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***Badania właściwości luminescencyjnych
mikrokrystalicznych materiałów Bi_3TeBO_9
domieszkowanych wybranymi jonami ziem rzadkich***

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Pragnę serdecznie podziękować wszystkim osobom, które wspierały mnie w trakcie realizacji pracy doktorskiej i całej drogi naukowej, która do niej doprowadziła. Na pierwszym miejscu kieruję wyrazy głębokiej wdzięczności do mojej Pani Promotor dr hab. Dobrosławy Kasprowicz, prof. PP za nieocenione wsparcie merytoryczne, inspirujące dyskusje, życzliwość i cierpliwość oraz za zaufanie i możliwość rozwijania się w tak twórczym i wymagającym środowisku.

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Streszczenie

Przedłożona rozprawa doktorska stanowi cykl pięciu artykułów dotyczących badań właściwości strukturalnych, oscylacyjnych oraz luminescencyjnych materiałów krystalicznych Bi_3TeBO_9 domieszkowanych wybranymi jonami ziem rzadkich: Nd^{3+} , Yb^{3+} i/lub Er^{3+} . W szczególności, badania te miały na celu określenie wpływu aktywnych jonów domieszek na dynamikę sieci, transfer energii oraz mechanizm luminescencji w materiałach krystalicznych Bi_3TeBO_9 domieszkowanych wyżej wymienionymi jonami.

W ramach rozprawy doktorskiej zsyntetyzowano mikrokryształiczne proszki $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$ oraz $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ zmodyfikowaną metodą Pechiniego oraz wykonano ceramiki $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ metodą wysokociśnieniowego, niskotemperaturowego spiekania. Charakterystyka strukturalna badanych materiałów obejmowała analizę wyników wykonanych metodą dyfrakcji rentgenowskiej pozwalającą na ocenę jednorodności fazowej oraz określenie struktury krystalograficznej ww. materiałów. Morfologia i skład atomowy badanych materiałów został określony przy wykorzystaniu elektronowego mikroskopu skaningowego oraz metody spektroskopii rentgenowskiej z dyspersją energii. Badania dynamiki sieci wykonano metodą spektroskopii Ramana i spektroskopii w podczerwieni. Analiza spektralna widm Ramana i widm w podczerwieni dotyczyła aktywności drgań związanych z grupami BO_3 , TeO_6 oraz jonami Bi^{3+} (Nd^{3+} , Yb^{3+} i/lub Er^{3+}) i Te^{6+} . Wykazano, że niska energia fononów matrycy Bi_3TeBO_9 sprzyja efektywnemu transferowi energii między jonami domieszek, minimalizując straty wynikające z relaksacji wielofononowej.

Właściwości luminescencyjne materiałów Bi_3TeBO_9 domieszkowanych wybranymi jonami ziem rzadkich (Nd^{3+} , Yb^{3+} i/lub Er^{3+}) badano metodami spektroskopii absorpcyjnej, emisyjnej oraz przez pomiar i analizę czasów zaniku luminescencji aktywnych jonów Bi^{3+} , Nd^{3+} , Yb^{3+} i/lub Er^{3+} . W mikrokryształicznych proszkach $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$ zarejestrowano emisję promieniowania z maksimum intensywności około 1064 nm związaną z konwersją energii z zakresu widzialnego do bliskiej podczerwieni. W przypadku materiałów $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$ oraz $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ zarejestrowano intensywną emisję w zakresie bliskiej podczerwieni około 975 oraz 1531 nm, która jest skutkiem efektywnego transferu energii pomiędzy jonami Bi^{3+} , Yb^{3+} i/lub Er^{3+} . Ponadto, w przypadku $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ zaobserwowano efekt konwersji energii w górę, prowadzący do emisji w zakresie widzialnym z maksimum intensywności około 523, 540 oraz 653 nm.

Dodatkowo, przeanalizowano wpływ parametrów spiekania wysokociśnieniowego na strukturę i właściwości luminescencyjne ceramiek $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$. W tym celu z mikrokryształicznego proszku $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ przygotowano próbki w postaci ceramiek przy zastosowaniu ciśnienia 2, 4, 6 lub 8 GPa. Stwierdzono, że wzrost ciśnienia spiekania prowadzi do poprawy krystaliczności, zmniejszenia defektów strukturalnych oraz zwiększenia intensywności emisji luminescencji jonów Er^{3+} .

Wykonane badania mają charakter podstawowy, poszerzając wiedzę na temat mechanizmów luminescencji i transferu energii w mikrokryształicznych materiałach boranowych Bi_3TeBO_9 domieszkowanych wybranymi jonami ziem rzadkich Nd^{3+} , Yb^{3+} i/lub Er^{3+} , a także aplikacyjny – badane materiały mogą znaleźć zastosowania jako optyczne konwertery promieniowania z konwersją energii w górę lub dół do zastosowań w fotowoltaice, optoelektronice lub fotonice.

Abstract

The presented doctoral dissertation comprises a series of five articles on the study of the structural, phonon and optical properties of Bi_3TeBO_9 crystalline materials doped with selected rare earth ions: Nd^{3+} , Yb^{3+} and/or Er^{3+} . The research aimed to determine the influence of active dopant ions on the lattice dynamics, energy transfer and luminescence mechanisms of Bi_3TeBO_9 crystalline materials doped with the above mentioned ions.

Microcrystalline powders $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$ were synthesized by a modified Pechini method and $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ ceramics were prepared by high-pressure low-temperature sintering. The structural characterization of the investigated materials included measurements and analysis of the results obtained by X-ray diffraction and scanning electron microscopy to verify phase homogeneity, crystallite size and the effect of sintering pressure on material morphology.

Lattice dynamics were studied using Raman and Fourier transform infrared spectroscopy. Spectral analysis of Raman and infrared spectra focused on the vibrational activity of BO_3 and TeO_6 groups, as well as Bi^{3+} (Nd^{3+} , Yb^{3+} and/or Er^{3+}) and Te^{6+} ions. The results confirmed that the low phonon energy of Bi_3TeBO_9 enables efficient energy transfer between dopant ions while minimizing losses due to multiphonon relaxation.

The luminescence properties of Bi_3TeBO_9 materials doped with selected rare earth ions (Nd^{3+} , Yb^{3+} and/or Er^{3+}) were investigated using absorption, emission spectroscopy, as well as by measuring and analysing the luminescence decay times of the active ions Bi^{3+} , Nd^{3+} , Yb^{3+} i/lub Er^{3+} . In microcrystalline $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$ powders, the emission was recorded with a maximum intensity around 1064 nm, due to energy transfer from the visible to near-infrared range. In the case of $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$ and $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$ materials, intense near-infrared emission around 975 nm for powders doped with Yb^{3+} ions and 1531 nm for those doped with Er^{3+} ions was recorded, which is due to efficient energy transfer between Bi^{3+} , Yb^{3+} and/or Er^{3+} ions. Furthermore, an up-conversion effect was observed for $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$, resulting in emission in the visible range with intensity maxima around 523, 540 and 653 nm.

Furthermore, the influence of high pressure sintering parameters on the structure and luminescence properties of $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ ceramics were analyzed. For this purpose, samples were prepared from $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ powder as ceramics using pressures of 2, 4, 6 or 8 GPa. It was found that an increase in sintering pressure leads to an improvement in crystallinity, a reduction in structural defects and an increase in luminescence emission intensity of active ions.

The research carried out is fundamental, extending knowledge of the luminescence and energy transfer mechanisms of microcrystalline borate Bi_3TeBO_9 materials doped with selected rare earth ions Nd^{3+} , Yb^{3+} and/or Er^{3+} , as well as applied indicating the potential to be used as a luminescent materials for photovoltaic, optoelectronics and photonics applications.

1. Wstęp

Obecnie jednym z najważniejszych wyzwań ekologicznych jest opracowanie nowych strategii i technologii produkcji energii bezpiecznej dla środowiska. W tym celu konieczne jest zbadanie potencjalnych naturalnych źródeł energii przyjaznej środowisku naturalnemu. Oprócz wielu naturalnych źródeł energii, takich jak pływy morskie, wiatr czy biomasa, słońce zapewnia najczystsza do pozyskania energię, którą można stosunkowo łatwo przekształcać w energię elektryczną [1–3]. Słońce dostarcza duże ilości energii w postaci promieniowania elektromagnetycznego, generowanego podczas fuzji jąder wodoru [3–5]. Chociaż energia słoneczna jest dostępna na całym świecie, jej wykorzystanie jest ograniczone wieloma czynnikami, w szczególności położeniem geograficznym, które determinuje czas potencjalnego wykorzystania energii słonecznej. Energia promieniowania słońca w pobliżu powierzchni Ziemi obejmuje szeroki zakres spektralny od 300 do 2500 nm i składa się z promieniowania ultrafioletowego (ang. ultraviolet – UV) około 7%, widzialnego (ang. visible – VIS) około 47% i podczerwonego (ang. infrared – IR) około 46% [6–8]. Energia słoneczna może być przekształcona w energię elektryczną za pomocą fotowoltaicznych ogniw słonecznych [9,10]. Wydajność konwersji energii słonecznej na energię elektryczną zależy w dużej mierze od rodzaju ogniw słonecznych [11,12]. W ostatnich latach zaobserwowano wysoką dynamikę modyfikacji ogniw słonecznych w celu poprawy wydajności konwersji naturalnej energii słonecznej na energię elektryczną poprzez efekt fotowoltaiczny [9–14]. Ogniw słoneczne pierwszej generacji były wykonane z krzemu monokrystalicznego (c-Si) lub krzemu polikrystalicznego (mc-Si) [4,15–19]. Ogniw słoneczne drugiej generacji to cienkowarstwowe ogniw słoneczne wykonane z następujących materiałów: c-Si, krzem amorficzny (a-Si), a także wieloskładnikowych materiałów półprzewodnikowych np. diselenek miedziowo-indowo-galowy $\text{Cu}(\text{In,Ga})(\text{Se})_2$, tellurek kadmu CdTe , siarczki miedziowo-cynkowo-cynowy $\text{Cu}(\text{Zn,Sn})(\text{S})_2$ lub związki z grup III-V (np. GaAs , InP lub GaInP). Materiały te umożliwiają tworzenie ogniw słonecznych składających się z wielu warstw półprzewodników o różnej wartości przerwy energetycznej (E_g) w celu wykorzystania możliwie szerokiego zakresu widma promieniowania słonecznego i osiągnięcia wyższej wydajności ogniw słonecznych [4,15–18]. Technologia ogniw słonecznych trzeciej generacji związana jest z wytwarzaniem następujących typów wielowarstwowych ogniw słonecznych: ogniw słoneczne $\text{Cu}_2\text{ZnSnS}_4$, ogniw słoneczne organiczne i polimerowe, ogniw słoneczne z kropkami kwantowymi lub perowskitowe ogniw słoneczne [4,15–18,20]. Fotowoltaiczne ogniw słoneczne czwartej generacji są kombinacją ogniw wytworzonych z materiałów poprzednich generacji z zastosowaniem dodatkowo grafenu jako składnika zwiększającego wydajność ogniw słonecznych [18, 21–22].

Głównym czynnikiem ograniczającym wydajność konwersji energii słonecznej w ogniwach słonecznych jest niedopasowanie pomiędzy energią padającego promieniowania słonecznego a energią E_g materiałów półprzewodnikowych stosowanych w ogniwach słonecznych [15,23,24]. Konwencjonalne półprzewodnikowe jednowarstwowe ogniwa słoneczne skutecznie absorbują tylko fotony o energiach zbliżonych do energii E_g materiału półprzewodnikowego [15,23,24]. Aktualnie rynek ogniw słonecznych na całym świecie głównie wykorzystuje ogniwa słoneczne c-Si (około 80%) [13,25], co jest związane z ich niskim kosztem wytwarzania, niską toksycznością, dobrze znanym procesem produkcyjnym i długą żywotnością (ponad 20 lat) [26–28]. Jednak zgodnie z modelem Shockley-Queissera wydajność ogniw słonecznych c-Si nie przekracza limitu 32-33% [13,26–29]. Również warto zauważyć, że konwencjonalne krzemowe ogniwa słoneczne mają wartość E_g równą 1,12 lub 1,75 eV odpowiednio dla c-Si lub a-Si, co odpowiada absorpcji promieniowania słonecznego o długości fali odpowiednio około 1107 i 708 nm [15,28]. Fotony o energiach mniejszych niż E_g nie są absorbowane, a ich energia nie jest wykorzystywana do generowania elektronów, podczas gdy fotony o energiach wyższych niż E_g są absorbowane, ale nadmiar energii jest tracony w wyniku procesów termicznych [23,24,30]. Aby wykorzystać szeroki zakres promieniowania słonecznego w ogniwach słonecznych stosowane są również materiały półprzewodnikowe z E_g w zakresie spektralnym VIS: InN (1,8–1,9 eV) [31], GaInP (1,8–1,9 eV) [32], AlGaInP (1,9–2,2 eV) [33], AlGaAs (1,42–2,16 eV dla różnych zawartości Al) [34], GaP (2,27 eV) [31], AlP (2,45 eV) [31]. Ostatnio, związki takie jak: CuInSe₂, CuGaSe₂, Cu(Ga,In)Se₂ lub (Cu,Ag)(In,Ga)Se₂ zostały uznane za najbardziej obiecujące absorbery dla polikrystalicznych cienkowarstwowych ogniw słonecznych, ponieważ ich E_g pokrywają szeroki zakres spektralny (VIS/NIR) odpowiedni do absorpcji promieniowania słonecznego w tym zakresie [26,29]. Niestety, sprawność konwersji tych ogniw słonecznych o szerokiej E_g jest niższa niż 20% [26,29].

Jednym z możliwych sposobów zwiększenia wydajności ogniw słonecznych c-Si jest zastosowanie konwerterów optycznych w technologii ich wytwarzania, które będą koncentrować promieniowanie słoneczne do zakresu widmowego odpowiadającego energii E_g krzemu. Konwertery optyczne mogą koncentrować promieniowanie słoneczne w wymaganym zakresie spektralnym, z którego energia słoneczna może być łatwo absorbowana, a następnie przekształcana w energię elektryczną poprzez efekt fotowoltaiczny [15,18,35]. Efekt koncentracji promieniowania słonecznego może być osiągnięty dzięki procesowi cięcia kwantowego (ang. quantum cutting), w którym jeden foton o wysokiej energii jest przekształcany na dwa fotony o niższych energiach korespondujących z zakresem energii E_g materiału półprzewodnikowego, z którego wykonane są ogniwa słoneczne [15,18,35]. Ponadto, proces konwersji energii w dół (ang. down-conversion)

skutecznie minimalizuje straty energii spowodowane procesami termicznymi par elektron-dziura w półprzewodnikach [15,36,37]. Przy zastosowaniu w technologii wytwarzania ogniw słonecznych c-Si materiałów z wykorzystaniem procesu konwersji energii w dół maksymalna wydajność procesu fotowoltaicznego może osiągnąć 39% [15,38].

Materiały krystaliczne domieszkowane pierwiastkami ziem rzadkich (ang. rare earth – RE) są często wykorzystywane jako konwertery spektralne ze względu na unikalną strukturę poziomów energetycznych pierwiastków RE, która umożliwia absorpcję lub emisję promieniowania w zakresie UV, VIS lub bliskiej podczerwieni (ang. near infrared – NIR). Ponadto, w materiałach tych zachodzą procesy transferu energii (ang. energy transfer – ET) między aktywnymi jonami RE^{3+} w procesach konwersji energii w górę (ang. up-conversion) lub w dół [36,39–42]. W celu zwiększenia wydajności fotowoltaicznej w konwencjonalnych krzemowych ogniwach słonecznych, warstwy materiałów domieszkowanych jonami RE^{3+} o wyżej wspomnianych właściwościach konwersji energii, mogą być umieszczane na górnej powierzchni panelu/ogniwa słonecznego, umożliwiając bardziej efektywne wykorzystanie promieniowania słonecznego [36,43].

Grupa pierwiastków RE obejmuje lantanowce (od lantanu do lutetu) oraz pierwiastki itr i skand. Właściwości luminescencyjne jonów RE^{3+} wynikają z ich charakterystycznej struktury elektronowych poziomów energetycznych [44,45]. Jony RE^{3+} mają częściowo zapełnioną powłokę 4f, która jest ekranowana od wpływu zewnętrznego pola matrycy przez zewnętrzne powłoki elektronowe 5s² i 5p⁶. Częściowo zapełniona powłoka 4f jonów RE^{3+} umożliwia przejścia w zakresie wewnętrznej powłoki 4f – 4f, a ich aktywność optyczna, w zależności od wybranych jonów, może obejmować szeroki zakres widmowy od obszaru próżniowego ultrafioletu (ang. vacuum ultraviolet – VUV) poprzez VIS aż do zakresu NIR [46].

Wyjątkowe właściwości jonów RE^{3+} sprawiają, że są one wykorzystywane w materiałach optoelektronicznych, co przyczynia się do intensywnych badań materiałów organicznych i nieorganicznych domieszkowanych pierwiastkami RE. W syntezie tego typu materiałów najczęściej stosuje się związki organiczne skoordynowane z jonami RE^{3+} oraz nieorganiczne układy, takie jak kryształy, szkła i ceramiki, zawierające domieszki jonów RE^{3+} . Najczęściej stosowane matryce do domieszkowania jonami RE^{3+} są wybierane spośród materiałów krystalicznych, takich jak: fluorki, tlenki, borany lub fosforany dzięki ich transparentności w szerokim zakresie spektralnym [47–50]. Wśród materiałów krystalicznych aktywowanych jonami RE^{3+} szczególne miejsce zajmują borany, które wyróżniają się korzystnymi właściwościami optycznymi, fizyko-chemicznymi oraz szerokim zakresem zastosowań w optoelektronice oraz fotonice [51–53]. Ponadto, borany są dobrze znaną grupą związków o niecentrosymetrycznych strukturach [51–53], dzięki czemu posiadają unikalne

nieliniowe właściwości optyczne (ang. nonlinear optical – NLO) i są znane jako bardzo efektywne materiały do wytwarzania emisji laserowej przez generowanie drugiej harmonicznej (ang. second harmonic generation – SHG) z zakresu NIR do VIS [54–56].

Właściwości optyczne kryształów boranowych są związane z ich strukturą, w szczególności z obecnością charakterystycznych grup boranowych BO_3 , BO_4 , B_3O_6 lub B_3O_7 [53,57]. Kryształy boranowe, takie jak $\beta\text{-BaB}_2\text{O}_4$ (BBO), LiB_3O_5 (LBO), CsB_3O_5 (CBO), $\text{KBe}_2\text{BO}_3\text{F}_2$ (KBBF), $\alpha\text{-BiB}_3\text{O}_6$, $\text{CsLiB}_5\text{O}_{10}$ lub $\text{Bi}_2\text{ZnOB}_2\text{O}_6$ są często używane jako materiały NLO [57–59]. Oprócz charakterystycznych grup boranowych kryształy boranowe często zawierają również jony metaliczne, które stabilizują strukturę i nadają im specyficzne właściwości optyczne i luminescencyjne [57–60].

Inna efektywna grupa kryształów zapewniająca uzyskanie unikalnych właściwości optycznych to materiały zawierające w swojej strukturze oktaedry MO_6 zawierające kationy takie jak $\text{M} = \text{Ti}^{4+}$, Nb^{5+} , Ta^{5+} , Mo^{6+} , W^{6+} lub Te^{6+} podatne na dystorsję Jahn-Tellera drugiego rzędu, co skutkuje lokalnym obniżeniem symetrii w strukturze kryształu, a w konsekwencji możliwościami generacji sygnałów SHG o dużej intensywności [61]. Efekt ten zaobserwowano na przykład w kryształach $\text{BaTeMo}_2\text{O}_9$ lub BaTeW_2O_9 [62].

Badane w ramach rozprawy doktorskiej materiały krystaliczne Bi_3TeBO_9 (BTBO) w literaturze po raz pierwszy zostały zaprezentowane w dwóch niezależnych publikacjach w 2016 roku [61,63]. BTBO to kryształy boranowe zawierające trzy rodzaje optycznie aktywnych jednostek: planarne grupy boranowe BO_3 , zniekształcone oktaedry TeO_6 i stereochemicznie aktywną parę elektronów w kationach Bi^{3+} [61]. Dodatkowy wkład tych trzech typów aktywnych optycznie grup skutkuje efektem synergicznym, prowadzącym do generacji sygnału SHG o dużej intensywności (około 20 razy większej w porównaniu do sygnału SHG w kryształ KH_2PO_4), wykazując największy efekt SHG wśród znanych NLO materiałów boranowych. W wyżej wspomnianym artykule została opisana struktura krystaliczna, struktura elektronowa i właściwości NLO kryształu BTBO [61]. Właściwości strukturalne, piezoelektryczne, termalne, optyczne i elastyczne kryształów BTBO były również badane przez innych autorów [63–67]. Ponadto, teoretyczne obliczenia *ab initio* wykonane dla kryształu BTBO przy użyciu funkcjonałów DFT-LDA i DFT-GGA pozwoliły na wyznaczenie następujących wartości E_g : 3,23 eV DFT-GGA [61], 3,21 eV DFT-GGA [64], 2,96 eV DFT-LDA [64], które porównano do wartości E_g otrzymanej eksperymentalnie 2,70 eV [61].

Celem rozprawy doktorskiej było wytworzenie oraz charakteryzacja materiałów mikrokrystalicznych w postaci proszków i ceramiek, które dzięki transferowi energii pomiędzy aktywnymi optycznie jonami matrycy krystalicznej oraz domieszkami jonów RE^{3+} skutecznie

konwertują energię promieniowania z zakresu UV/VIS do NIR dzięki czemu mogą znaleźć zastosowanie w fotowoltaice, optoelektronice lub fotonice.

Materiały BTBO zawierające domieszki wybranych jonów Nd^{3+} , Yb^{3+} i/lub Er^{3+} zostały po raz pierwszy wykonane i scharakteryzowane w ramach badań przedstawionych w przedłożonej pracy doktorskiej. BTBO krystalizuje w strukturze heksagonalnej, w grupie przestrzennej $P6_3$ (nr 173), komórka elementarna zawiera 2 jednostki strukturalne ($Z = 2$), a jej parametry wynoszą: $a = 8,7510(12) \text{ \AA}$, $c = 5,8981(12) \text{ \AA}$ i $V = 391,16(11) \text{ \AA}^3$ [61]. Jony Nd^{3+} , Yb^{3+} i Er^{3+} wbudowują się w pozycje jonów Bi^{3+} w matrycy BTBO. Związane jest to z podobieństwem promieni jonowych Nd^{3+} (0,983 $\text{ \AA}$), Yb^{3+} (0,868 $\text{ \AA}$) oraz Er^{3+} (0,89 $\text{ \AA}$) do wartości promienia jonów Bi^{3+} (1,03 $\text{ \AA}$) [68]. W szczególności, badania przedstawione w rozprawie doktorskiej wykonano dla mikrokrystalicznych proszków BTBO domieszkowanych wybranymi jonami Nd^{3+} , Yb^{3+} lub Er^{3+} oraz podwójnie domieszkowanych jonami Yb^{3+} i Er^{3+} .

Wybór jonów Nd^{3+} , Yb^{3+} lub Er^{3+} do domieszkowania matrycy Bi_3TeBO_9 został dokonany ze względu na ich unikalne właściwości spektroskopowe oraz zdolność do efektywnej emisji w zakresie VIS i/lub NIR, korzystnej do zastosowań w fotowoltaice i optoelektronice na skutek efektywnego transferu energii.

Jony Nd^{3+} cechują się przejściami $f - f$ ($^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ oraz $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$) w zakresie NIR, obejmującym strategiczne długości fal wykorzystywane w komunikacji optycznej i technologiach laserowych (890, 1064 oraz 1350 nm) [69–71]. Ponadto, w materiałach domieszkowanych jonami Nd^{3+} mogą zachodzić procesy konwersji energii, co może istotnie zwiększyć zastosowanie tych materiałów w ogniwach fotowoltaicznych nowej generacji lub w układach optoelektronicznych [72–74].

Jony Yb^{3+} charakteryzują się dwupoziomową strukturą energetyczną, ograniczoną do przejścia $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ oraz dużym przekrojem absorpcji przy długości fali około 975 nm [75,76]. Jony Yb^{3+} są także doskonałymi sensybilizatorami, dzięki efektywnemu transferowi energii z jonów Yb^{3+} do innych aktywnych jonów w układach domieszkowanych innymi RE^{3+} [75,76].

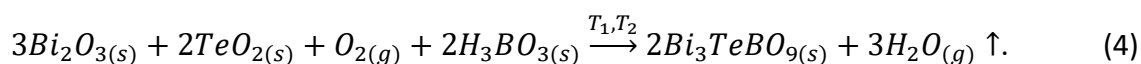
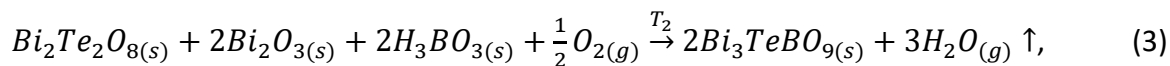
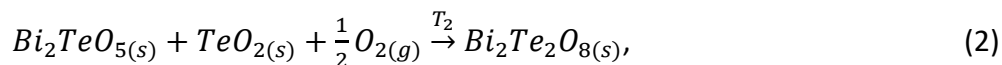
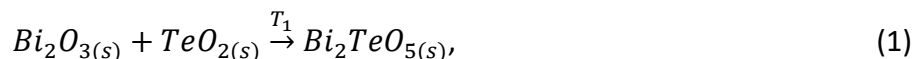
Jony Er^{3+} zostały wybrane do domieszkowania matrycy BTBO ze względu na ich emisję w zakresie VIS (przejścia $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ oraz $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$) oraz NIR (przejście $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$). Ponadto, w obecności Yb^{3+} , emisja Er^{3+} w obszarze VIS lub NIR może być dodatkowo wzmacniana w wyniku transferu energii z Yb^{3+} do Er^{3+} , prowadząc do znacznego zwiększenia intensywności luminescencji jonów Er^{3+} [76,77].

W związku z powyżej opisanymi właściwościami, wybór jonów Nd^{3+} , Yb^{3+} i/lub Er^{3+} do domieszkowania BTBO wynikał ze strategicznego połączenia ich właściwości luminescencyjnych,

zdolności do udziału w procesach transferu energii oraz kompatybilności strukturalnej z matrycą BTBO, umożliwiającą optymalizację właściwości luminescencyjnych domieszkowanych układów przy jednoczesnym zachowaniu uporządkowanej struktury krystalicznej.

Proszek krystaliczny BTBO syntetyzowano przy zastosowaniu zmodyfikowanej metody Pechiniego [78]. Do syntezy wykorzystano następujące materiały: tlenek bizmutu (Bi_2O_3 , 99,9%), dwutlenek telluru (TeO_2 , 99,99%), kwas borowy (H_3BO_3 , 99,5%), kwas cytrynowy ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, 99,4%), mannitol ($\text{C}_6\text{H}_8(\text{OH})_6$, 99,5%), wodę dejonizowaną (rezystancja właściwa $\rho = 15 \text{ M}\Omega \cdot \text{cm}$) oraz kwas azotowy (HNO_3 , 65% wag., cz.d.a.). Ponadto, w przypadku syntezy proszków domieszkowanych jonami RE^{3+} , do wyżej wymienionych w materiałów dodawany był również materiał zawierający właściwą domieszkę (tlenki neodymu, iterbu lub erbu (Nd_2O_3 , Yb_2O_3 lub Er_2O_3 , 99,99%). W celu przygotowania roztworów początkowych, odpowiednie ilości tlenków: Bi_2O_3 i TeO_2 rozpuszczano w minimalnej objętości HNO_3 w obecności kwasu cytrynowego (czynnik kompleksujący) przy mieszaniu i ogrzewaniu w temperaturze 80°C . W procesie syntezy tellur musi być dostarczony w odpowiednim nadmiarze (ok. 12% mol.) ze względu na jego znaczną lotność podczas pirolizy w metodzie Pechiniego. Kwas cytrynowy został wybrany jako czynnik kompleksujący ze względu na ligandy cytrynianowe tworzące stabilne kompleksy dla Bi^{3+} i Te^{4+} w silnie kwaśnych roztworach [79]. Stosunek molowy kwasu cytrynowego do ilości kationów metali wynosił 3:1. W tych warunkach zapewniono całkowite rozpuszczenie tlenków metali. Po uzyskaniu przezroczystego i jednorodnego roztworu zawierającego kompleksy metali, do roztworu dodawano odpowiednią ilość H_3BO_3 (z 10% molowym nadmiarem) i kontynuowano mieszanie. Ten nadmiar boru był wymagany, aby zapobiec niestechiometrii spowodowanej odparowaniem B_2O_3 w wyższych temperaturach. Stosunek molowy użytych substratów Bi_2O_3 , TeO_2 i H_3BO_3 wynosił 3,00:2,24:2,20. Po wtórnej homogenizacji do roztworu dodawano mannitol. Stosunek molowy kwasu cytrynowego do mannitolu był stały i wynosił 3:1. Po rozpuszczeniu wszystkich odczynników mieszanie roztworu kontynuowano przez około 1 godzinę w temperaturze 90°C w celu zainicjowania poliestryfikacji. Przygotowany zol przenoszono następnie do tygla z tlenku glinu i umieszczano w piecu wyposażonym w regulator temperatury. Zawartość tygla utrzymywano przez około 24 h w temperaturze 100°C w celu odparowania rozpuszczalników (H_2O – HNO_3) i przeprowadzenia poliestryfikacji. Następnie temperaturę zwiększano do 350°C na 3 h w celu usunięcia resztek wody i wysuszenia żelu. Aby rozpocząć proces pirolizy i pozbyć się części organicznych, temperaturę stopniowo zwiększano do 500°C i utrzymywano na tym poziomie przez 24 h. Następnie temperaturę zwiększano do 650°C i kontynuowano proces wygrzewania przez 48 h. Taki czas trwania syntezy (72 h pirolizy) jest wymagany do zapewnienia całkowitego utlenienia jonów Te^{4+} do Te^{6+} .

Po zakończeniu procesu wygrzewania sproszkowany materiał został dokładnie zmielony w moździerzu agatowym. Proces syntezy BTBO zgodny z metodą Pechiniego zachodzi zgodnie z następującymi reakcjami:



W trakcie syntezy jony telluru mogą być utleniane ze stanu +4 do +6 (przez fazę pośrednią $Bi_2Te_2O_8$, zawierającą parę telluru przy stopniu utlenienia +4 i +6, dzięki obecności atmosfery tlenu/powietrza w wysokiej temperaturze. Reakcja (1) zachodzi w temperaturze T_1 (poniżej 500°C), reakcje (2) i (3) zachodzą jednocześnie, ale tylko w odpowiednio wysokiej temperaturze T_2 (650°C). Równanie (4) opisuje reakcję sumaryczną zachodzącą w tym procesie. Po zakończeniu syntezy tygiel był wyjęty z pieca i szybko schłodzony do temperatury pokojowej. Jego zawartość pokruszono i zmielono w moździerzu agatowym, uzyskując bardzo drobne, prawie bezbarwne proszki BTBO. Przedstawiona powyżej procedura syntezy umożliwia określenie i obliczenie dokładnych ilości Bi_2O_3 oraz substancji zawierających jony domieszek, które należy użyć w syntezie każdego z układów BTBO:RE³⁺.

Do wykonania ceramiek BTBO:Yb³⁺/Er³⁺ zastosowano mikrokryształiczny proszek BTBO:Yb³⁺/Er³⁺ zsyntetyzowany opisaną wyżej metodą Pechiniego. Ceramiki wykonaną metodą ściskania przy wysokim ciśnieniu w niskiej temperaturze (ang. High-Pressure Low-Temperature – HPLT) [80]. W tym celu przygotowano wstępnie próbki proszku pod ciśnieniem 0,2 GPa w temperaturze pokojowej w postaci pastylek o średnicy około 5 mm i wysokości około 2 mm przy użyciu cylindrycznej komórki. Następnie próbki umieszczano w specjalnie ukształtowanym ceramicznym pojemniku wykonanym z $CaCO_3$ wyposażonym w grzejnik grafitowy, który umieszczano w półprzewodnikowej komorze wysokociśnieniowej w celu ich spiekania. Próbki były poddawane spiekaniu w temperaturze około 500°C przez 1 minutę pod ciśnieniem 2, 4, 6 lub 8 GPa w celu uzyskania ceramicznych próbek. Po zakończeniu procesu spiekania i chłodzenia, ceramiki były polerowane papierem ściernym o różnej ziarnistości w celu uzyskania powierzchni o odpowiedniej jakości do badań. W rezultacie uzyskano cztery próbki ceramiczne wytworzone pod różnymi ciśnieniami oznaczone jako 2 GPa, 4 GPa, 6 GPa i 8 GPa.

Badania materiałów mikrokrystalicznych BTBO:RE³⁺ przedstawione w pracy doktorskiej dotyczą ich unikalnych właściwościach strukturalnych, oscylacyjnych i luminescencyjnych, które otwierają możliwości ich zastosowania w fotowoltaice, optoelektronice lub fotonice. Celem tych badań było kompleksowe określenie struktury, dynamiki sieci, mechanizmu transferu energii oraz właściwości luminescencyjnych mikrokrystalicznych materiałów BTBO domieszkowanych wybranymi jonami Nd³⁺, Yb³⁺ i/lub Er³⁺.

W szczególności badania te obejmowały:

1. Badania struktury krystalicznej i dynamiki sieci:

- analiza teorii grup i charakteryzacja *ab initio* modów fononowych w centrum strefy Brillouina,
- analiza właściwości oscylacyjnych BTBO na podstawie pomiarów metodą spektroskopii

Ramana i spektroskopii podczerwieni w zakresie bliskiej i średniej podczerwieni (ang. Fourier transform infrared/ medium infrared – FT-IR/MIR),

- rejestracja dyfraktogramów przy zastosowaniu metody XRD,
- analiza morfologii i składu atomowego metodą SEM i EDX.

2. Badania mechanizmu transferu energii i właściwości luminescencyjnych:

• badanie procesów absorpcji i emisji promieniowania w BTBO domieszkowanym jonami Nd³⁺, Yb³⁺ i/lub Er³⁺,

• analiza procesu transferu energii pomiędzy jonami Bi³⁺ a RE³⁺, w tym wyznaczenie wartości współczynników efektywności transferu energii (ang. energy transfer efficiency – ETE) i współczynników wydajności kwantowej (ang. quantum efficiency – QE),

• optymalizacja koncentracji aktywnych jonów Nd³⁺, Yb³⁺ i/lub Er³⁺ w matrycy BTBO w celu maksymalizacji intensywności emisji w zakresie NIR oraz VIS.

3. Badania wpływu warunków procesów technologicznych na właściwości ceramiek BTBO:Yb³⁺/Er³⁺:

• analiza wpływu parametrów procesu wytworzenia ceramiek (temperatura oraz ciśnienie spiekania) na krystaliczność, defekty strukturalne oraz intensywność luminescencji aktywnych jonów Yb³⁺ i Er³⁺,

• określenie optymalnych warunków spiekania metodą HPLT ceramiek BTBO:Yb³⁺/Er³⁺ w celu poprawy ich właściwości strukturalnych i luminescencyjnych.

2. Badane materiały oraz techniki pomiarowe

Mikrokryształiczne proszki	Koncentracja domieszki (at.%)
Bi_3TeBO_9	-
$\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$	0,5; 1,0; 2,5; 5,0; 7,5; 10,0
$\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$	0,5; 1,0; 2,5; 4,0; 5,0; 7,5
$\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$	1,0
$\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$	5,0/1,0
Ceramiki	Ciśnienie stosowane przy wytworzeniu ceramik, P [GPa]
$\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ (5,0/1,0 at.%)	2; 4; 6; 8

Mikrokryształiczne proszki BTBO domieszkowane jonami RE^{3+} (Nd^{3+} , Yb^{3+} i/lub Er^{3+}) zostały zsyntetyzowane przy użyciu zmodyfikowanej metody Pechiniego na Wydziale Nowych Technologii i Chemii Wojskowej Akademii Technicznej w Warszawie. Wyżej wymienione mikrokryształiczne proszki zostały scharakteryzowane metodą XRD na Wydziale Nowych Technologii i Chemii Wojskowej Akademii Technicznej w Warszawie, w Instytucie Fizyki Polskiej Akademii Nauk w Warszawie oraz na Wydziale Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej.

Ceramiki BTBO domieszkowane jonami Yb^{3+} oraz Er^{3+} zostały wytworzone z mikrokryształicznych proszków $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ metodą HPLT w Instytucie Niskich Temperatur i Badań Strukturalnych Polskiej Akademii Nauk we Wrocławiu. Pomiary z wykorzystaniem elektronowego mikroskopu skaningowego (ang. scanning electron microscope – SEM) proszków $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ i ceramik $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ oraz badania metodą spektrometrii dyspersji energii promieniowania rentgenowskiego (ang. energy-dispersive X-ray spectroscopy – EDX) proszków $\text{Bi}_3\text{TeBO}_9:\text{Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$ i ceramik $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ zostały wykonane w Wielkopolskim Centrum Zaawansowanych Technologii Uniwersytetu im. Adama Mickiewicza oraz na Wydziale Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej. Pomiary mikrokryształicznych proszków BTBO metodą spektroskopii FT-IR/MIR wykonano w Instytucie Fizyki Molekularnej Polskiej Akademii Nauk w Poznaniu. Badania metodą spektroskopii Ramana materiałów BTBO domieszkowanych jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} zostały wykonane na Wydziale Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej. Ponadto, we współpracy z Instytutem Fizyki Materii Skondensowanej Narodowej Akademii Nauk

Ukrainy we Lwowie wykonano teoretyczne obliczenia dynamiki sieci krystalicznej BTBO obejmujące analizę teorii grup i charakteryzację *ab initio* modów fononowych przy użyciu funkcjonału gęstości (ang. generalized gradient approximation – GGA) w parametryzacji Perdew-Burke-Ernzerhofa oraz funkcjonału korelacji metodą Grimme'a (DFT-D3). Pomiary właściwości luminescencyjnych badanych materiałów (rejestracja widma odbicia, wzbudzenia, emisji oraz pomiary czasów zaniku) wykonano metodami spektroskopii optycznej w Instytucie Niskich Temperatur i Badań Strukturalnych Polskiej Akademii Nauk we Wrocławiu. Analiza oraz obliczenia dotyczące pomiarów badanych materiałów wykonanych wyżej wymienionymi metodami w tym: opracowanie widm Ramana, widm odbicia, widm wzbudzenia, widm emisji, analiza mechanizmów relaksacji energii, obliczenia czasów zaniku, obliczenia kinetyki luminescencji metodą Inokuti – Hirayama, obliczenia współczynników ETE oraz QE, a także obliczenia związane z uzyskaniem informacji o liczbie fotonów uczestniczących w procesach konwersji energii w górę zostały wykonane na Wydziale Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej.

Szczegółowe informacje dotyczące technik wytwarzania badanych materiałów, badawczych metod i aparatury pomiarowej są zawarte w artykułach wchodzących w skład rozprawy doktorskiej [publikacje [P1–P5](#)].

3. Opis prac wchodzących w skład rozprawy

Pracę doktorską stanowi cykl pięciu oryginalnych artykułów opublikowanych w czasopismach z listy filadelfijskiej (ang. journal citation reports – JCR). Ponadto, dla każdego artykułu podano wartości współczynnika wpływu (ang. Impact Factor – IF) oraz liczbę punktów według kategoryzacji Ministerstwa Nauki i Szkolnictwa Wyższego (MNiSW) ze stanem na rok publikacji artykułu.

- P1** D. Kasprowicz, **T. Zhezhera**, A. Łapiński, M. Chrunik, A. Majchrowski, A.V. Kityk, Ya. Shchur, “Lattice dynamics of Bi_3TeBO_9 microcrystals: μ -Raman/IR spectroscopic investigation and *ab initio* analysis”, *Journal of Alloys and Compounds*, 782 (2019) 488–495, (IF: 4,650; MNISW: 100 pkt).
- P2** **T. Zhezhera**, P. Gluchowski, M. Nowicki, M. Chrunik, A. Majchrowski, K. M. Kosyl and D. Kasprowicz, “Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors”, *Journal of Materials Science*, 57 (2022) 185–203, (IF: 4,500; MNISW: 100 pkt).
- P3** **T. Zhezhera**, P. Gluchowski, M. Nowicki, M. Chrunik, A. Majchrowski and D. Kasprowicz, “Enhanced near-infrared emission of Er^{3+} as a synergistic effect of energy transfers in $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$ phosphors”, *Journal of Luminescence*, 258 (2023) 119774, (IF: 3,300; MNISW: 100 pkt).
- P4** **T. Zhezhera**, P. Gluchowski, M. Nowicki, M. Chrunik, A. Miklaszewski and D. Kasprowicz, Pressure modified upconversion luminescence of Yb^{3+} and Er^{3+} -doped Bi_3TeBO_9 ceramics, *Journal of Luminescence* 268 (2024) 120401, (IF: 3,300; MNISW: 100 pkt).
- P5** **T. Zhezhera**, P. Gluchowski, M. Nowicki, M. Chrunik, B. Szczęśniak, D. Kasprowicz, Efficient Yb^{3+} emission sensitized by Bi^{3+} excitation in $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}$ phosphors, *The Journal of Physical Chemistry C*, 128(34) (2024) 14357–14367, (IF: 3,300; MNISW: 140 pkt).

W pracy **P1** przedstawiono wyniki pomiarów dynamiki sieci krystalicznej BTBO (w zakresie drgań oscylacyjnych) metodą spektroskopii μ -Ramana oraz FT-IR/MIR w połączeniu z obliczeniami *ab initio* parametrów modów fononowych matrycy BTBO. Heksagonalna struktura z grupą przestrzenną $P6_3$ proszków mikrokrystalicznych BTBO została potwierdzona na podstawie pomiarów XRD. Widma μ -Ramana i FT-IR/MIR zarejestrowano w szerokim zakresie spektralnym ($100 - 1500 \text{ cm}^{-1}$), analizując zarówno drgania wewnętrzne jak i zewnętrzne matrycy BTBO. Wyniki eksperymentalne porównano z przewidywaniami teorii grup i charakteryzacją *ab initio* modów

fononowych przy użyciu funkcjonałów gęstości GGA oraz DFT-D3. W strukturze BTBO występują dwie jednostki strukturalne: trygonalne grupy BO_3 oraz zdeformowane oktaedry TeO_6 . Z teoretycznej analizy dynamiki sieci wynika, że komórka elementarna BTBO składa się z 28 atomów, dających 84 drgania fundamentalne. Całkowita nieredukowalna reprezentacja, opisująca drgania normalne w mikrokryształicznych proszkach BTBO ma następującą postać: $\Gamma = 14A + 14B + 14E_1 + 14E_2$. Mody fononowe typu A , E_1 i E_2 są aktywne w widmach Ramana podczas gdy mody A i E_1 są aktywne w widmach IR. Mody o symetrii B są nieaktywne zarówno w widmach Ramana jak i IR. Wyniki obliczeń *ab initio* parametrów modów fononowych są zgodne z wynikami eksperymentu. Z analizy widm Ramana i FT-IR/MIR wynika, że drgania występujące w matrycy BTBO można podzielić na: drgania niskoczęstotliwościowe (poniżej 350 cm^{-1}) związane z translacjami i libracjami grup BO_3 i TeO_6 oraz jonów Bi^{3+} i Te^{6+} , drgania w zakresie średnich częstotliwości ($350 - 700\text{ cm}^{-1}$) przypisane modom zginającym grup BO_3 i TeO_6 oraz drgania o wysokiej częstotliwości ($700 - 1500\text{ cm}^{-1}$), dla których w widmach dominują drgania rozciągające grup BO_3 i TeO_6 z pasmami o najwyższej intensywności w zakresie $1200 - 1400\text{ cm}^{-1}$.

W publikacji **P1** doktorant współuczestniczył w pomiarach, opracowaniu, analizie i interpretacji wyników otrzymanych metodą spektroskopii Ramana. Ponadto, na podstawie danych krystalograficznych uzyskanych z literatury doktorant opracował graficznie strukturę BTBO przy zastosowaniu oprogramowania Diamond 2.1c i przygotował graficzną ilustrację struktury kryształu.

W publikacji **P2** przedstawiono wyniki pomiarów właściwości luminescencyjnych mikrokryształicznych proszków BTBO:Nd^{3+} . W szczególności przeanalizowano procesy związane z emisją promieniowania w zakresie NIR badanych materiałów. Główny cel pracy dotyczył wyjaśnienia mechanizmu transferu energii między jonami Bi^{3+} i Nd^{3+} , określenia optymalnej koncentracji domieszki Nd^{3+} oraz zbadania właściwości oscylacyjnych i luminescencyjnych materiałów BTBO:Nd^{3+} . Badane mikrokryształiczne proszki BTBO domieszkowane jonami Nd^{3+} o różnych koncentracjach (0,5; 1,0; 2,5; 5,0; 7,5 i 10,0 at.%) zostały zsyntetyzowane przy wykorzystaniu zmodyfikowanej metody Pechiniego. W celu potwierdzenia jednorodności fazowej oraz określenia struktury krystalograficznej badanych proszków zastosowano metodę XRD. BTBO:Nd^{3+} krystalizuje w układzie heksagonalnym (grupa przestrzenna $P6_3$). Analizę morfologiczną BTBO:Nd^{3+} wykonano przy użyciu mikroskopu SEM, natomiast spektroskopia EDX pozwoliła na określenie zawartości poszczególnych atomów w mikrokryształicznych proszkach BTBO:Nd^{3+} . Na podstawie widm Ramana mikrokryształicznych proszków BTBO:Nd^{3+} określono energię fononów matrycy BTBO związaną z drganiami charakterystycznych grup molekularnych BO_3 i TeO_6 oraz zewnętrznymi drganiami sieci (translacje i libracje grup BO_3 i TeO_6 oraz jonów $\text{Bi}^{3+}/\text{Nd}^{3+}$). Z analizy

widm wynika, że domieszkowanie mikrokrystalicznych proszków BTBO jonami Nd^{3+} o różnych koncentracjach nie powoduje zmian w widmach Ramana w porównaniu do widma czystego proszku BTBO. Stosunkowo niska energia fononów matrycy BTBO umożliwia efektywny, wspomagany fononami, transfer energii pomiędzy aktywnymi jonami Bi^{3+} i Nd^{3+} . W celu zbadania właściwości luminescencyjnych proszków BTBO: Nd^{3+} w temperaturze pokojowej zmierzono i przeanalizowano widma odbicia, wzbudzenia, emisji oraz czasy zaniku charakterystycznej emisji jonów Nd^{3+} (przejście $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$). Widma odbicia proszków BTBO oraz BTBO: Nd^{3+} zostały zarejestrowane w zakresie spektralnym 250 – 1000 nm. W widmach odbicia zaobserwowano pasma związane z przejściami $f-f$ jonów Nd^{3+} oraz szerokie pasma zarejestrowane w zakresie spektralnym 200 – 370 nm, z maksimum intensywności przy około 330 nm, pochodzą od przejścia $^1\text{S}_0 \rightarrow ^3\text{P}_1$ jonów Bi^{3+} . Pasma z maksymalną intensywnością około 515 i 530 nm są związane z przejściami $(^4\text{G}_{7/2} + ^4\text{G}_{9/2}) \rightarrow ^4\text{I}_{9/2}$ oraz $^2\text{K}_{13/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} . Piki o największej intensywności zlokalizowane w zakresie 570 – 610 nm zostały przypisane przejściom $(^4\text{G}_{5/2} + ^2\text{G}_{7/2}) \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} . Słabe pasma w zakresie spektralnym 670 – 700 nm odpowiadają przejściom $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} . Pasma w zakresie spektralnym 730 – 775 nm i 780 – 835 nm wynikają z przejść $(^4\text{F}_{7/2} + ^4\text{S}_{3/2}) \rightarrow ^4\text{I}_{9/2}$ i $(^4\text{F}_{5/2} \rightarrow ^2\text{H}_{9/2}) \rightarrow ^4\text{I}_{9/2}$, a piki zlokalizowane w zakresie widmowym 850 – 890 nm przypisano przejściom $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} .

Widma wzbudzenia proszków BTBO: Nd^{3+} zostały zarejestrowane w zakresie spektralnym 250 – 900 nm przez monitorowanie przejścia $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ jonów Nd^{3+} , odpowiadające emisji o długości fali 1064 nm. W widmach wzbudzenia zarejestrowano przejścia $(^4\text{G}_{7/2} + ^4\text{G}_{9/2}) \rightarrow ^4\text{I}_{9/2}$, $^2\text{K}_{13/2} \rightarrow ^4\text{I}_{9/2}$, $(^4\text{G}_{5/2} + ^2\text{G}_{7/2}) \rightarrow ^4\text{I}_{9/2}$, $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$, $(^4\text{F}_{7/2} + ^4\text{S}_{3/2}) \rightarrow ^4\text{I}_{9/2}$, $(^4\text{F}_{5/2} \rightarrow ^2\text{H}_{9/2}) \rightarrow ^4\text{I}_{9/2}$ oraz $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$. Ponadto, dodatkowo zostały zarejestrowane bardzo słabe piki z maksymalną intensywnością około 430 nm odpowiadające przejściom $^2\text{P}_{1/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} . Słabe pasma w zakresie od 450 do 490 nm można przypisać przejściom $^2\text{K}_{15/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} . Ponadto, pasma w zakresie spektralnym 620 – 640 nm odpowiadają przejściom $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{9/2}$ jonów Nd^{3+} .

Widma emisji proszków BTBO: Nd^{3+} zostały zarejestrowane przy wzbudzeniu 327 nm (wzbudzenie jonów Bi^{3+}) i 586 nm (wzbudzenie jonów Nd^{3+}) w zakresie spektralnym 800 – 1200 nm. Pasma emisji o największej intensywności w bliskiej podczerwieni zarejestrowano w widmach BTBO: Nd^{3+} domieszkowanych jonami Nd^{3+} o koncentracjach 0,5 i 5,0 at.% po wzbudzeniu odpowiednio w zakresie widmowym UV i VIS. Czas zaniku luminescencji monitorowany dla emisji o długości fali 1064 nm dla proszków BTBO: Nd^{3+} wykazuje charakter jedno- lub dwuwykładniczy w zależności od koncentracji jonów Nd^{3+} . W pracy przedyskutowano mechanizmy relaksacji energii po wzbudzeniu badanych proszków BTBO: Nd^{3+} w zakresie UV (wzbudzenie jonów Bi^{3+}) lub VIS (wzbudzenie jonów Nd^{3+}). Praca przedstawia szczegółową analizę luminescencji mikrokrystalicznych

proszków BTBO:Nd³⁺ uwzględniając procesy konwersji energii w dół wspomagane wzbudzeniami fononów matrycy. Badane mikrokrystaliczne proszki BTBO:Nd³⁺ skutecznie konwertują promieniowanie z zakresu UV/VIS do zakresu NIR i mogą być potencjalnie stosowane jako efektywne konwertery spektralne. Na podstawie otrzymanych wyników określono optymalną koncentrację Nd³⁺ na poziomie 5,0 at.% w matrycy BTBO, a także stwierdzono istotną rolę niskiej energii fononów w efektywnym transferze energii pomiędzy jonami Bi³⁺ oraz Nd³⁺.

W publikacji **P2** doktorant wykonał pomiary metodą spektroskopii Ramana jak również współuczestniczył w pomiarach właściwości luminescencyjnych. W szczególności, na podstawie widm Ramana doktorant przeanalizował występujące w matrycy BTBO drgania charakterystycznych grup molekularnych BO₃ i TeO₆ oraz zewnętrzne drgania sieci krystalicznej związane z translacjami oraz libracjami grup BO₃, TeO₆ i jonów Bi³⁺/Nd³⁺. Doktorant przedstawił również analizę kinetyki zaniku luminescencji dla badanych materiałów rozszerzając analizę o wyniki otrzymane z wykorzystaniem teoretycznego modelu zaproponowanego przez Inokuti-Hirayama. Ponadto, doktorant współuczestniczył w opracowaniu, analizie i interpretacji wyników eksperymentalnych oraz współuczestniczył w redagowaniu tekstu manuskryptu.

W publikacji **P3** przedstawiono wyniki pomiarów właściwości luminescencyjnych mikrokrystalicznych proszków BTBO domieszkowanych jonami Yb³⁺ i/lub Er³⁺. W szczególności przeanalizowano proces transferu energii oraz emisji w zakresie NIR badanych materiałów. Celem badań było wyjaśnienie mechanizmów wzmocnienia emisji jonów Er³⁺ około 1531 nm przez synergiczne oddziaływania aktywnych jonów Bi³⁺, Yb³⁺ i Er³⁺ oraz określenie potencjalnych zastosowań mikrokrystalicznych proszków BTBO:Yb³⁺/Er³⁺ w technologii fotowoltaicznej. W publikacji zostały opisane badania mikrokrystalicznych proszków BTBO:Yb³⁺, BTBO:Er³⁺ oraz BTBO:Yb³⁺/Er³⁺ syntezowanych zmodyfikowaną metodą Pechiniego. Koncentracje domieszek wynosiły odpowiednio: 5,0 at.% dla Yb³⁺ oraz 1,0 at.% dla Er³⁺. Badania XRD potwierdziły heksagonalną strukturę (grupa przestrzenna P6₃) mikrokrystalicznych proszków BTBO:Er³⁺, BTBO:Yb³⁺ oraz BTBO:Yb³⁺/Er³⁺ z niezmienną symetrią przy wprowadzonych domieszkach. Średnie rozmiary krystalitów, obliczone metodą Scherrera, były w zakresie od 39 do 58 nm. Morfologia badanych próbek BTBO:Er³⁺, BTBO:Yb³⁺ oraz BTBO:Yb³⁺/Er³⁺ została określona przy zastosowaniu techniki SEM. Wyniki badań metodą spektroskopii Ramana wykazały niską energię fononów matrycy BTBO, co sprzyja efektywnemu transferowi energii między aktywnymi jonami Bi³⁺, Yb³⁺ i Er³⁺, natomiast pasma zarejestrowane w widmach w zakresie 100 – 1000 cm⁻¹ przypisano drganiom charakterystycznych grup molekularnych BO₃ i TeO₆ oraz zewnętrznym drganiom sieci (translacje i libracje grup BO₃ i TeO₆ oraz jonów Bi³⁺, Yb³⁺ i/lub Er³⁺).

W celu zbadania właściwości luminescencyjnych materiałów BTBO:Yb³⁺, BTBO:Er³⁺ i BTBO:Yb³⁺/Er³⁺ zmierzono widma odbicia, wzbudzenia i emisji. Widma odbicia wyżej wspomnianych mikrokrystalicznych proszków zostały zarejestrowane w zakresie spektralnym 250 – 2500 nm w temperaturze pokojowej. Wyniki pozwoliły na identyfikację pasm przypisanych do jonów Bi³⁺, Yb³⁺ oraz Er³⁺. Silne i szerokie pasma zarejestrowane w zakresie 210 – 460 nm z maksymalną intensywnością około 260/326 nm, związane są z przejściami ¹S₀ → ³P₁ jonów Bi³⁺. W badanych układach jony Bi³⁺ pełniły rolę sensybilizatora, które po wzbudzeniu efektywnie przekazują energię do jonów Yb³⁺ i Er³⁺. Pasma w zakresie 460 – 560 nm oraz 620 – 690 nm przypisano przejściom wzbudzonych jonów Er³⁺. W zakresie 890 – 1040 nm zidentyfikowano przejścia jonów Yb³⁺ (²F_{5/2} → ²F_{7/2}) oraz Er³⁺ (⁴F_{7/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2}, ²H_{11/2} → ⁴I_{15/2}, ⁴F_{9/2} → ⁴I_{15/2}, ⁴I_{11/2} → ⁴I_{15/2} i ⁴I_{13/2} → ⁴I_{15/2}). Charakterystyczne pasma emisji jonów Er³⁺ w zakresie 1420 – 1600 nm z maksymalną intensywnością emisji przy około 1531 nm w BTBO:Er³⁺ i BTBO:Yb³⁺/Er³⁺ przypisano przejściom ⁴I_{13/2} → ⁴I_{15/2} jonów Er³⁺. Na podstawie widm odbicia, zgodnie z modelem Kubelka-Munk'a i przy użyciu metody Tauc'a, wyznaczono energię pasma wzbronionego E_g dla BTBO:Yb³⁺/Er³⁺, która wyniosła 2,98 eV. Wartość ta jest zgodna z wartościami E_g obliczonymi teoretycznie przy użyciu funkcjonatów DFT-LDA i DFT-GGA (2,96 i 3,21 eV) [64]. Widma wzbudzenia wyżej wspomnianych materiałów zarejestrowano w zakresie spektralnym 250 – 700 nm monitorując emisję związaną z przejściem ²F_{5/2} → ²F_{7/2} jonów Yb³⁺ (około 975 nm) oraz emisję związaną z przejściem ⁴I_{13/2} → ⁴I_{15/2} jonów Er³⁺ (około 1531 nm). W widmach zostały zarejestrowane szerokie i intensywne pasma w zakresie 285 – 374 nm z maksimum intensywności około 333 nm, które odpowiadają przejściu ¹S₀ ← ³P₁ jonów Bi³⁺. Ponadto, w widmach wzbudzenia przy monitorowaniu emisji 1531 nm (⁴I_{13/2} → ⁴I_{15/2}) zostały zarejestrowane następujące pasma przypisane przejściom jonów Er³⁺: (²K_{15/2} + ⁴G_{7/2}) ← ⁴I_{15/2}, ⁴G_{11/2}; _{9/2} ← ⁴I_{15/2}, ²H_{9/2} ← ⁴I_{15/2}, ⁴F_{5/2}; _{3/2} ← ⁴I_{15/2}, ⁴F_{7/2} ← ⁴I_{15/2}, ²H_{11/2} ← ⁴I_{15/2}, ⁴S_{3/2} ← ⁴I_{15/2} oraz ⁴F_{9/2} ← ⁴I_{15/2}. Widma emisji proszków BTBO:Yb³⁺, BTBO:Er³⁺ i BTBO:Yb³⁺/Er³⁺ oraz niedomieszkowanego BTBO zarejestrowano w zakresach 430 – 650 nm oraz 800 – 1650 nm po wzbudzeniu jonów Bi³⁺ około 327 nm. W pierwszym zakresie dla wszystkich próbek zarejestrowano szerokie pasma emisji z maksimum około 560 nm, przypisane przejściom ³P₀ → ¹S₀ jonów Bi³⁺, co sugeruje, że jony Bi³⁺ obecne w matrycy BTBO mogą być wykorzystane jako sensybilizatory przez absorpcję energii w zakresie UV, przekazywanej następnie do jonów Yb³⁺ i Er³⁺. W drugim zakresie wykryto typową emisję jonów Er³⁺ z maksymalną intensywnością około 1531 nm (przejście ⁴I_{13/2} → ⁴I_{15/2}) dla BTBO:Er³⁺ i BTBO:Yb³⁺/Er³⁺ oraz jonów Yb³⁺ z maksymalną intensywnością około 975 nm (przejście ²F_{5/2} → ²F_{7/2}) dla BTBO:Yb³⁺ oraz BTBO:Yb³⁺/Er³⁺. Należy zauważyć, że intensywność pasm emisji przy 975 nm jest wyższa dla BTBO:Yb³⁺ niż dla BTBO:Yb³⁺/Er³⁺ ze względu na fakt, że w przypadku BTBO:Yb³⁺ całkowita energia

wzbudzonych jonów Bi^{3+} jest przekazywana do jonów Yb^{3+} , a w przypadku $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ energia ze wzbudzonych jonów Bi^{3+} jest przekazywana do jonów Yb^{3+} oraz do jonów Er^{3+} . Co więcej, pasma emisji przy 1531 nm zarejestrowane w widmie $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ miały wyższą intensywność niż pasma zarejestrowane dla $\text{BTBO}:\text{Er}^{3+}$, co jest wynikiem transferu energii ze wzbudzonych jonów Bi^{3+} bezpośrednio do jonów Er^{3+} , jak również transferu energii z jonów Yb^{3+} (wzbudzonych przez jony Bi^{3+}) do jonów Er^{3+} . Ten synergiczny efekt transferu energii między aktywnymi jonami Bi^{3+} , Yb^{3+} i Er^{3+} spowodował emisję o większej intensywności około 1531 nm jonów Er^{3+} mikrokrystalicznych proszków $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$. Widma emisji proszków $\text{BTBO}:\text{Er}^{3+}$ i $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ zarejestrowano również w zakresie spektralnym 1400 – 1650 nm przy wzbudzeniu diodą laserową z emisją o długości fali 975 nm. W widmach zarejestrowano szerokie pasma o maksymalnej intensywności około 1531 nm, przypisane przejściom $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ jonów Er^{3+} , przy czym intensywność pasm tej emisji jest wyższa dla $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$. Obserwowana silna emisja jonów Er^{3+} wynika z dodatkowego transferu energii ze wzbudzonych jonów Yb^{3+} do wzbudzonych poziomów jonów Er^{3+} . Na podstawie zmierzonych czasów zaniku emisji związanych z przejściem $^3\text{P}_0 \rightarrow ^1\text{S}_0$ jonów Bi^{3+} oraz przejściem $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ jonów Yb^{3+} badanych próbek wykonano obliczenia ETE oraz QE, które potwierdziły efektywny transfer energii pomiędzy jonami Bi^{3+} i Yb^{3+} oraz Yb^{3+} i Er^{3+} .

Na podstawie otrzymanych wyników można wnioskować, że układ $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ wykazuje wysoką efektywność transferu energii pomiędzy aktywnymi jonami Bi^{3+} , Yb^{3+} oraz Er^{3+} . Wyniki te wskazują na potencjał tego materiału do zastosowań w technologii fotowoltaicznej jako wydajnego konwertera spektralnego.

W publikacji **P3** doktorant wykonał pomiary metodą spektroskopii Ramana. Na podstawie analizy widm Ramana doktorant wyznaczył parametry spektralne pasm związanych z drganiami charakterystycznych grup molekularnych BO_3 i TeO_6 oraz drgań sieciowych (translacje i libracje grup BO_3 i TeO_6 oraz jonów Bi^{3+} , Yb^{3+} i/lub Er^{3+}) występujących w matrycy BTBO. Doktorant współuczestniczył w pomiarach widm wzbudzenia, emisji i czasów zaniku oraz przedstawił analizę kinetyki zaniku luminescencji, wykonał obliczenia wydajności transferu energii pomiędzy aktywnymi jonami i wydajności kwantowej badanych materiałów. Ponadto, doktorant współuczestniczył w opracowaniu, analizie oraz interpretacji otrzymanych wyników i w redagowaniu tekstu manuskryptu.

W publikacji **P4** przeanalizowano wpływ ciśnienia stosowanego podczas procesu wytwarzania ceramiek $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ na ich właściwości luminescencyjne. Głównym celem pracy było wyjaśnienie, jak parametry procesu HPLT wpływają na strukturę krystaliczną, efektywność emisji w procesie konwersji energii w górę, czas zaniku luminescencji oraz mechanizm transferu energii

między aktywnymi jonami Yb^{3+} oraz Er^{3+} w badanych materiałach. Mikrokrystaliczne proszki $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ o koncentracji domieszek 5,0 at.% Yb^{3+} oraz 1,0 at.% Er^{3+} wykonano, przy użyciu zmodyfikowanej metody Pechiniego. Natomiast próbki w formie ceramiek przygotowano opisaną wcześniej metodą HPLT. Analiza XRD ceramiek $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ potwierdziła strukturę heksagonalną (grupa przestrzenna $P6_3$) ceramiek otrzymanych przy zastosowaniu ciśnienia 2, 4, 6 lub 8 GPa. Ponadto, na podstawie obliczeń stwierdzono różnicę parametrów komórki elementarnej dla poszczególnych ceramiek, wynikającą z procesu technologicznego HPLT. Dodatkowo, na podstawie obliczeń wielkości krystalitów stwierdzono zmniejszenie rozmiaru krystalitów w ceramikach w porównaniu z proszkiem $\text{BTBO} \text{Yb}^{3+}/\text{Er}^{3+}$, z którego zostały wytworzone ceramiki (97 nm dla proszków oraz 32 – 40 nm dla ceramiek). W widmach Ramana ceramiek $\text{BTBO} \text{Yb}^{3+}/\text{Er}^{3+}$ zarejestrowano pasma związane z charakterystycznymi drganiami wewnętrznymi grup BO_3 i TeO_6 oraz drganiami sieciowymi (translacje i libracje grup BO_3 i TeO_6 oraz jonów $\text{Bi}^{3+}, \text{Yb}^{3+}$ i/lub Er^{3+}). Dodatkowo stwierdzono, że niska energia fononów w matrycy BTBO sprzyjała efektywnemu transferowi energii między aktywnymi jonami Yb^{3+} oraz Er^{3+} , co jest kluczowe dla wzmocnienia procesu konwersji energii w górę w układach $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$. Właściwości luminescencyjne ceramiek $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ przeanalizowano na podstawie zarejestrowanych widm emisji w zakresie 450 – 750 nm przy wzbudzeniu diodą laserową z emisją promieniowania o długości fali 975 nm. Zarejestrowane pasma emisji przypisano przejściom energetycznym jonów Er^{3+} : $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ (ok. 523 nm), $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ (ok. 540 nm) oraz $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ (ok. 653 nm). Zaobserwowana emisja była wynikiem procesu transferu energii między jonami Yb^{3+} i Er^{3+} . Na podstawie otrzymanych wyników stwierdzono, że intensywność pasm wzrasta dla próbek wytworzonych pod ciśnieniem 2, 4, 6 lub 8 GPa zastosowanym w procesie spiekania, osiągając maksymalną wartość dla ceramiek spiekanych pod ciśnieniem 8 GPa. Z analizy czasów życia wyżej wspomnianych emisji wynika, że czasy życia luminescencji (523, 540 oraz 653 nm) osiągają najwyższe wartości dla ceramiki spiekanej pod ciśnieniem 8 GPa i są prawie dwukrotnie większe w porównaniu do czasów życia próbek proszkowych, głównie z powodu mniejszej liczby defektów w strukturze ceramiek. Podsumowując, praca **P4** zawiera analizę procesów luminescencji w ceramikach $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$, uwzględniając wpływ ciśnienia stosowanego w procesie spiekania metodą HPLT na strukturę i morfologię oraz efektywność emisji jonów Er^{3+} w zakresie VIS. Z wykonanych badań ceramiek $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$ wynika, że odpowiednio dobrane parametry spiekania metodą HPLT, zwłaszcza ciśnienie, mogą znacząco poprawić właściwości luminescencyjne materiału $\text{BTBO}:\text{Yb}^{3+}/\text{Er}^{3+}$, co czyni ten materiał obiecującym do zastosowań w technologii fotowoltaicznej, optoelektronice lub fotonice.

W publikacji **P4** doktorant współuczestniczył w wytwarzaniu ceramicznych próbek oraz w pomiarach XRD, SEM oraz pomiarach metodami spektroskopii optycznej. Ponadto, doktorant samodzielnie wykonał pomiary metodą spektroskopii Ramana oraz wykonał obliczenia, związane z określeniem liczby fotonów uczestniczących w procesach konwersji energii w górę, a także czasów życia luminescencji. Doktorant współuczestniczył w opracowaniu, analizie i interpretacji uzyskanych wyników eksperymentalnych oraz w redagowaniu tekstu manuskryptu.

W publikacji **P5** badano procesy luminescencji w mikrokryształicznych proszkach BTBO domieszkowanych jonami Yb^{3+} . Celem pracy było zbadanie mechanizmów transferu energii z jonów Bi^{3+} do Yb^{3+} oraz określenie wpływu różnych koncentracji domieszki na wydajność emisji jonów Yb^{3+} w zakresie NIR.

W szczególności przedmiotem pracy **P5** było zbadanie możliwości użycia matrycy BTBO jako sensybilizatora promieniowania UV, wspomagającego emisję jonów Yb^{3+} w zakresie NIR. Mikrokryształiczne proszki BTBO: Yb^{3+} o koncentracjach domieszki 0,5; 1,0; 2,5; 4,0 oraz 7,5 at.% zostały zsyntetyzowane zmodyfikowaną metodą Pechinigo, a ich struktura, morfologia i skład atomowy były analizowane przy zastosowaniu technik XRD, SEM oraz EDX. Badania XRD potwierdziły heksagonalną strukturę (grupa przestrzenna $P6_3$) mikrokryształicznych proszków BTBO: Yb^{3+} . Na podstawie pomiarów SEM stwierdzono różnice w rozmiarach ziaren (od 1 do 30 μm) zależnie od koncentracji jonów Yb^{3+} w badanych próbkach BTBO: Yb^{3+} . Ponadto, porównano teoretyczne i eksperymentalne zawartości jonów Yb^{3+} i Bi^{3+} w matrycy BTBO na podstawie danych EDX oraz obliczeń wykonanych dla poszczególnych koncentracji domieszek. Obliczono również stosunek ilościowy jonów $\text{Yb}^{3+}/\text{Bi}^{3+}$ dla BTBO: Yb^{3+} o różnych koncentracjach jonów Yb^{3+} , który jest kluczowy dla wyjaśnienia wpływu domieszkowania na właściwości strukturalne i luminescencyjne badanych materiałów. W widmach Ramana BTBO: Yb^{3+} o różnych koncentracjach jonów Yb^{3+} stwierdzono obecność pasm związanych z charakterystycznymi drganiami wewnętrznymi grup BO_3 i TeO_6 oraz zewnętrznym drganiami sieci (translacje i libracje grup BO_3 i TeO_6 oraz jonów $\text{Bi}^{3+}/\text{Yb}^{3+}$). W celu uzyskania informacji o właściwościach luminescencyjnych proszków BTBO: Yb^{3+} zmierzono i przeanalizowano widma wzbudzenia, widma emisji oraz czasy życia luminescencji jonów Bi^{3+} i Yb^{3+} w zakresach VIS oraz NIR. W widmach wzbudzenia zarejestrowanych w zakresie 270 – 800 nm, występują szerokie pasma z maksimum około 330 nm przypisane przejściu $^1\text{S}_0 \leftarrow ^3\text{P}_1$ jonów Bi^{3+} . W widmach emisji, zarejestrowanych w zakresie 425 – 640 nm występują szerokie pasma z maksymalną intensywnością około 550 nm (przejścia $^3\text{P}_0 \rightarrow ^1\text{S}_0$ jonów Bi^{3+}), natomiast w widmach zarejestrowanych w zakresie 900 – 1100 nm występują pasma emisji z maksimum intensywności około 975 nm (przejście $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ jonów Yb^{3+}). Czas życia emisji jonów Bi^{3+} (emisja w zakresie VIS

z maksymalną intensywnością około 550 nm) zmniejsza się wraz ze wzrostem koncentracji jonów Yb^{3+} . Ponadto, w przypadku emisji jonów Yb^{3+} (emisja w zakresie NIR z maksymalną intensywnością około 975 nm) wartości czasów życia wzrastały z 248 μs dla próbek BTBO: Yb^{3+} o koncentracji 0,5 at.% jonów Yb^{3+} do 381 μs dla próbek BTBO: Yb^{3+} o koncentracji 4,0 at.% jonów Yb^{3+} , a następnie malały dla wyższych koncentracji jonów Yb^{3+} . Obliczone współczynniki ETE oraz QE wynoszą odpowiednio 13,5% oraz 113,5% dla optymalnej koncentracji jonów Yb^{3+} w mikrokryształicznych proszkach BTBO: Yb^{3+} wynoszącej 4,0 at.%, co czyni ten materiał obiecującym konwerterem spektralnym z zakresu UV do NIR. W pracy wykazano, że jony Bi^{3+} mogą pełnić funkcję efektywnego sensybilizatora UV dla emisji jonów Yb^{3+} w NIR, dzięki czemu mikrokryształiczne proszki BTBO: Yb^{3+} mogą potencjalnie znaleźć zastosowanie jako konwertery spektralne w technologii krzemowych (c-Si) ogniw słonecznych.

W publikacji [P5](#) doktorant samodzielnie wykonał pomiary metodą spektroskopii Ramana, przedstawił analizę kinetyki zaniku luminescencji, wykonał obliczenia wydajności transferu energii i wydajności kwantowej badanych materiałów oraz zaproponował mechanizm transferu energii między jonami Bi^{3+} oraz Yb^{3+} . Doktorant współuczestniczył także w opracowaniu, analizie i interpretacji uzyskanych wyników eksperymentalnych oraz w redagowaniu tekstu manuskryptu.

4. Podsumowanie i wnioski

Rozprawa doktorska, stanowiąca cykl spójnych tematycznie pięciu artykułów naukowych **P1–P5**, prezentuje wyniki badań właściwości strukturalnych, oscylacyjnych oraz luminescencyjnych mikrokrystalicznych materiałów BTBO domieszkowanych wybranymi jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} . Badane mikrokrystaliczne proszki wykonano przy zastosowaniu zmodyfikowanej metody Pechiniego, natomiast ceramiki domieszkowane jonami $\text{Yb}^{3+}/\text{Er}^{3+}$ wytworzone zostały metodą HPLT. Głównym celem badań było określenie wpływu jonów domieszek na strukturę krystaliczną, dynamikę sieci oraz mechanizmy luminescencji w procesach konwersji energii w górę lub w dół. Na podstawie wykonanych badań właściwości strukturalnych, oscylacyjnych oraz luminescencyjnych mikrokrystalicznych proszków BTBO: Nd^{3+} , BTBO: Yb^{3+} , BTBO: Er^{3+} i BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ oraz ceramiek BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ uzyskano wyniki dotyczące zależności pomiędzy strukturą krystaliczną, a właściwościami luminescencyjnymi i mechanizmami transferu energii pomiędzy aktywnymi jonami Bi^{3+} oraz Nd^{3+} , Yb^{3+} i/lub Er^{3+} .

Badania mikrokrystalicznych proszków BTBO domieszkowanych wybranymi jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} techniką XRD wykazały, że materiały te krystalizują w układzie heksagonalnym (grupa przestrzenna $P6_3$). Jony Nd^{3+} , Yb^{3+} i/lub Er^{3+} wbudowują się w pozycje jonów Bi^{3+} matrycy BTBO ze względu na zbliżone wartości promieni jonowych dla Nd^{3+} (0,983 Å), Yb^{3+} (0,868 Å) oraz Er^{3+} (0,89 Å) do wartości promienia jonowego jonu Bi^{3+} (1,03 Å). Wprowadzenie jonów Nd^{3+} , Yb^{3+} lub Er^{3+} do struktury BTBO nie powodowało zmiany symetrii ani pojawienia się dodatkowych faz, co świadczy o skutecznej inkorporacji domieszek do struktury krystalicznej matrycy BTBO. Dodatkowo, z analizy Rietvelda wykonanej dla próbek BTBO: Nd^{3+} , BTBO: Yb^{3+} , BTBO: Er^{3+} lub BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ wynika, że domieszki jonów Nd^{3+} , Yb^{3+} i/lub Er^{3+} nie wprowadzają zaburzeń w strukturze krystalicznej BTBO, a zaobserwowane zmiany objętości komórki elementarnej są wynikiem różnicy promieni jonowych RE^{3+} wbudowujących się w pozycje jonów Bi^{3+} . Zachowanie jednorodnej fazy nawet przy zwiększonej koncentracji domieszek potwierdza wysoką stabilność struktury BTBO i możliwości wbudowania jonów RE^{3+} bez destabilizacji sieci krystalicznej [**P2–P5**].

Na podstawie badań SEM wykonanych dla proszków i ceramiek BTBO domieszkowanych jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} stwierdzono obecność ziaren o rozmiarach w zakresie od kilkuset nanometrów do kilku mikrometrów, co jest typowe dla materiałów otrzymywanych metodą Pechiniego. W przypadku ceramiek BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ zaobserwowano zwartą mikrostrukturę z dobrze rozwiniętymi ziarnami o wyraźnych granicach, co potwierdza wysoką jakość procesu spiekania metodą HPLT, prowadzącego do poprawy krystaliczności i zmniejszenia defektów strukturalnych [**P2–P5**].

Analiza składu atomowego wykonana na podstawie pomiarów metodą EDX potwierdziła obecność pierwiastków matrycy: Bi, Te, B, O oraz domieszek Nd, Yb i/lub Er w proporcjach zgodnych z zaplanowanymi w procesie technologicznym. Ponadto, rozkład domieszek w analizowanej objętości wskazuje na efektywne ich wprowadzenie do matrycy BTBO [P2,P4 i P5].

Z zarejestrowanych widm FT-IR/MIR dla czystego BTBO oraz widm Ramana dla czystego i domieszkowanego BTBO jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} uzyskano wiele istotnych informacji na temat dynamiki sieci krystalicznej. W przypadku czystego BTBO zaobserwowano charakterystyczne pasma przypisane drganiom wewnętrznym jednostek BO_3 i TeO_6 oraz zewnętrznym drganiom sieci: translacje i libracje grup BO_3 i TeO_6 oraz jonów Bi^{3+} (Nd^{3+} , Yb^{3+} i/lub Er^{3+}) i Te^{6+} . Najintensywniejsze pasma zlokalizowane w zakresie $700 - 800 \text{ cm}^{-1}$ przypisano symetrycznym drganiom rozciągającym B–O oraz Te–O. Stwierdzono, że wprowadzenie jonów Nd^{3+} , Yb^{3+} i/lub Er^{3+} do struktury matrycy BTBO nie spowodowało znaczących zmian w widmach Ramana. Parametry spektralne wybranych pasm w widmach Ramana (szerokość połówkowa oraz intensywność integralna) świadczy o tym, że jony RE^{3+} zostały skutecznie wprowadzone w pozycje Bi^{3+} bez formowania oddzielnych faz, co jest zgodne z wynikami analiz strukturalnych wykonanych metodą XRD [P1–P5].

Właściwości luminescencyjne mikrokryształicznych materiałów BTBO domieszkowanych jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} zostały zbadane i przeanalizowane biorąc pod uwagę w szczególności: efektywność emisji promieniowania w zakresie VIS i NIR, mechanizmy transferu energii oraz możliwość zastosowania tych materiałów jako materiały konwertujące promieniowanie elektromagnetyczne z zakresu UV/VIS do NIR (proszki BTBO:Nd^{3+} , BTBO:Yb^{3+} , BTBO:Er^{3+} lub $\text{BTBO:Yb}^{3+}/\text{Er}^{3+}$) lub z NIR do VIS (ceramiki $\text{BTBO:Yb}^{3+}/\text{Er}^{3+}$) [P2–P5].

W przypadku materiałów domieszkowanych jonami Nd^{3+} zaobserwowano intensywną emisję w zakresie $870 - 1380 \text{ nm}$, przypisaną przejściom $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$, $^4\text{I}_{11/2}$ i $^4\text{I}_{13/2}$ jonów Nd^{3+} . Badania wykazały, że transfer energii ze wzbudzonych poziomów jonów Bi^{3+} oraz Nd^{3+} może prowadzić do emisji w zakresie NIR w procesie konwersji energii w dół [P2].

W materiałach domieszkowanych Yb^{3+} i/lub Er^{3+} stwierdzono wzmocnienie emisji około 975 i/lub 1531 nm będącą skutkiem transferu energii z jonów Bi^{3+} do Yb^{3+} i/lub Er^{3+} . Wykonane pomiary wykazały, że jony Yb^{3+} pełnią rolę efektywnego sensybilizatora w układach $\text{BTBO:Yb}^{3+}/\text{Er}^{3+}$, przekazując energię do jonów Er^{3+} , co znacząco zwiększa intensywność emisji jonów Er^{3+} [P3].

Zjawisko konwersji energii w górę zaobserwowane w ceramikach $\text{BTBO:Yb}^{3+}/\text{Er}^{3+}$ wzbudzonych promieniowaniem laserowym o długości fali 975 nm skutkowało emisją w zakresie VIS (523 , 540 oraz 653 nm), przypisaną mechanizmowi transferu energii w górę z jonów Yb^{3+} do Er^{3+} . Efektywność procesu konwersji energii w górę była zależna od stosunku molowego $\text{Yb}^{3+}/\text{Er}^{3+}$, ale

również od ciśnienia stosowanego w trakcie wytwarzania ceramiek. Badania luminescencji ceramiek BTBO:Yb³⁺/Er³⁺ wykazały, że wzrastające ciśnienie stosowane w trakcie wytwarzania ceramiek prowadzi do znacznego wzrostu intensywności emisji ceramiek BTBO:Yb³⁺/Er³⁺ około 523, 540 oraz 653 nm odpowiadające przejściom ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} oraz ⁴F_{9/2} → ⁴I_{15/2}. Ponadto, wyniki wskazują, że próbka ceramiczna wytworzona przy ciśnieniu 8 GPa osiąga najwyższą intensywność emisji dla wyżej wymienionych przejść emisji [P4].

W mikrokryształicznych proszkach domieszkowanych jonami Yb³⁺ występuje efektywny mechanizm transferu energii z jonów Bi³⁺ do jonów Yb³⁺, prowadzący do emisji w zakresie NIR około 975 nm. Taki transfer energii matrycy BTBO do domieszkowanych jonów Yb³⁺ może mieć istotne znaczenie dla optymalizacji domieszkowania materiałów luminescencyjnych aktywowanych jonami Yb³⁺ w matrycy BTBO [P5].

Wykonane w ramach pracy doktorskiej badania umożliwiły realizację założonego celu, jakim było otrzymanie i szczegółowa charakterystyka materiałów mikrokryształicznych BTBO domieszkowanych jonami Nd³⁺, Yb³⁺ i/lub Er³⁺. Wytworzone materiały wykazały zdolność do efektywnej konwersji promieniowania z zakresu UV/VIS do NIR (proszki BTBO:Nd³⁺, BTBO:Yb³⁺, BTBO:Er³⁺ lub BTBO:Yb³⁺/Er³⁺) oraz z NIR do VIS (ceramiki BTBO:Yb³⁺/Er³⁺). Mechanizmy transferu energii pomiędzy matrycą BTBO (jony Bi³⁺) a jonami Nd³⁺, Yb³⁺ i/lub Er³⁺ zostały szczegółowo przeanalizowane i opisane w publikacjach P2, P3 oraz P5.

Otrzymane wyniki świadczą o potencjale materiałów BTBO domieszkowanych jonami Nd³⁺, Yb³⁺ i/lub Er³⁺ do zastosowań jako konwertery promieniowania z zakresu UV/VIS do NIR (BTBO:Nd³⁺, BTBO:Yb³⁺, BTBO:Er³⁺, BTBO:Yb³⁺/Er³⁺) oraz z NIR do VIS (BTBO:Yb³⁺/Er³⁺), w których możliwe jest precyzyjne sterowanie procesami emisji i transferu energii poprzez dobór odpowiedniego rodzaju i koncentracji domieszek. Możliwość efektywnego transferu energii zarówno pomiędzy jonami domieszek Yb³⁺ → Er³⁺ jak i możliwością transferu energii z matrycy BTBO (jony Bi³⁺) a jonami Nd³⁺, Yb³⁺ i/lub Er³⁺, otwiera nowe perspektywy dla projektowania materiałów o ulepszonych właściwościach luminescencyjnych (np. wyższa intensywność emisji, dłuższe czasy życia, wyższe wartości ETE oraz QE) [P2–P5].

Obserwowane zjawiska konwersji energii w dół lub górę, efektywna emisja w zakresie NIR i/lub VIS, a także możliwość wzmacniania luminescencji przez parametry zewnętrzne (ciśnienie stosowane w trakcie wytwarzania ceramiek) wskazują na potencjał aplikacyjny badanych materiałów m.in. w takich obszarach jak:

- fotowoltaika – jako konwertery optyczne z zakresu UV/VIS do zakresu NIR stosowane w technologii ogniw fotowoltaicznych w celu zwiększenia efektywności konwersji słonecznej w energię elektryczną,

- optoelektronika – jako źródła emisji w strategicznych zakresach długości fal (np. 975 i 1531 nm) do zastosowań telekomunikacyjnych,

- fotonika – ze względu na możliwość wykorzystania emisji w zakresie NIR w nowoczesnych technologiach optycznych (bioobrazowanie, czujniki i detektory optyczne).

Zróżnicowanie morfologiczne badanych materiałów krystalicznych BTBO domieszkowanych jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} (mikrokrystaliczne proszki i/lub ceramiki), zastosowane metody syntezy oraz techniki pomiarowe, a także analiza właściwości strukturalnych, oscylacyjnych i luminescencyjnych świadczą o dużym potencjale układów BTBO domieszkowanych jonami Nd^{3+} , Yb^{3+} i/lub Er^{3+} do zastosowań w wymienionych wyżej obszarach.

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Lattice dynamics of Bi₃TeBO₉ microcrystals: μ -Raman/IR spectroscopic investigation and ab initio analysis



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ABSTRACT

A Bi₃TeBO₉ crystal is an excellent nonlinear optical material as well as an efficient host matrix for luminescent rare earth ions. Investigated Bi₃TeBO₉ microcrystals were synthesized by means of the modified Pechini method. XRD measurements of Bi₃TeBO₉ confirmed its hexagonal structure with noncentrosymmetric P6₃ space group. The vibrational properties of Bi₃TeBO₉ were studied using μ -Raman and FT-IR/MIR spectroscopy. The theoretical lattice dynamics study of Bi₃TeBO₉ crystal at room temperature comprises the group theory analysis and the ab initio calculations of phonon mode spectrum in Brillouin zone centre. The unpolarized Raman and IR spectra were analyzed in details on the basis of group theory predictions and the results of ab initio calculations of phonon spectra.

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1. Introduction

Nonlinear optical (NLO) crystals are widely used for frequency conversion of laser radiation [1]. The tuning/conversion of the fundamental wavelengths of laser emission of active ions can be realized in NLO crystals by second or third harmonics generation, sum or difference frequency generation or optical parametric oscillations [2]. To expand the laser emission possibilities, the search for new highly efficient NLO materials is a continuous subject of interest. Recently, some novel NLO materials were suggested basing on first-principle calculations [3–5]. Moreover, the effectivity of nonlinear processes as well as energy transfer between the active ions in laser crystals strongly depends on the crystals properties, especially their lattice dynamics.

From among NLO crystals, borates are known as very effective NLO materials for frequency conversion of laser emission from near infrared through visible and ultraviolet, to vacuum-ultraviolet spectral regions [6–8]. The optical properties of borate crystals

are related to their molecular structure, especially the presence of anionic groups such as BO₃, BO₄, B₃O₆ or B₃O₇ [9]. Several borate crystals such as β -BaB₂O₄, LiB₃O₅, CsB₃O₅, α -BiB₃O₆, CsLiB₅O₁₀ or Bi₂ZnOB₂O₆ are constructed from the network of these basic structural units and are often used as second-order NLO materials [9,10]. Another effective group of NLO crystals contains in their structure other NLO active units, i.e. MO₆ octahedra, containing cations (such as M = Ti⁴⁺, Nb⁵⁺, Ta⁵⁺, Mo⁶⁺, W⁶⁺ or Te⁶⁺) susceptible to second-order Jahn–Teller distortions, resulting in asymmetric coordination environments in the crystal structure and consequently in the large second harmonic generation (SHG) responses [11]. This effect was observed for example in BaTeMo₂O₉ or BaTeW₂O₉ crystals [12].

Recently, M. Xia et al. [11] reported synthesis of a novel Bi₃TeBO₉ (abbreviated as BTBO) crystal, which contains three types of NLO-active units, planar borate BO₃ groups, second-order Jahn–Teller distorted octahedra TeO₆ and stereochemically active lone pair of electrons in Bi³⁺ cations [11]. The additive contribution from these three types of NLO active groups results in a synergetic effect that is an extremely large SHG response in BTBO (about 20 times that of KDP), exhibiting the largest SHG effect from among the known

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borate NLO materials. The crystal structure, electronic structure, and some optical properties of BTBO were reported by M. Xia et al. [11]. Moreover, some of the structure, optical, elastic, and spectroscopic properties of BTBO were also reported by other authors [13–15]. *Ab initio* calculation of electronic structure and photoinduced phenomena of BTBO was recently published in paper [14].

Investigated BTBO microcrystals were synthesized by means of the modified Pechini method and their phase uniformity was examined using x-ray diffraction (XRD) analysis. In this paper, we present a systematic lattice dynamics study of BTBO on the basis of μ -Raman and Fourier transform infrared (FT-IR) spectroscopy measurements and *ab initio* analysis. The unpolarized Raman and IR spectra of BTBO were recorded in the range of external and internal vibrations and the modes assignment was made on the basis of group theory analysis and first-principle calculations. To the best of our knowledge, the complex lattice dynamics study of BTBO crystal at room temperature (RT) that comprises the experimental Raman, IR spectra investigation, the group theory analysis and the calculation of phonon mode spectrum in Brillouin zone centre are presented for the first time.

2. Synthesis procedure of BTBO

BTBO powder was synthesized by means of a modified Pechini method [16]. The following precursor materials were used for the synthesis, without additional purification: commercial bismuth oxide (Bi_2O_3 , SIAL, 99.9%), tellurium dioxide (TeO_2 , MERCK, 99.99%), boric acid (H_3BO_3 , STENMARK, 99.5%), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, POCH, 99.4%), mannitol ($\text{C}_6\text{H}_8(\text{OH})_6$, CHEMDREAMLAND, 99.5%), deionized water (MILIPORE, resistivity $\rho = 15 \text{ M}\Omega \text{ cm}$) and nitric acid (HNO_3 , 65 % wt., POCH, pure p.a.). In order to prepare the initial solutions, the proper quantities of oxides: Bi_2O_3 and TeO_2 were dissolved in a minimal volume of HNO_3 in the presence of citric acid (complexing agent) under stirring and heating at 80°C . Tellurium source must be provided in proper excess (here 12% mol.) due to its considerable volatility during pyrolysis in the Pechini method (not observed while heating the raw individual substrate). Citric acid was chosen as a complexing agent due to the fact that the citrate ligands form rather stable complexes of both Bi^{3+} and Te^{4+} in strongly acidic solutions [17]. The molar ratio between citric acid and metal cations was set to be 3:1. Under these conditions, the complete dissolution of metal oxides was secured. When transparent and homogeneous solution containing metal complexes was obtained, a proper amount of H_3BO_3 (with 10.0% mol. excess) was charged into the solution and the mixing was continued. This boron excess is required to prevent the non-stoichiometry due to the evaporation of B_2O_3 at higher temperatures. The overall molar ratio of used Bi_2O_3 , TeO_2 and H_3BO_3 substrates was 3:2.24:2.2. After secondary homogenization, the mannitol (polymeric agent) was added into the solution. The molar ratio of citric acid to mannitol was constant and set to 3:1. After dissolving of all the reagents, the solution mixing was continued for about 1 h at 90°C in order to initialize the polyesterification. Prepared sol was then transferred into an alumina crucible (INCERAMICS S.A.) and put inside a furnace equipped with an EUROTHERM 906S temperature controller. The content was kept for about 24 h at 100°C in order to evaporate the solvents (H_2O – HNO_3 azeotrope) and to accomplish the polyesterification. A yellowish, foamy-like viscous gel was obtained. The temperature was raised up to 350°C for 3 h in order to remove the water residuals and dry the gel until it turned into black, brittle resin. To start the pyrolysis process and to get rid of the organic part, the temperature was gradually raised up to 500°C and kept at that value for 24 h. After that, the temperature was increased to 650°C and the process was continued for 48 h. In between these stages and after finishing, the powder material was

thoroughly ground in an agate mortar. Such a duration of synthesis (72 h of pyrolysis) is required to ensure the complete oxidation of Te^{4+} to Te^{6+} .

3. Experimental methods

The diffraction pattern of synthesized BTBO powder was collected using a BRUKER D8 Discover diffractometer equipped with a $\text{CuK}\alpha$ radiator ($\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$, 40 kV voltage and 40 mA current in operating mode). The Bragg-Brentano diffraction and Göbel FGM2 mirror geometry were applied. The diffraction angle $2\theta_B$ was varied from 18° to 70° with a step of 0.01° and acquisition time of 2 s per step. The measurements were made at room temperature. For the data processing the DIFFRAC.SUITE EVA application was used, allowing the $\lambda_{\text{K}\alpha 2}$ signal component deconvolution and removal, background subtraction and data smoothing (using the fast Fourier transform). The phase analysis was performed with the support of the Crystallography Open Database (COD). The FullPROF ver. 3.0 program was used for Rietveld refinement and calculations of accurate unit cell parameters.

The Raman spectra were recorded in back-scattering geometry using a Renishaw InVia Raman microscope equipped with a confocal DM 2500 Leica optical microscope and CCD detector. The excitation source was an Ar^+ laser emitting light of 514.5 nm wavelength. The unpolarized Raman spectrum detected in the range $100\text{--}1500 \text{ cm}^{-1}$ was measured using an edge filter in single scan with 30 s exposure time of CCD detector and 10 mW of the applied power. The low-excitation Raman spectra were detected using a NeXT filter (to stray Rayleigh light rejection), which allows measurements of modes as far as 10 cm^{-1} from the Rayleigh line, for 30 s exposure time and 20 mW of the applied power. The position of the Raman peaks was calibrated before data collection using an Si reference sample as an internal standard. The spectral resolution of the Raman system was better than 2 cm^{-1} .

The vibrational absorption spectra of BTBO were investigated at room temperature using the FT-IR Bruker Equinox 55 spectrometer equipped with the Hyperion 2000 microscope; the spectral resolution was 2 cm^{-1} . The IR spectra of the investigated compound dispersed in Nujol mulls ($c = 1:50$) and the KBr pellets ($c = 1:2000$) were recorded in two spectral regions from 50 to 700 and from 400 to 7500 cm^{-1} , respectively.

4. Result and discussion

4.1. XRD measurements

The XRD diffraction pattern of BTBO powder recorded at room temperature is presented in Fig. 1.

As shown in Fig. 1, diffraction pattern of BTBO powder is in good agreement with the reference COD card (No. 96-412-5286), which means that it represents the hexagonal class with non-centrosymmetric $P6_3$ (173) space group ($Z = 2$). The reference Crystallographic Information File (CIF) of BTBO phase used for Rietveld refinement was received from the supplementary data given in Ref. [18]. The refined unit cell parameters of BTBO microcrystals are: $a = 8.7505(2) \text{ \AA}$, $c = 5.8871(3) \text{ \AA}$, $Z = 2$, $V = 390.39 \text{ \AA}^3$ and correspond to those determined by M. Xia et al. [11]. The average crystallite size of BTBO equal to 149 nm was estimated on the basis of XRD patterns analysis by means of the Debye-Scherrer equation [18,19].

4.2. Crystal structure

The BTBO crystal is formed by two covalently bonded ionic

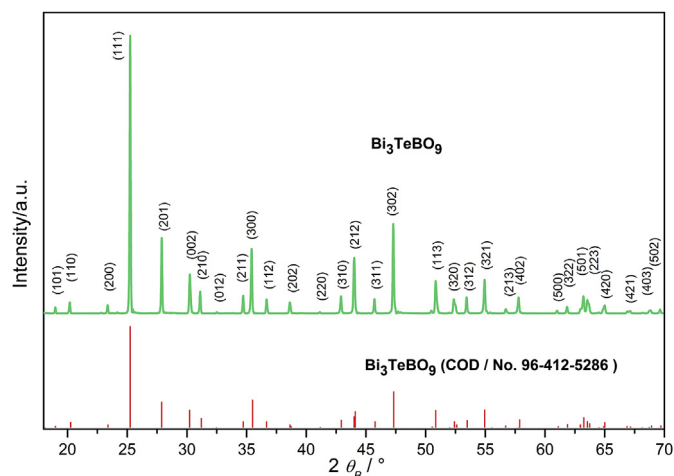


Fig. 1. The XRD patterns of BTBO powder.

complexes, octahedral TeO_6^{6-} and trigonal-planar BO_3^{3-} groups. Along the c -axis the BO_3 layers are alternate with cationic layers made of TeO_6 octahedra and Bi^{3+} ions. The BO_3 and TeO_6 groups are arranged similarly along the a and b axis, creating the alternate rows of BO_3 and TeO_6 groups (Fig. 2a) [11].

In the BTBO structure, the bismuth Bi and oxygen O atoms occupy the 6c Wyckoff positions, while the boron B and tellurium Te atoms are located at the 2a and 2b Wyckoff positions, respectively [11]. B atoms are surrounded by three O atoms to form the planar BO_3 groups (D_{3h} symmetry) with a uniform B–O bond length equal to 1.378 Å (Fig. 2b). Te^{6+} cations are coordinated by six O atoms with three B–O bond lengths equal to 1.921 Å and the other three B–O bond lengths equal to 1.925 Å. The TeO_6 octahedra are slightly deformed from the regular octahedral configuration. Moreover, the Bi^{3+} cations are surrounded by O atoms resulted in six Bi–O bonds are: three shorter Bi–O bond lengths equal to 2.214, 2.264 and 2.267 Å and three longer Bi–O bond lengths equal to 2.505, 2.506 and 2.514 Å [11]. For better clarity of Fig. 2b some of the B–O bonds were omitted.

4.3. μ -Raman and FT-IR investigation

The unpolarized Raman and IR spectra of investigated BTBO crystalline powder were recorded in the spectral range of external and internal vibrations at room temperature (Fig. 3).

As follows from Fig. 3, the Raman and IR spectra could be divided into the high-frequency vibration range separated by a broad gap of 530 cm^{-1} from the middle/low-frequency part of the spectra, extending from 690 to 100 cm^{-1} containing the majority of Raman and IR active bands. In general, the modes positioned in the spectral range 1500 – 600 cm^{-1} are assigned to the stretching vibrations of BO_3 groups or TeO_6 octahedra. The bending modes of BO_3 and TeO_6 groups occur in the spectral range 660 – 350 cm^{-1} . The external/lattice modes assigned to translational and librational motions of BO_3 and TeO_6 groups as rigid units appear in the spectral range below 350 cm^{-1} . The low wavenumber phonons were detected in Raman spectra using the NEXt filter in the spectral range below 100 cm^{-1} (Fig. 4).

The very weak line observed at 27 cm^{-1} in the low-frequency Raman spectrum is an optical ghost of the system, while the three modes centered at around 67, 80 and 86 cm^{-1} as well as the corresponding IR modes centered at 76, 85 and 106 cm^{-1} are intrinsic BTBO low-frequency vibrations. The spectroscopic parameters of all Raman active bands were analyzed by the fitting

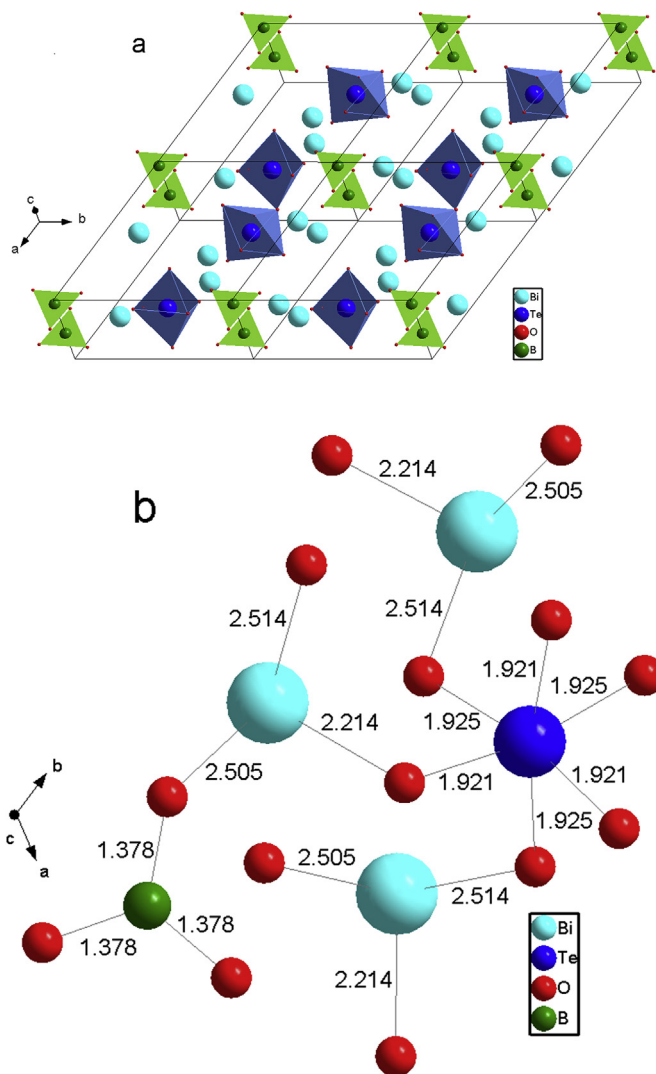


Fig. 2. The structure of BTBO (a) and the structural unit of BTBO (b) The program Dimond [20] was used for visualization of crystal structure..

procedure using the Lorentzian-like function, while for the bands active in the IR spectra the centre positions were determined. The experimental wavenumbers of Raman and IR modes are given together with those predicted from theoretical ab initio calculations of BTBO in Table 5. Moreover, the detailed assignment of experimental lines based on symmetry analysis and ab initio calculations is presented in Discussion (section 7).

5. Symmetry analysis of normal modes

The experimental Raman and IR data can be interpreted on the basis of group theory analysis. The primitive unit cell of BTBO crystal comprises two formula units and contains 28 atoms, giving 84 fundamental vibrations, which are classified in Γ point according to irreducible representations (irreps) of $P6_3$ space group, as follows:

$$\Gamma = 14A + 14B + 14E_1 + 14E_2$$

Since E_1 and E_2 are two-dimensional irreps, all modes that are transformed according to them are two-fold degenerated. The phonon modes of A, E_1 and E_2 types are Raman active, whereas the modes of A and E_1 species are IR active. The modes of B symmetry

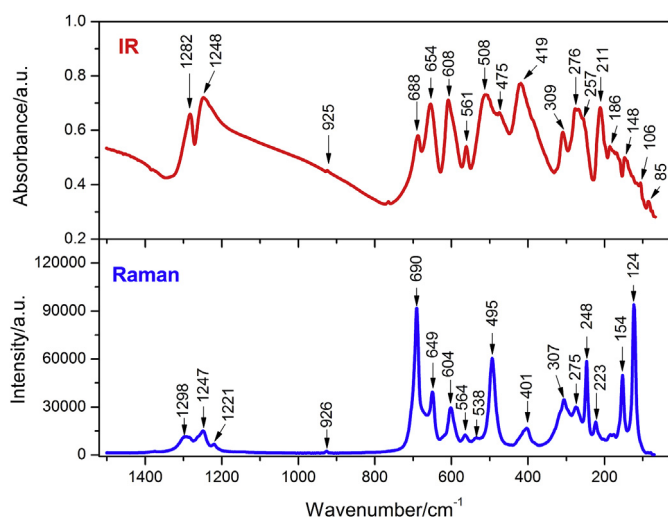


Fig. 3. The unpolarized Raman and IR spectra recorded in the 100–1500 cm^{-1} range of BTBO powder at RT.

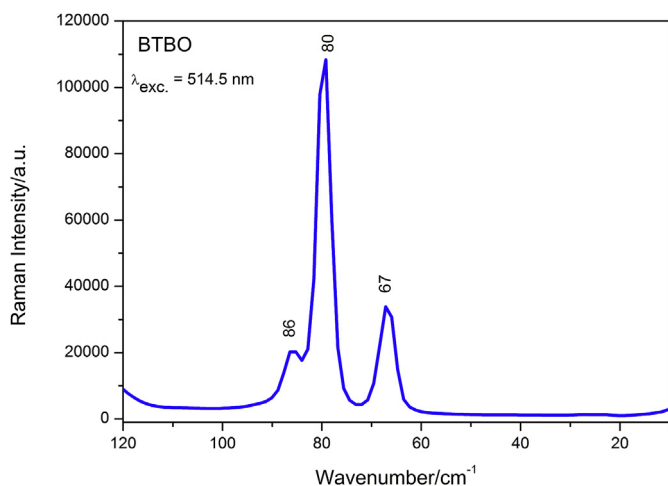


Fig. 4. The low-wavenumber Raman spectrum detected in the 10–100 cm^{-1} range of BTBO powder at RT.

are inactive both in Raman and IR spectra. However, this symmetry restriction is valid only for the ideal crystal structure. In real crystals, as we consider it later on, this strict symmetry demand may evidently be violated due to structural peculiarities.

Considering the characteristic features of BTBO crystal structure, it is possible to obtain a general distribution of phonon modes over the frequency range. As mentioned above, there are two covalently bonded ionic complexes, octahedral TeO_6^{6-} and trigonal-planar BO_3^{3-} groups, each of them has its own characteristic internal vibrations. Both structural motives are not directly linked (see Fig. 2a), therefore their internal frequencies should not significantly influence each other. In the ideal octahedral TeO_6 unit with O_h symmetry, the internal stretching or bending ν_1 , ν_2 and ν_5 vibrations are Raman active, whereas the ν_3 and ν_4 modes are IR active; the ν_6 internal mode is inactive both in Raman and IR spectra. In particular, the symmetric stretching vibrations ν_1 are expected at about 700 cm^{-1} ; the doubly and triply degenerate asymmetric bending vibrations ν_2 and ν_3 , respectively, occur in 500–650 cm^{-1} spectral range; the triply degenerate asymmetric bending vibrations ν_4 are in the range 400–500 cm^{-1} , while the symmetric bending ν_5 modes occur below 400 cm^{-1} . Similar spectroscopic activity is valid for

internal vibrations, μ_1 , μ_2 , μ_3 , μ_4 , of the ideal triangular planar BO_3 groups with D_{3h} symmetry, namely, μ_1 , μ_3 , μ_4 modes are Raman active while μ_2 , μ_3 , μ_4 are IR active. The characteristic vibrations of isolated BO_3 ion can be classified into four fundamental modes: the symmetric stretching mode μ_1 (~950 cm^{-1}), the doubly degenerate asymmetric stretching mode μ_3 (1250–1400 cm^{-1}), the doubly degenerate planar bending mode μ_4 (~600 cm^{-1}) and the infrared active out-of-plane bending mode μ_2 (700–800 cm^{-1}) [10,21]. However, the frequencies of internal vibrations of TeO_6 and BO_3 groups are significantly dependent on crystal environment and may considerably deviate in various host compounds (see Table 1). Applying group theory treatment [22], one may construct the compatibility relations between internal modes of octahedral TeO_6 and triangular BO_3 groups, their site symmetry and crystal point group symmetry (see Table 2) and, finally, one may derive the general classification of BTBO normal modes in Γ point (see Table 3). Note that normally the frequencies of external lattice vibrations (translational and rotational) are located below ~350 cm^{-1} . Since the ν_5 normal mode has nearly the same frequency, we should not expect the strict frequency gap in our experimental spectra between external lattice and internal vibrations.

6. Ab initio calculations

Our calculations were performed within the density functional perturbation approach using the generalized gradient approximation (GGA) [29] in Perdew-Burke-Ernzerhof parameterization [30] as implemented in the ab initio package ABINIT [31,32]. We also used another form of exchange-correlation functional properly accounting for the long-range dispersion effects by the Grimme and co-authors' method [33]. Hereinafter, the results obtained by uncorrected GGA approach will be denoted as GGA and those obtained within Grimme's method as DFT-D3. Norm-conserving ONCVSP pseudopotentials were utilized in our calculations with Bi ($5d^{10}6s^26p^3$), Te ($4d^{10}5s^25p^4$), B ($2s^22p^1$) and O ($2s^22p^4$) valence states. After convergence analysis we chose a 4^*4^*4 grid for Brillouin zone sampling using the Monkhorst-Pack scheme [34]. The cut-off energy of plane-wave basis was set to a rather high value of $E_{\text{cut}} = 1632$ eV. Our calculation was performed on the basis of experimental crystal structure refined in Ref. [11]. Structural optimization was made within the Broyden-Fletcher-Goldfarb-Shanno algorithm [35] and a very high stability of crystal lattice was achieved, i.e. the maximal forces acting on each atom were reduced to the values lower than 5^*10^{-7} eV/Å. The lattice parameters and Te–O and B–O distances within covalently bonded TeO_6 and BO_3 groups calculated using various exchange-correlation functionals are listed in Table 4. As follows from this table, both approaches give quite acceptable results but the deviation of DFT-D3 data from the experimental results [11] is smaller comparing with that of GGA data, not exceeding even 1% for lattice parameters and B–O distances. Comparatively higher discrepancy between the calculation and experiment, less than 3%, observed for Te–O distances within both GGA and DFT-D3 approaches, may be explained by the distortion of TeO_6 structural units occurred in real BTBO crystal.

The phonon frequencies calculated near the Brillouin zone centre within both exchange-correlation functionals, GGA and DFT-D3, with the experimental Raman and IR data obtained in our work are compared in Table 5.

All modes are classified there according to the irreps of $P6_3$ group in Γ point. Calculated frequencies nicely correspond to the general demands of group theory. One acoustic mode has A symmetry and two other acoustic modes are of E_1 species. The modes of E_1 and E_2 types are two-fold degenerated satisfying two-dimensionality of these irreps. However, the degeneration of E_1 symmetry modes is lifted due to the transverse-longitudinal TO-LO

Table 1
Frequencies of internal modes of TeO₆ and BO₃ ionic groups in different compounds.

TeO ₆							BO ₃					
ν_5	ν_4	ν_2	ν_3	ν_1	Compound	Ref.	μ_4	μ_2	μ_1	μ_3	Compound	Ref.
355	470	540	640	700	Li ₆ (TeO ₆)	[23]	610	713–788	944	1285	Pr(BO ₃)	[26]
355	470	540	640	700	α -Li ₆ (TeO ₆)	[24]	637	740,764		1200–1260	Sc(BO ₃)	[26]
368	455	512	695		Mg ₃ (TeO ₆)	[25]	647	743	944	1205	CaSn(BO ₃) ₂	[27]
			650–675	708–730	H ₆ (TeO ₆)	[26]	545	648,668	1060	1428–1490	H ₃ (BO ₃)	[28]
		536	675	780	Na ₂ H ₄ (TeO ₆)	[25]						

Table 2
Correlation diagram of internal modes of TeO₆ ($\nu_1 - \nu_6$) and BO₃ ($\mu_1 - \mu_4$) groups and factor-group of BTBO crystal.

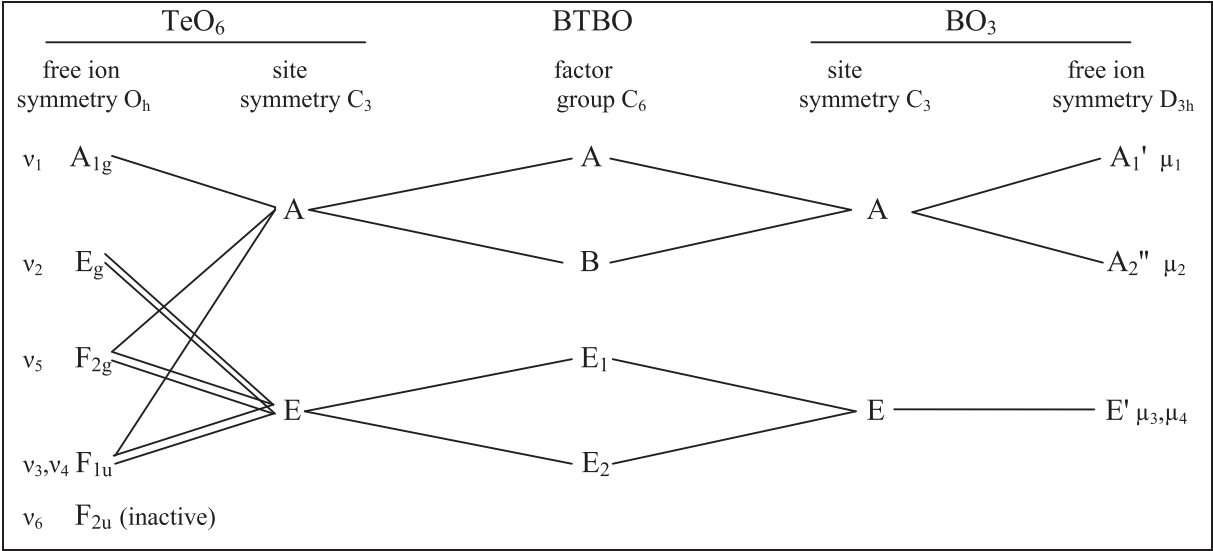


Table 3
Normal mode classification in Γ point according to irreps of $P6_3$ space group of BTBO crystal. R and IR indicate the activity in the Raman and IR spectra, respectively.

irreps.	translations+librations	internal
14 A (R, IR)	1 acoust + 6	7 ($\nu_1, \nu_3, \nu_4, \nu_5, \nu_6, \mu_1, \mu_2$)
14 B	7	7 ($\nu_1, \nu_3, \nu_4, \nu_5, \nu_6, \mu_1, \mu_2$)
14 E ₁ (R, IR)	1 acoust + 6	7 ($\nu_2, \nu_3, \nu_4, \nu_5, \nu_6, \mu_3, \mu_4$)
14 E ₂ (R)	7	7 ($\nu_2, \nu_3, \nu_4, \nu_5, \nu_6, \mu_3, \mu_4$)

splitting, which is inherent for dielectric BTBO crystal. All modes with z-polarized dipole moment are transformed according to A irrep, whereas the modes with dipole moments lying in (x, z) plane are of E₁ symmetry. Note that our calculation was carried out in the Cartesian coordinate system x, y, z, which is directed according to the hexagonal crystallographic system, a, b, c, as follows, x || a, y ⊥ (a, c), z || c.

Table 4
Comparison of lattice parameters and interatomic distances of covalently bonded atoms obtained within two different functionals with experimental values (experimental Te – O and B – O distances are listed in Fig. 2). The deviation from experiment [11] is indicated in parentheses.

	a [Å]	c [Å]	Te – O [Å]	B – O [Å]
GGA	8.8951 (1.65%)	5.9952 (1.65%)	1.966 (2.40%) 1.981 (2.91%)	1.383 (0.36%)
DFT-D3	8.8236 (0.83%)	5.9470 (0.83%)	1.959 (2.03%) 1.979 (2.81%)	1.380 (0.15%)
Exp./this paper	8.7505(2)	5.8871(3)		
Experim. [11]	8.7510	5.8981		

Some of the experimental Raman frequencies appear twice in Table 5 since our experiment was performed on the powder sample and we are not aware of the precise symmetry of detected frequencies. As seen from this table, the frequencies calculated within both approaches, GGA and DFT-D3, well agree with the experimental Raman and IR data. However, the DFT-D3 data give the better agreement with the experiment. It follows from the average deviation between calculated and experimental Raman frequencies, i.e. 1.3% vs. 2.8% for A irrep, 1.6% vs. 2.3% for E₁ irrep and 1.2% vs. 1.7% for E₂ irrep for DFT-D3 vs. GGA functional, respectively. For all irreps DFT-D3 approach gives better description of experimental result.

It is quite instructive to look closer at Born effective charges of nonequivalent atoms of BTBO. The Born effective charge, $Z_{k,\alpha\beta}^*$, is treated as a proportionality coefficient relating the polarization per unit cell, created along the direction β , and the displacement along the direction α of the atoms belonging to the sublattice κ , under the

Table 5

Comparison between the calculated near Brillouin zone centre and experimental Raman/IR frequencies in cm^{-1} . TO and LO indicate transverse and longitudinal frequencies of A and E_1 species, respectively.

A						B		E_1				E_2		
calcul				Raman	IR	calcul		calcul		Raman	IR	calcul		Raman
GGA	DFT-D3					GGA	DFT-D3	GGA	DFT-D3			GGA	DFT-D3	
TO	acoustic	TO	LO					TO	acoustic					
76.4	76.5	78.7	79.0	80	76	58.1	62.1	TO	64.9	68.7		66.5	69.3	
90.0	113.9	98.8	113.2		106	84.9	86.0	LO	66.9	70.2		66.5	69.3	
115.0	145.2	114.4	152.4	124	148	111.0	114.7	TO	81.9	85.3	86	79.9	83.9	80
150.8	163.6	158.3	168.5	154	160	139.2	144.1	LO	82.1	85.5		79.9	83.9	
194.7	214.0	201.2	219.4	223	200	196.5	199.0	TO	150.5	149.1		84.7	90.0	
230.6	230.7	231.6	232.1			219.0	223.8	LO	151.6	150.6	155			
267.2	306.4	270.0	312.7	319	276	257.5	260.6	TO	168.2	169.6		151.2	151.2	
408.4	457.6	408.5	458.7	401	403	279.3	284.8	LO	180.1	183.1	186	151.2	151.2	154
457.7	477.9	458.9	480.2		475	435.8	434.7	TO	195.9	198.4		177.9	180.0	177
549.0	585.1	556.3	592.7	593	561	514.8	518.0	LO	209.9	211.2	215	177.9	180.0	
635.3	637.2	646.2	649.0	649	654	539.4	548.1	TO	240.6	247.5	248	204.2	207.2	204
676.0	688.9	676.7	691.0	690	688	631.3	641.0	LO	275.6	278.9	275	204.2	207.2	
903.0	903.1	910.0	910.2	926	925	726.8	727.6	TO	284.9	286.1	288	264.1	266.6	
						893.3	900.6	LO	295.0	300.9		264.1	266.6	
								TO	379.0	381.8		296.8	300.8	307
								LO	414.5	418.9	417	296.8	300.8	
								TO	464.0	466.9		385.3	388.2	
								LO	505.6	508.3	495	385.3	388.2	
								TO	527.3	532.8		466.9	471.1	
								LO	530.8	536.8	538	466.9	471.1	
								TO	573.0	578.3		508.3	513.9	
								LO	578.0	591.0	593	508.3	513.9	
								TO	601.7	610.3	604	563.4	568.9	564
								LO	627.4	637.7	621	563.4	568.9	
								TO	1233.5	1248.5	1257	603.5	610.4	604
								LO	1266.8	1281.3	1298	603.5	610.4	621
												1205.5	1220.1	1221
												1205.5	1220.1	1247

condition of a zero electric field [36]. In general, the Born effective charge is a tensor, whose peculiar form is defined by the site symmetry of a respective ion. Since the site symmetry of Bi, O_1 , O_2 and O_3 ions is 1, whereas the site symmetry of Te and B atoms is 3, one may expect the general form of Born effective charge tensor in the former case and some symmetric form of such a tensor in the latter case. The Born effective charges of non-equivalent Bi, O_1 , O_2 , O_3 , Te, B ions and their principal values λ_α calculated within both approaches, DFT-D3 and GGA, are listed in Table 6.

As follows from Table 6, both exchange-correlation functionals give very similar results. To analyze the Born effective charges it is more convenient to transform them into the principal basis in which they adopt a diagonal form. As shown in Table 6, all constituent ions manifest the effective charge anisotropy. However, the charge anisotropy of Bi ions not involved in covalent bonding is comparatively small (directional deviation from the isotropic value

is -10% , -4% , 14%). Similarly small charge anisotropy (9%, 9%, -18%) is observed for Te ions incorporated into the comparatively uniform space bonding of TeO_6 octahedra. The charge anisotropy of all other atoms is much higher which is the consequence of the strong covalent bonding inherent for TeO_6 and BO_3 groups. The triangular planar shape of BO_3 groups inspires the drastic charge redistribution of both B and O_3 ions in the (x, y) plane making, e.g., the effective charge of B ion along z direction smaller by one order of magnitude relative to those along x and y directions. The Born effective charges of all non-equivalent oxygen atoms also demonstrate significant anisotropy. Note that this characteristic feature is relevant for many compounds possessing the non-equivalent covalently bonded oxygen atoms in their structure (see e.g. Ref. [37]).

Table 6

Born effective charges of non-equivalent atoms of BTBO crystal calculated within both DFT-D3 and GGA approaches. The principal values of responsible Born effective charge tensor are indicated in brackets; percentage corresponds to their deviations from isotropic spherical charge.

	Z_{Bi}^*	Z_{Te}^*	Z_{O1}^*	Z_{O2}^*	Z_{O3}^*	Z_{B}^*
DFT-D3	$\begin{pmatrix} 4.55 & 0.08 & 0.03 \\ 0.07 & 4.36 & 0.29 \\ 0.14 & 0.40 & 5.23 \end{pmatrix}$ [4.23 4.54 5.36] -10% -4% 14%	$\begin{pmatrix} 5.46 & 0.09 & 0.00 \\ -0.10 & 5.46 & 0.00 \\ 0.00 & 0.00 & 4.09 \end{pmatrix}$ [5.46 5.46 4.09] 9% 9% -18%	$\begin{pmatrix} -2.80 & -0.01 & 0.22 \\ 0.06 & -1.89 & 1.05 \\ -0.05 & 0.97 & -2.33 \end{pmatrix}$ [-1.08 -2.85 -3.09] -54% 22% 32%	$\begin{pmatrix} -2.62 & 0.07 & 0.14 \\ -0.32 & -2.07 & 1.06 \\ 0.23 & 0.95 & -2.49 \end{pmatrix}$ [-1.27 -2.58 -3.34] -47% 8% 38%	$\begin{pmatrix} -2.25 & 0.03 & 0.96 \\ 0.28 & -2.99 & 0.13 \\ 0.98 & 0.20 & -1.88 \end{pmatrix}$ [-3.03 -3.03 -1.05] 28% 28% -56%	$\begin{pmatrix} 3.11 & -0.21 & 0.00 \\ 0.21 & 3.12 & 0.00 \\ 0.00 & 0.00 & 0.30 \end{pmatrix}$ [3.12 3.12 0.30] 43% 43% -87%
GGA	$\begin{pmatrix} 4.53 & 0.09 & 0.13 \\ 0.10 & 4.28 & 0.38 \\ 0.03 & 0.30 & 5.13 \end{pmatrix}$ [4.15 4.53 5.13] -10% -2% 10%	$\begin{pmatrix} 5.48 & -0.06 & 0 \\ 0.06 & 5.48 & 0 \\ 0 & 0 & 3.94 \end{pmatrix}$ [5.48 5.48 3.94] 9% 9% -21%	$\begin{pmatrix} -2.81 & 0.06 & -0.07 \\ -0.01 & -1.87 & 0.96 \\ 0.21 & 1.03 & -2.28 \end{pmatrix}$ [-1.06 -2.88 -3.02] -54% 24% 30%	$\begin{pmatrix} -2.65 & 0.09 & 0.12 \\ -0.32 & -2.02 & 1.04 \\ 0.22 & 0.94 & -2.42 \end{pmatrix}$ [-1.22 -2.6 -3.25] -48% 11% 38%	$\begin{pmatrix} -2.20 & 0.30 & 0.99 \\ 0.07 & -3.01 & 0.15 \\ 0.97 & 0.07 & -1.84 \end{pmatrix}$ [-3.02 -3.02 -1.00] 29% 29% -57%	$\begin{pmatrix} 3.13 & 0.24 & 0 \\ -0.24 & 3.19 & 0 \\ 0 & 0 & 0.29 \end{pmatrix}$ [3.13 3.13 0.29] 44% 44% -87%

7. Discussion

To analyze the experimental data, it is reliable to distinguish the external and internal vibrations since the latter (i) normally appear in higher frequency range when compared with that of the external modes and (ii) they are well classified according to irreps and reveal different spectroscopic activity (Raman or IR). From among 28 internal modes of TeO_6 and BO_3 groups, 11 vibrations should be active in the Raman spectrum ($3A(\nu_1, \nu_5, \mu_1) + 4E_1(\nu_2, \nu_5, \mu_3, \mu_4) + 4E_2(\nu_2, \nu_5, \mu_3, \mu_4)$) and 7 modes are expected in the IR spectrum ($3A(\nu_3, \nu_4, \mu_2) + 4E_1(\nu_3, \nu_4, \mu_3, \mu_4)$). Note once again that all modes of E_1 and E_2 symmetry are twice degenerated, therefore the total amount of Raman and IR active normal modes is 19 and 11, respectively. Strictly speaking, this classification is valid only for the ideal octahedral TeO_6 and triangular BO_3 groups. Any crystal imperfections or crystal field at the certain site symmetry may distort the ideal polyhedral shape violating the spectroscopic selection rules or symmetry compatibility relations. According to the structural analysis, the TeO_6 groups are not the regular octahedra in BTBO crystal due to the inequality of two tellurium-oxygen distances in these ionic groups, i.e. $R(\text{Te}-\text{O}_1) = 1.921 \text{ \AA}$, $R(\text{Te}-\text{O}_2) = 1.924 \text{ \AA}$ [11]. Structural data published in Ref. [13] give even more distortion of TeO_6 , namely $R(\text{Te}-\text{O}_1) = 1.906 \text{ \AA}$, $R(\text{Te}-\text{O}_2) = 1.933 \text{ \AA}$. All these reasons may cause a lift of mode degeneration resulting in observation of a higher number of lines in the spectra than those allowed by group symmetry rules.

As we already mentioned, the transverse-longitudinal TO-LO splitting is inherent for BTBO crystal. The TO-LO splitting is the specific feature of A and E_1 symmetry modes polarized along the z axes or within (x, y) plane, respectively, and may be observed both in Raman and IR spectra. Since our spectra are recorded of the powder sample, the modes of both A and E_1 species may effectively present there any value between TO and LO frequency.

Let us consider the highest frequency range. As follows from Fig. 3 and Table 1, the modes in the spectral range $1500\text{--}600 \text{ cm}^{-1}$ are assigned to the stretching vibrations BO_3 groups or TeO_6 octahedra. In particular, the highest frequency region of Raman spectrum should include μ_3 internal vibrations of BO_3 groups. According to the symmetry demands (see Table 3), only 2 twice degenerated μ_3 modes ($1E_1 + 1E_2$) may be visible in the Raman spectrum. This symmetry demand is satisfied by our ab initio calculation of BTBO phonon spectrum (see Table 5). However, our experimental data give 6 instead of 4 modes in the highest frequency part of Raman spectrum, i.e. $1384, 1298, 1284, 1262, 1247$ and 1221 cm^{-1} (see Table 5). In particular, the Raman spectrum showed the medium intensity modes at $1298, 1247$ and 1221 cm^{-1} , while the IR spectrum contained the strong and very strong modes at 1282 and 1248 cm^{-1} , respectively. Very weak Raman mode at 1384 cm^{-1} may be eliminated from our examination since it is probably a result of higher order Raman scattering. Moreover, our ab initio calculations give the highest frequency near 1281 cm^{-1} (DFT-D3). A similar conclusion is relevant for the two experimental Raman lines, i.e. 1298 and 1284 cm^{-1} . The calculation predicts only one mode in this highest frequency range. It means that one of these two experimental modes should be a result of either crystal imperfection or the violation of spectroscopic selection rules.

The very weak intensity modes detected at 926 and 925 cm^{-1} in the Raman and IR spectra, respectively, are probably not a result of a many-phonon process but originate from A type μ_1 internal vibration of BO_3 complex and correlate well with the calculated value of 910 cm^{-1} . Neglecting this weak line, one may say that there is a rather broad gap of an order of 530 cm^{-1} between the high frequency μ_3 vibrations and the main part of the Raman spectrum, extending from 690 to 100 cm^{-1} (see Fig. 3). Interpretation of this wide frequency range is not so straightforward as that of the

highest frequency range presented above. The assignment of many lines in the intermediate frequency range is to a great extent approximate because of the mixed character of many modes. The bands detected in the Raman and IR spectra in the region from 690 to 600 cm^{-1} originate by μ_4, μ_2 (BO_3) and strong stretching ν_3, ν_1 (TeO_6) vibrations. In particular, the most intensive modes recorded in this spectral range at 690 and 688 cm^{-1} in the Raman and IR spectra, respectively, are assigned to the ν_1 stretching vibrations of TeO_6 . The strong and very strong modes occurring at 649 and 654 cm^{-1} in the Raman and IR spectra, respectively, were attributed to doubly degenerated ν_3 stretching modes of BO_3 groups. The modes at 621 (weak) and 604 (strong) cm^{-1} in the Raman spectrum and the very strong mode at 608 cm^{-1} in the IR spectrum were assigned to the μ_4 vibration of BO_3 .

The bending modes of BO_3 and TeO_6 groups occur in the spectral range of $660\text{--}350 \text{ cm}^{-1}$. Only the weak mode at 564 cm^{-1} and the medium mode at 561 cm^{-1} detected in the Raman and IR spectra, respectively, can be assigned to the μ_4 vibrations of BO_3 . The other bands in the Raman and IR spectra in the considered spectral range of $660\text{--}350 \text{ cm}^{-1}$ were assigned to the vibrations of TeO_6 octahedra. In particular, the shoulder at 593 cm^{-1} detected in the Raman and IR spectra and the weak mode at 538 cm^{-1} detected in the Raman spectrum can be assigned to the ν_2 vibrations; very strong modes centered at 495 and 508 cm^{-1} in the Raman and IR spectra, respectively, and the strong mode at 475 cm^{-1} in the IR spectrum arise from the ν_4 vibrations; the very strong mode centered at 419 cm^{-1} and a shoulder at 417 cm^{-1} detected in the IR and Raman spectra, respectively, can be related to the ν_4 vibrations; the medium-frequency mode at 401 cm^{-1} in the Raman spectrum and the corresponding shoulder at 403 cm^{-1} in the IR spectrum were assigned to the ν_5 vibrations. On the basis of the analysis of calculated eigenvectors, it follows that the lowest frequency part of the spectrum below $\sim 350 \text{ cm}^{-1}$ originates from the external lattice vibrations of Bi or Te atoms and TeO_6 and BO_3 complexes as the rigid units. In particular, the Raman and IR modes recorded in the spectral range $120\text{--}300 \text{ cm}^{-1}$ mainly correspond to the librational or translational motions of BO_3 or TeO_6 groups. The highest intensity modes in this range were centered at 124 and 154 cm^{-1} in the Raman spectrum. The other modes located in the spectral range $300\text{--}360 \text{ cm}^{-1}$ can be assigned to the vibrations of BiO_6 units. The low wavenumber phonons detected in the Raman spectrum in the range below 100 cm^{-1} , the three modes centered at around $67, 80$ and 86 cm^{-1} as well as the corresponding modes centered at $76, 85$ and 106 cm^{-1} in the IR spectrum can be assigned to the translations of Bi^{3+} and/or Te^{6+} ions. These low energy vibrations are connected with the relatively large atomic masses of Bi and Te atoms [10]. However, to a great extent, the low-frequency modes below $\sim 300 \text{ cm}^{-1}$ are of mixed type.

8. Conclusions

We performed exhaustive lattice dynamics study of BTBO crystal at room temperature based on the experimental Raman, IR spectra investigation, group theory analysis and calculations of phonon mode spectrum in the Brillouin zone centre. Experimental spectra were analyzed in detail on the basis of the group theory predictions and results of ab initio calculations. Both exchange-correlation functionals, uncorrected GGA in Perdew-Burke-Ernzerhof formulation and that corrected by the long-range dispersion by Grimme's method (DFT-D3) gave quite a satisfactory agreement with the experimental fundamental frequencies. However, DFT-D3 approach results agree better with the experiment as the total average deviation from Raman data was lower than 1.4%.

Acknowledgments

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Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors

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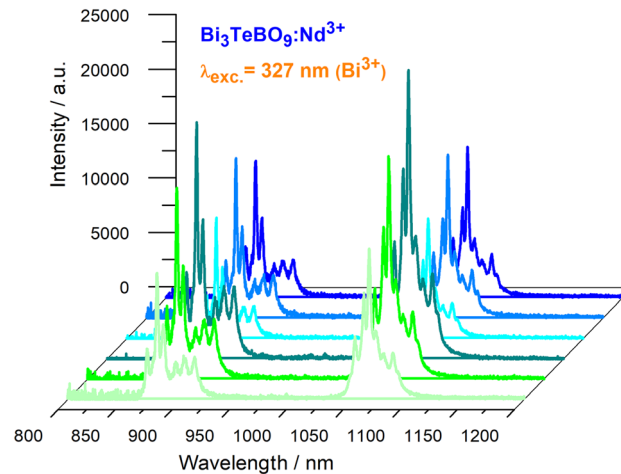
ABSTRACT

An efficient near-infrared quantum cutting process by cooperative down-conversion of active Bi^{3+} and Nd^{3+} ions was demonstrated in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors. In particular, the near-infrared emission of Nd^{3+} ions enhanced by Bi^{3+} ions of a series of novel $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ microcrystalline powders doped with Nd^{3+} ions in various concentrations was investigated. In order to investigate the luminescent properties of BTBO:Nd^{3+} powders, the excitation and emission spectra and the fluorescence decay time were measured and analyzed. In particular, the emission of $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ at 890 and 1064 nm was excited at 327 nm (via energy transfer from Bi^{3+} ions) and at 586.4 nm (directly by Nd^{3+} ions). The highest intensity emission bands in near-infrared were detected in the spectra of $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ doped with 5.0 and 0.5 at.% of Nd^{3+} ions upon excitation in ultraviolet and visible spectral range, respectively. The fluorescence decay lifetime monitored at 1064 nm for $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ powders shows the single- or double-exponential character depending on the concentrations of Nd^{3+} ions. The possible mechanisms of energy relaxation after excitation $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ powders in ultraviolet or visible spectral range were discussed. The investigated $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors efficiently concentrate the ultraviolet/visible radiation in the near-infrared spectral range and can be potentially used as effective spectral converters.

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GRAPHICAL ABSTRACT



Introduction

The efficiency of spectral converters based on rare earth (RE) ions doped crystalline materials is related to the characteristic energy level structures of RE ions, which allows up- and/or down-conversion processes by resonant energy transfer between lanthanide ions [1]. Besides many other applications of such materials, they can be used in the solar cells technology to achieve high efficiency in conversion of solar energy into electric current, by the concentration of solar radiation in the appropriate spectral range, leading thus to enhancement of the photovoltaic effect. Solar energy near the Earth's surface is distributed in a wide spectral range from 300 to 2500 nm and consists of ultraviolet (UV) in 7%, visible (VIS) in 47% and infrared (IR) in 46% radiation [2]. Conventional single-junction semiconductor solar cells effectively convert only the photons of energies close to the semiconductor band gap (E_g) as a result of the mismatch between the incident solar spectrum range and the spectral absorption range of the semiconductor material [3]. The photons with energies smaller than E_g are not absorbed and their energy is not used for electrons generation, while the photons with energies higher than E_g are absorbed, but the excess energy is lost due to thermalization of the generated electrons [4]. These spectral losses in a

single-junction crystalline silicon (c-Si) solar cells limit the efficiency of solar energy conversion into electricity. One of the solutions to overcome this limitation is to use the RE doped materials as spectral converters in c-Si solar cells technology, which concentrate the solar radiation into the required NIR spectral range in the process of down-conversion (known as quantum cutting process) [1]. In other words, the high-energy region of the solar spectrum cannot be utilized by conventional c-Si solar cells as silicon has a band gap $E_g = 1.12$ eV, corresponding to the absorption in the NIR spectral range ≈ 1100 nm [5]. The proposed solution is to convert the high-energy part of the solar spectrum into the low energy NIR region, from which the solar energy can be efficiently absorbed by the c-Si solar cells.

In this study, we used a complex borate Bi_3TeBO_9 (abbreviated as BTBO) micro-crystals doped with Nd^{3+} ions. Oxide crystals are considered important for photonic applications, thanks to the excellent transparency window from UV to NIR as well as high RE^{3+} doping ability [6–8]. The synthesis, crystal structure, electronic structure, some optical and spectroscopic properties of undoped BTBO were already reported [9–12]. Recently, the first complex study of vibrational properties based on experimental results of IR and Raman spectroscopy supported by the ab initio calculations for undoped BTBO micro-crystalline powders were reported by us [13].

Among the RE^{3+} ions, Nd^{3+} ones are particularly attractive as spectral converters because of their characteristic electronic energy level structure, which allows efficient down-conversion of the electromagnetic spectrum from UV/VIS to NIR [14]. In this study the specific Nd^{3+} emissions of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions under excitation in UV and VIS spectral range were investigated in BTBO: Nd^{3+} system. Moreover, there are many reports available on the use of Bi^{3+} ions (present in BTBO matrix) as sensitizers for RE^{3+} ions [15, 16]. The ground state of Bi^{3+} ion with $6s^2$ electronic configuration is expressed as $^1\text{S}_0$. The $6s6p$ excited states consist of $^1\text{P}_1$, $^3\text{P}_2$, $^3\text{P}_1$ and $^3\text{P}_0$ states. The transition from $^1\text{P}_1$ to the ground state generally occurs in the UV region, whereas the location of the emission band originating from $^3\text{P}_1$ and $^3\text{P}_0$ can be observed in the range of shorter wavelengths (in UV or VIS range) depending on the host lattice. Although the transition from the ground state to the first excited level ($^1\text{S}_0 \rightarrow ^3\text{P}_0$) of Bi^{3+} is strongly forbidden, the transitions from the $^1\text{S}_0$ ground state to the $^3\text{P}_2$, $^3\text{P}_1$ and $^3\text{P}_0$ states are observed in optical excitation spectra. Depending on the host material, the structure of the energy levels of Bi^{3+} ions may change and a lowering of the excited states energy is typically observed in comparison with the structure of electronic levels of isolated Bi^{3+} ions [17–19]. Particularly, for oxide-based lattices, the structure of electronic levels of Bi^{3+} ions strongly depends on the configuration of the nearest oxygen surrounding of Bi^{3+} ions [17]. In the BTBO structure, Bi^{3+} ions occur in octahedral coordination BiO_6 being six-coordinated by the oxygen atoms forming BiO_6 octahedra [13]. Due to the close location of some excited states of Bi^{3+} and Nd^{3+} ions in the considered BTBO: Nd^{3+} system, the orbitals for energy transfer from the Bi^{3+} to the RE^{3+} levels overlap and an efficient NIR quantum-cutting process (converting photons of high energy into photons of lower energy) is possible [15]. Thus, the synergy effect of cooperative down-conversion of Bi^{3+} and Nd^{3+} ions from UV/VIS to NIR spectral range results in efficient NIR emission in BTBO: Nd^{3+} system.

Efficiency of the spectral conversion of the proposed BTBO: Nd^{3+} system strongly depends on the concentration of RE^{3+} active ions. Usually, increase in the RE^{3+} ions concentration should improve the luminescence. However, too short distances between the active RE^{3+} ions in the host matrix may increase the probability of energy transfer between them,

which results in luminescence suppression. This phenomenon, known as Luminescence Concentration Quenching (LCQ), was widely observed in lanthanide-based luminescent materials [20, 21], but it can be avoided by using limited RE^{3+} concentration [22, 23]. To obtain the optimal concentration of active Nd^{3+} ions, we investigated BTBO microcrystalline powders doped with different concentrations of Nd^{3+} ions (0.5, 1.0, 2.5, 5.0, 7.5 and 10.0 at. %). On the other hand, another condition required for efficient RE^{3+} luminescence emission of the doped phosphors is a long emission lifetime, which significantly depends on the lack of radiationless transitions. The phosphors radiationless transition occurs due to the multiphonon relaxation from the excited states of active ions to the matrix, or to the above-mentioned energy transfer process between the excited and unexcited states of RE^{3+} active ions. These processes may also quench the emission of RE^{3+} active ions and are undesirable for achieving efficient emissions of RE^{3+} ions in the host matrix. The most desirable are the matrices with lower phonon energy as well as optimal separation between the active dopant ions. Raman investigation presented in this paper shows that BTBO has a low-energy phonon matrix.

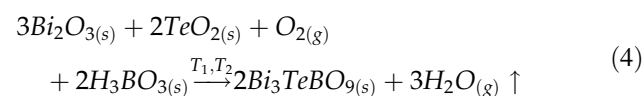
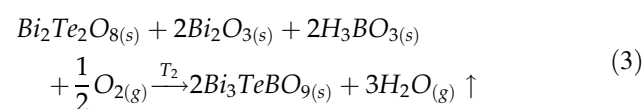
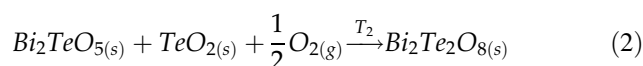
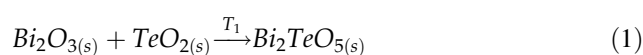
The mentioned above new BTBO: Nd^{3+} powders were synthesized by means of the modified Pechini method. In this paper we present for the first time the synthesis as well as structure, morphology, μ -Raman and luminescence properties of BTBO: Nd^{3+} powders. In particular, the excitation spectra monitored at 1064 nm, emission in NIR under excitation at 327 and 586.4 nm as well as decay lifetimes monitored at 1064 nm for BTBO: Nd^{3+} powders are presented. Moreover, the energy transfer mechanism between Bi^{3+} and Nd^{3+} ions, which leads to NIR emission of BTBO: Nd^{3+} , was discussed. Additionally, using the Inokuti–Hirayama model, the kinetics of the luminescence was analyzed and some parameters related with the energy transfer processes (from excited to neighboring unexcited Nd^{3+} ions) were determined for BTBO: Nd^{3+} powder (0.5 at. %).

Synthesis procedure

BTBO powders were synthesized by means of the modified Pechini method [24]. The following precursor materials were used for the synthesis without additional purification: commercial bismuth oxide

(Bi_2O_3 , SIAL, 99.9%), tellurium dioxide (TeO_2 , MERCK, 99.99%), neodymium oxide (Nd_2O_3 , ALFA 99.999%), boric acid (H_3BO_3 , STENMARK, 99.5%), citric acid ($\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$, POCH, 99.4%), mannitol ($\text{C}_6\text{H}_8(\text{OH})_6$, CHEMDREAMLAND, 99.5%), deionized water (MILIPORE, resistivity $\rho = 15 \text{ M}\Omega \cdot \text{cm}$) and nitric acid (HNO_3 , 65% wt., POCH, pure p.a.). In order to prepare the initial solutions, the proper quantities of the oxides: Bi_2O_3 , (along with proper amount of Nd_2O_3 dopant) and TeO_2 were dissolved in a minimal volume of HNO_3 in the presence of citric acid (complexing agent) upon stirring and heating at 80°C . Tellurium source must be provided in proper excess (here 12% mol.) because of its considerable volatility during pyrolysis in the Pechini method (not observed while heating the individual raw substrate). Citric acid was chosen as a complexing agent because citrate ligands can form rather stable complexes of both Bi^{3+} and Te^{4+} in strongly acidic solutions as well as of Nd^{3+} ions [25]. The molar ratio between citric acid and metal cations was set to be 3:1. Under these conditions, the complete dissolution of the metal oxides was secured. When transparent and homogeneous solutions containing metal complexes were obtained, a proper amount of H_3BO_3 (with required 10.0% mol. boron excess applied to prevent non-stoichiometry due to the presence of adsorbed water and a possible evaporation of B_2O_3 at elevated temperatures) was charged into the solution and the stirring was kept on. The overall molar ratio of the used Bi_2O_3 , TeO_2 and H_3BO_3 substrates was 3:2.24:2.2, respectively (counted for undoped BTBO). After secondary homogenization, mannitol (polymeric agent) was added into the solution. In all the syntheses carried out, the molar ratio of citric acid to mannitol was constant and set to 3:1. After dissolving all the reagents, the solution mixing was continued for about 1 h at 90°C in order to initialize the polyesterification. Each prepared sol was then transferred into an alumina crucible (INCERAMICS S.A.) and put inside a furnace equipped with an EUROTHERM 906S temperature controller. The content was kept for about 24 h at 100°C in order to evaporate the solvents (H_2O - HNO_3 azeotrope) and to complete the polyesterification. A yellowish, foamy-like viscous gel was obtained. The temperature was raised up to 350°C for 3 h in order to remove the water residuals and dry the gel until it turned into black, brittle resin. To start the pyrolysis process and to get rid of the organic part, the

temperature was gradually raised up to 500°C and kept for 24 h. After that, the temperature was increased to 650°C and the process was still carried out for 48 h. In between these stages and after their completion, the powder materials were thoroughly ground in an agate mortar. Such a long duration of the synthesis (including 72 h of pyrolysis) is required to ensure complete oxidation from Te^{4+} to Te^{6+} . From the analytical point of view, the chemical reactions that take place between the initial reagents during the synthesis at a proper temperature and within a sufficient process time according to the Pechini method (for undoped BTBO) can be written by the following equations:



The sequence given above is the most probable, while BTBO is the only documented existing phase that consists of bismuth, tellurium and boron at the same time. Tellurium ions can be oxidized from +4 to +6 state (through the intermediate $\text{Bi}_2\text{Te}_2\text{O}_8$ phase, containing a tellurium pair at both +4 and +6 states), thanks to the presence of oxygen/air atmosphere at high temperature. It explains such a long duration of this process. Even if reaction (1) can occur at T_1 (below 500°C), reactions (2) and (3) can run simultaneously, but only at a suitably high temperature T_2 . Reaction (4) describes the summary reaction taking place in this process. One can see that the final product (BTBO) is formed as a result of redox reaction. In our study, T_1 was equal to 500°C and T_2 was set to 650°C . After the reaction completion, the crucible was taken out of the furnace and rapidly cooled to room temperature. Its contents were crushed and ground in an agate mortar and very fine, almost colorless BTBO: Nd^{3+} powders were obtained. Synthesis procedure provided above makes it possible to determine and calculate the precise amounts of Nd_2O_3 and Bi_2O_3 one should use in the synthesis of each of the BTBO: Nd^{3+} systems (for 0.5,

1.0, 2.5, 5.0, 7.5 and 10.0 at.% of Nd^{3+}). According to the literature data given for other borates, i.e. $\text{Bi}_2\text{ZnOB}_2\text{O}_6$ [8] or $\delta\text{-BiB}_3\text{O}_6$ [26], we assumed that it is possible to substitute effectively the Bi^{3+} with Nd^{3+} ions, what was later confirmed by XRD measurements. In this work, the Nd dopant concentration is expressed in at.% of Nd^{3+} ions substituting Bi^{3+} ions, which is determined as Nd and Bi atoms content, relative to three Bi atoms in the structure unit of Bi_3TeBO_9 (Table 1).

On the basis of synthesis reaction stoichiometry (Reaction (4)) and mutual molar proportions, it can be calculated that 0.69894 g of Bi_2O_3 should be used for the synthesis of 1 mmol of undoped BTBO, while for the synthesis of the same amount of doped BTBO:Nd^{3+} with Nd^{3+} concentration equal to 5.0% at, it requires 0.66399 g of Bi_2O_3 and 0.02524 g of Nd_2O_3 , respectively. These calculations show that the molar ratio of Nd^{3+} to Bi^{3+} ions in target BTBO:Nd^{3+} systems should be exactly the same as the molar ratio of used oxides: Nd_2O_3 and Bi_2O_3 in the initial mixture of needed reagents. Based on the above mentioned (and the information concerning the necessary excesses of Te and B), it is possible to determine the absolute masses of all reagents needed for the process.

Characterization

Experimental methods

The diffraction patterns of the synthesized BTBO:Nd^{3+} powders were collected using the BRUKER D8 Discover diffractometer equipped with the CuK_α radiator ($\lambda_{K\alpha1} = 1.540598 \text{ \AA}$, $\lambda_{K\alpha2} = 1.544426 \text{ \AA}$, Siemens KFL CU 2 K, 40 kV voltage and 40 mA current in operating mode) and Göbel FGM2 mirror. The Bragg–Brentano diffraction geometry was applied. The diffraction angle $2\theta_B$ ranged from 18 to 70° with a step of 0.01° and acquisition time of 2 s per step. All the measurements were carried out at 298 K in the temperature-stabilized Anton Paar HTK 1200 N chamber. For data processing, the

DIFFRAC.SUITE EVA application was used, allowing the $\lambda_{K\alpha2}$ signal component deconvolution and removal, background subtraction and data smoothing (using the fast Fourier transform). The phase analysis was made with the support of the Crystallography Open Database (COD). For crystallographic calculations, the FullPROF ver. 3.0 program was used. This application allowed the Rietveld refinement and calculation of the precise unit cell parameters according to the diffraction profile fitting.

The microscopic analysis of BTBO:Nd^{3+} powders was performed with the scanning electron microscope (SEM/FEI Quanta 250FEG). The samples were analyzed in the low vacuum mode at the pressure 70 Pa. The images were recorded in secondary electron mode at an accelerating voltage of 5 kV. Energy dispersive X-ray (EDX) analysis was performed with the Edax Octane SDD system at an accelerating voltage of 30 kV.

The Raman investigations were performed in the back-scattering geometry using the Renishaw InVia Raman microscope equipped with the confocal the DM 2500 Leica optical microscope and the CCD detector. The unpolarized Raman spectra were excited with the Ar laser emitting light of 488 nm wavelength and recorded in single scan with 30 s exposure time and 1 mW of the applied power. The position of the Raman peaks was calibrated before data collection using the Si reference sample as an internal standard with the peak position at 520.3 cm^{-1} . The diffraction-limited optical spatial resolution depended on the excitation wavelength and for the used $50\times$ LWD objective it was approximately equal to $1.5 \mu\text{m}$. The instrumental resolution of the spectrometer was better than 2 cm^{-1} . Spectral analysis was performed with the software packages WiRE3.1/Renishaw.

The reflectance spectra were measured with the Varian Model 5E UV–VIS–NIR spectrophotometer equipped with two excitation sources: the tungsten halide lamp in NIR/VIS and the deuterium arc UV range. As detectors were used the Hamamatsu R928 PMT in UV/VIS and Peltier-cooled PbS photocell in NIR range. All spectra were corrected for sources,

Table 1 The Nd and Bi content of the series of investigated BTBO:Nd^{3+} samples

BTBO:Nd^{3+}	0.5 at.%	1.0 at.%	2.5 at.%	5.0 at.%	7.5 at.%	10.0 at.%
Nd	0.015	0.030	0.075	0.150	0.225	0.300
Bi	2.985	2.970	2.925	2.850	2.775	2.700

detectors and gratings characteristics. The excitation and emission spectra as well as decay kinetics and quantum yield measurements of BTBO:Nd³⁺ crystalline powders were recorded using the FLS980 Fluorescence Spectrometer (Edinburgh Instruments) equipped with the holographic grating of 1800 lines/mm, blazed at 300 mm focal length monochromators in Czerny Turner configuration. The excitation and emission spectra were obtained using a 450 W Xenon lamp. For decay times measurements, the 450 W excitation source was replaced with the 150 W lamp (μ F2) with external triggering. The emission spectra and decay times in the visible range were recorded on the Hammamatsu C5680 streak camera with time resolution below 50 ps and effective spectral range from 200 to 1000 nm. An excitation source was the Coherent Libra-S-laser (femtosecond laser, wavelength 800 nm, pulse width of less than 100 fs and energy of 1 mJ at 1 kHz repetition rate) paired with the Coherent OPerA Solo Optical Parametric Oscillator (two-stage amplifier of white continuum) that allows generation of pulses in the range of wavelengths from 230 to 2800 nm.

Results and discussion

Crystal structure

BTBO crystallizes in hexagonal structure of $P6_3$ space group with two formula units in the unit cell. The unit-cell parameters of BTBO crystal are: $a = 8.7510(12)$ Å, $c = 5.8981(12)$ Å and $V = 391.16$ Å³ [9]. The crystal structure of BTBO is formed by two covalently bonded ionic complexes, octahedral TeO₆^{6−} and trigonal-planar BO₃^{3−} groups. In particular, B atoms are surrounded by three O atoms to form the trigonal-planar BO₃ groups with uniform B – O bond lengths, while Te⁶⁺ cations are coordinated by six O atoms with different Te – O bond lengths. (The TeO₆ octahedra are slightly deformed from the regular octahedral configuration.) Owing to the size similarity of the ionic radii of the Nd³⁺ and Bi³⁺ ions, in the doped BTBO microcrystals, Bi³⁺ ions can be efficiently substituted by Nd³⁺ ions. In the crystal structure of BTBO, the BO₃ layers are alternate with the cationic layers made of TeO₆ octahedra and Bi³⁺ ions along the z -axis. The BO₃ triangles are

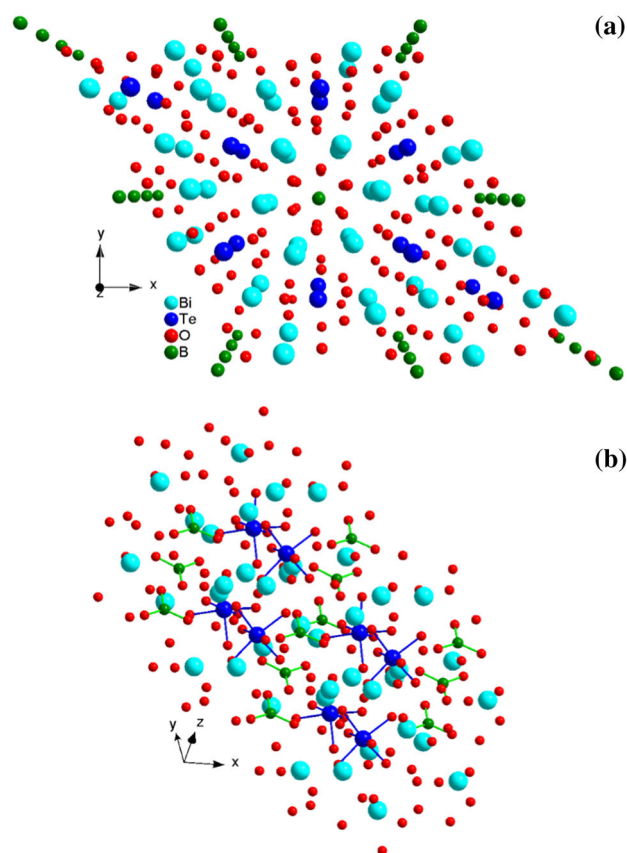


Figure 1 Structure of BTBO crystal (a) a view along the c axis (b) structure projection according to the xyz orientation [27].

placed in staggered arrangement along the z direction. Moreover, the BO₃ and TeO₆ groups are arranged similarly along the x and y axis, creating the alternate rows of BO₃ and TeO₆ groups (Fig. 1) [10, 13]. The structure of BTBO crystal presented in Fig. 1 was prepared based on the structure data involved in the Ref. [9]. The reference system (xyz) was defined by the following convention: x is parallel to a , y is perpendicular to a and z is parallel to c and perpendicular to the xy plane. In the used notation, a and c denote the crystallographic axes of the hexagonal system.

In particular, Fig. 1a presents the perspective view of BTBO structure along the c axis with the following coordination of B, Te and Bi atoms: (0, 0, 0.425(3)), (2/3, 1/3, 0.0813(2)) and (0.29827(3), 0.34622(3), 0.10689(12)), respectively [9]. In Fig. 1b, the structure projection according to the xyz orientation with some planar BO₃ groups and TeO₆ octahedra is presented. Moreover, we have already presented the detailed

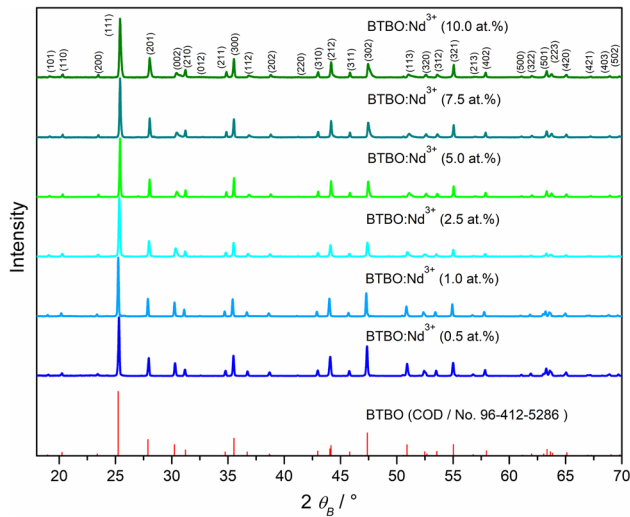


Figure 2 A set of experimental powder XRD patterns of BTBO:Nd³⁺ samples.

description of BTBO structure in our previous paper [13].

The results of diffraction measurements of BTBO:Nd³⁺ powders are presented in Fig. 2. All presented diffraction patterns of the synthesized BTBO:Nd³⁺ are in good agreement with the reference COD card (No. 96–412–5286), what means that all of them represent hexagonal class with $P6_3$ (173) space group ($Z = 2$). No diffraction lines originating from impurities, side products or unreacted reagents are observed, what indicates that BTBO:Nd³⁺ is the only reaction product. The reference Crystallographic Information File (CIF) of BTBO phase used for Rietveld refinement was received from the supplementary data given in Ref. [9]. The results for BTBO:Nd³⁺ compounds show that the original symmetry group of the crystal remains undisturbed when the Nd³⁺ ions are incorporated into the BTBO matrix.

The unit cell parameters of each synthesized sample are presented in Table 1. The values of effective ionic radius of Bi³⁺ and Nd³⁺ are equal to 1.03 and 0.983 Å, respectively [28]. Smaller Nd³⁺ ions radius can suggest that isovalent substitution of Bi³⁺ ions with Nd³⁺ should lead to progressive decrease in the BTBO:Nd³⁺ unit cell volume.

The results in Table 2 reveal irregular changes in the BTBO:Nd³⁺ unit cell parameters and its volume vs. the content of Nd³⁺ ions. In particular, the lattice constant a increases with increasing Nd³⁺ content up to 5.0 at.% Nd³⁺ ions in BTBO:Nd³⁺ and then decreases, while c shows a distinguished decrease with increasing Nd³⁺ content. It is also seen that the only factor that increases progressively with Nd³⁺ content is the a/c ratio, and at around 10 at.% Nd³⁺ it stabilizes, as shown in Table 2. It may suggest that the geometry of BTBO:Nd³⁺ unit cell is slightly changing (with unchanged symmetry class) and can affect its non-centrosymmetry. Different character of the courses of changes in the lattice constants a and c can be explained by the anisotropic behavior of these structure parameters and various distribution of Nd³⁺ dopant in the BTBO:Nd³⁺ microcrystals on the surface and the volume of the grains, depending on the Nd³⁺ concentration. The threshold Nd³⁺ concentration in BTBO:Nd³⁺ from which this volume compression starts is ca. 2.5 at. % Nd³⁺ ions. In particular, due to microscale of investigated polycrystalline materials, the distribution of Nd³⁺ dopant may vary within a single grain and a significant increase in their effective surface area takes place. As a result, the Nd³⁺ dopant may more preferably concentrate closer to the surface of the BTBO:Nd³⁺ microcrystals and then it is more bound to its surface than in its volume. Especially, when the concentration of Nd³⁺ ions is low, it may more readily build up

Table 2 Calculated unit cell parameters of BTBO:Nd³⁺ powders

Compound	Unit cell parameters [Å]			V/Å ³
	A	c	a/c	
BTBO [9]	8.7510(12)	5.8981(12)	1.4837	391.16
BTBO [13]	8.7505(2)	5.8871(2)	1.4864	390.39
BTBO:Nd ³⁺ (0.5 at.%)	8.7483(2)	5.8879(2)	1.4858	390.25
BTBO:Nd ³⁺ (1.0 at.%)	8.7520(1)	5.8877(1)	1.4865	390.56
BTBO:Nd ³⁺ (2.5 at.%)	8.7570(3)	5.8855(4)	1.4879	390.86
BTBO:Nd ³⁺ (5.0 at.%)	8.7592(1)	5.8716(2)	1.4918	390.12
BTBO:Nd ³⁺ (7.5 at.%)	8.7544(2)	5.8639(2)	1.4929	389.20
BTBO:Nd ³⁺ (10.0 at.%)	8.7523(3)	5.8618(3)	1.4931	388.87

in the near-surface regions. Then, despite maintaining the parental BTBO (hexagonal) structure, the local strains in the crystal lattice may occur, which will result in an increase in the lattice constants and volume of the BTBO:Nd³⁺ unit cell. On the other hand, as the concentration of the Nd³⁺ dopant increases, the possibility of filling the near-surface regions with it begins to decrease, which in turn necessitates the need for further incorporation of the dopant into the BTBO:Nd³⁺ microcrystals volume. Then, the changes in geometry of the BTBO: Nd³⁺ cell are closer to those predicted theoretically, showing progressive compression of BTBO. Moreover, for BTBO samples with higher Nd³⁺ concentrations (5.0, 7.5 and 10.0 at.%), we observed decreasing unit cell volume as a result of the smaller Nd³⁺ ionic radius (substituting ions) in comparison with the substituted Bi³⁺ ions. As a result, Nd³⁺-Nd³⁺ distances are shortened with increasing Nd³⁺ concentration in BTBO matrix. This effect can consequently lead to LCQ and different character of luminescence decay time of excited Nd³⁺ ions for samples doped with 5.0, 7.5 and 10.0 at.% of Nd³⁺ ions.

SEM and EDX analysis

Microscopic observation of the BTBO:Nd³⁺ samples revealed their morphology. All the materials discussed had different irregular microstructures (Fig. 3).

The sample BTBO:Nd³⁺(0.5 at.%) (Fig. 3a) has both large grains from 7 to 15 microns in size and smaller grains between 3 and 5 microns in size. The large grains are often agglomerations of much smaller ones, of up to a micrometer in size. However, large portions of the large grains are monolithic. The

sample BTBO:Nd³⁺(1.0 at.%) (Fig. 3b) has a very similar microstructure to that previously described. The only significant difference is that the sizes of the largest agglomerates reach 30 microns. The sample BTBO:Nd³⁺(2.5 at.%) (Fig. 3c) has a similar microstructure. Compared to previous ones, there are no such large agglomerates made of small grains, and the largest observed grains are monolithic. Their diameters are between 7 and 14 microns. The sizes of small, non-aggregating grains are mostly between 0.5 and 2.5 microns. From among all analyzed samples, BTBO:Nd³⁺(5.0 at.%) (Fig. 3d) has the morphology most closely resembling large crystals with clearly visible faces. The sizes of their edges are from 2 to 8 μm . For BTBO:Nd³⁺ (7.5 at.%) (Fig. 3e), we observe the largest grains with the size of tens of micrometers with a small amount of grains with the size of 1–2 μm . Increase in the Nd³⁺ content to 10.0 at% (Fig. 3f) resulted in a reduction of the grains size to 1–4 μm and a change in their edges that became strongly curved. However, their crystalline nature can be observed, but is less visible than for the sample in Fig. 3d. Moreover, in the SEM images Fig. 3a–f of all samples, the nano-sized crystals can be also observed.

The EDX analysis of investigated samples allows to determine the elements content for BTBO:Nd³⁺ systems. In Fig. 4, the EDX spectrum for the selected BTBO:Nd³⁺ (10.0 at.%) sample is presented.

Selected scanned areas of the sizes 28 $\times$ 36 μm^2 of all investigated samples were subjected to the EDX analysis. It should be noted that due to inhomogeneous morphology of the investigated samples, the EDX analysis of Nd atoms used at a low content, provides very local information. Moreover, the EDX

Figure 3 SEM micrographs of BTBO:Nd³⁺ (0.5 at.%) (a), BTBO:Nd³⁺(1.0 at.%) (b), BTBO:Nd³⁺ (2.5 at.%) (c), BTBO:Nd³⁺ (5.0 at.%) (d), BTBO:Nd³⁺ (7.5 at.%) (e) and BTBO:Nd³⁺ (10.0 at.%) (f) in magnification of 30 000x.

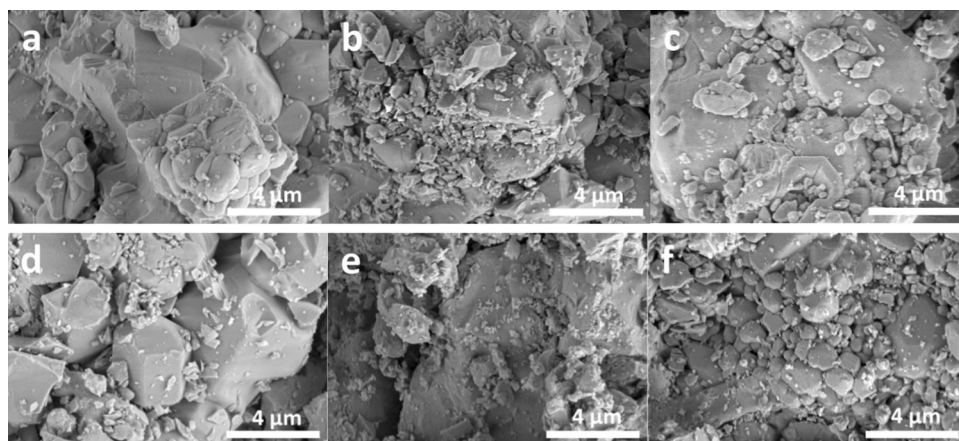


Figure 4 The EDX spectrum for BTBO:Nd³⁺ (10.0 at.%) sample.

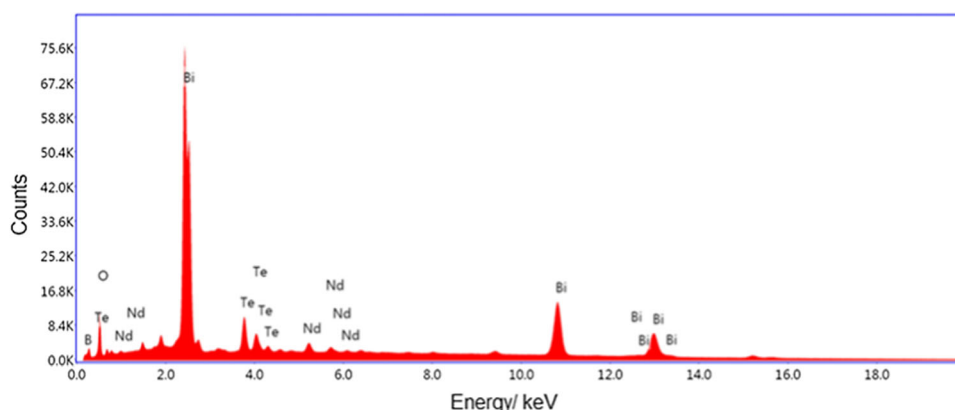


Table 3 The elements content in BTBO:Nd³⁺(10.0 at.%) sample

BTBO:Nd ³⁺ (10.0 at.%)	Element	Weight %	Atomic %	Error %
	B	8.26	37.85	4.63
	O	13.42	41.55	9.31
	Te	11.26	4.37	5.32
	Nd	3.08	1.06	6.89
	Bi	63.98	15.17	2.61

measurement of elements present at very low concentrations is charged with a relatively large uncertainty. The weight and atomic content of particular elements (relative to the structure unit Bi₃TeBO₉) in a selected exemplary BTBO:Nd³⁺ (10.0 at.%) sample are given in Table 3.

The theoretically calculated content of Nd and Bi atoms, relative to all atoms in the structure unit of Bi₃TeBO₉ (three Bi atoms, one Te atom, one B atom and nine O atoms) and the experimentally measured content of Nd atoms (on the basis of EDX data) for the series of investigated samples are given in Table 4.

As seen from Table 4, the Nd content in the studied samples increases with increasing concentration from 0.5 to 10 at.%, both for theoretical as well as experimental values, as expected. The same Nd content

observed for experimental value for 7.5 and 10.0 at.% may be results on the measured data mostly from the surface than from volume of microcrystals. As already mentioned, the volume in comparison with surface location of Nd³⁺ ions are more preferred in higher Nd³⁺ doped samples.

μ-Raman investigation

BTBO crystallizes in hexagonal structure with *P*6₃ space group. The primitive unit cell of BTBO crystal comprises two formula units and contains 28 atoms engaged in 84 fundamental vibrations. The zone-center optic modes predicted from the group theory analysis for BTBO crystals can be classified according to the following formula: 14A + 14B + 14E₁ + 14E₂. The phonon modes of A, E₁ and E₂ types are Raman active, whereas the modes of A and E₁ species are IR

Table 4 The theoretical and experimental contents of Nd atoms with the estimated absolute uncertainty for the series of BTBO:Nd³⁺ samples

Compound	Content of Nd atoms in the structure unit	
	Theoretical value	Experimental value
BTBO:Nd ³⁺ (0.5 at.%)	0.107	0.03 ± 0.01
BTBO:Nd ³⁺ (1.0 at.%)	0.214	0.12 ± 0.01
BTBO:Nd ³⁺ (2.5 at.%)	0.536	0.23 ± 0.02
BTBO:Nd ³⁺ (5.0 at.%)	1.071	0.52 ± 0.05
BTBO:Nd ³⁺ (7.5 at.%)	1.607	1.06 ± 0.08
BTBO:Nd ³⁺ (10.0 at.%)	2.143	1.06 ± 0.07

active. The modes of B symmetry are inactive both in the Raman and IR spectra [13, 29, 30]. The BTBO structure is formed by octahedral TeO_6 and trigonal-planar BO_3 molecular groups, which have their own characteristic internal vibrations. In the ideal, isolated octahedra TeO_6 unit with point group symmetry O_h , the internal vibrations can be classified into six fundamental modes: three Raman-active—the symmetric stretching vibrations ν_1 ($\sim 700\text{ cm}^{-1}$), doubly degenerate asymmetric bending vibrations ν_2 ($500\text{--}650\text{ cm}^{-1}$) and triply degenerate symmetric bending ν_5 modes (below 400 cm^{-1}); two IR-active modes—the triply degenerate asymmetric bending vibrations ν_3 ($500\text{--}650\text{ cm}^{-1}$), triply degenerate asymmetric bending vibrations ν_4 ($400\text{--}500\text{ cm}^{-1}$) and one ν_6 internal mode inactive both in the Raman and IR spectra [31]. The triangular planar BO_3 groups with D_{3h} symmetry have their four characteristic internal vibrations named: μ_1 , μ_2 , μ_3 , μ_4 . Some of them are Raman-active (μ_1 , μ_3 , μ_4) and/or IR-active modes (μ_2 , μ_3 , μ_4). The vibrations of an ideal, isolated BO_3 group can be classified into four fundamental modes: symmetric stretching mode μ_1 ($\sim 950\text{ cm}^{-1}$), doubly degenerate asymmetric stretching mode μ_3 ($1250\text{--}1400\text{ cm}^{-1}$), doubly degenerate planar bending mode μ_4 ($\sim 600\text{ cm}^{-1}$) and infrared active out-of-plane bending mode μ_2 ($700\text{--}800\text{ cm}^{-1}$) [13, 32, 33]. Moreover, the frequencies of external lattice vibrations (translations or librations of Bi (Nd) or Te atoms and BO_3 and TeO_6 groups) are located below $\sim 350\text{ cm}^{-1}$.

The unpolarized Raman spectra of undoped BTBO and BTBO:Nd^{3+} crystalline powders were recorded in the $100\text{--}1500\text{ cm}^{-1}$ spectral range at room temperature (Fig. 5).

The spectroscopic parameters of all Raman-active bands were analyzed by the fitting procedure using the Lorentzian-like function. The detailed assignment of all Raman-active bands and their determined wavenumbers values are presented in Table S1.

As follows from Fig. 5, Table S1 and the data given for undoped BTBO powder presented in our previous paper [13], the bands from the spectral range $1500\text{--}600\text{ cm}^{-1}$ were assigned to the stretching vibrations of BO_3 groups or TeO_6 octahedra. The medium intensity bands at 1297 , 1283 , 1262 , 1241 cm^{-1} and weak bands at 1221 cm^{-1} were assigned to the stretching modes of BO_3 units. The very weak Raman band at 1384 cm^{-1} is probably a result of higher order Raman scattering (according to

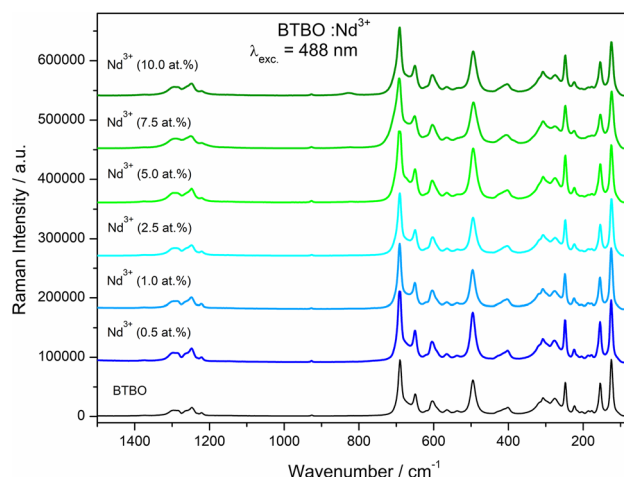


Figure 5 Unpolarized Raman spectra of undoped BTBO and BTBO:Nd^{3+} powders, detected at 300 K.

our ab initio calculations) [13]. The very weak intensity modes detected at 926 cm^{-1} originate from A type μ_1 internal stretching vibration of BO_3 complex. The modes in the spectral range $690\text{--}350\text{ cm}^{-1}$ correspond to the vibrations of BO_3 and TeO_6 groups. Many bands in this spectral range have the mixed character. The bands detected in the Raman spectra in the spectral region $690\text{--}600\text{ cm}^{-1}$ originate from the stretching vibrations μ_4 and μ_2 of BO_3 or ν_3 and ν_1 of TeO_6 groups. In particular, the most intensive modes recorded in this spectral range at 691 cm^{-1} and the medium modes occurring at 649 cm^{-1} were assigned to the ν_1 and ν_3 stretching vibrations of TeO_6 groups, respectively. The weak modes at 620 cm^{-1} , the medium modes at 604 cm^{-1} and the weak modes at 564 cm^{-1} detected in the spectra were attributed to the μ_4 bending vibrations of BO_3 groups. The other bands in the Raman spectra in the considered spectral range of $660\text{--}350\text{ cm}^{-1}$ were assigned to the vibrations of TeO_6 octahedra. In particular, the shoulder at 596 cm^{-1} and the weak mode at 537 cm^{-1} detected in the spectra can be assigned to the bending ν_2 vibrations; the very strong modes centered at 497 cm^{-1} and a shoulder at 414 cm^{-1} arise from the ν_4 vibrations; the medium-intensity modes at 401 cm^{-1} in the spectra were assigned to the ν_5 vibrations. According to the analysis of the calculated eigenvectors, the lowest frequency part of the spectrum, below $\sim 350\text{ cm}^{-1}$, originates from the external lattice vibrations of Bi(Nd) or Te atoms and TeO_6 and BO_3 complexes, as the rigid units, and mainly corresponds to the librational or translational motions of these molecular groups. In particular, the

highest intensity modes in this range were centered at 124 and 154 cm^{-1} in the spectra. The low wavenumber/energy phonons detected in the Raman spectra in the range below $\sim 360 \text{ cm}^{-1}$ are of mixed type and are related to the relatively large atomic masses of Bi and Te atoms [8]. All above-given wavenumbers were determined for BTBO: Nd^{3+} (0.5 at.%) sample. Moreover, the spectral analysis of the Raman spectra of undoped and Nd^{3+} -doped BTBO powders allows to conclude that low Nd^{3+} concentrations used in this study do not influence on vibrational properties of BTBO matrix. The results of Raman scattering method show the low phonon energy of BTBO matrix, which is important in phonon-assisted energy transfer processes between active Bi^{3+} and Nd^{3+} ions.

Luminescence

All the bands present in the reflectance, excitation and absorption spectra, assigned to the energy levels of active Nd^{3+} ions, were identify on the basis of the Dieke's diagram [33].

The reflectance spectra of undoped BTBO and BTBO: Nd^{3+} powders detected in 250–1000 nm spectral range at 300 K are presented in Fig. 6.

In the reflectance spectra of BTBO: Nd^{3+} powders it can be observed the f - f transitions from Nd^{3+} ions as well as band assigned to the transition from Bi^{3+} ions. The broad bands recorded in the range 200–370 nm, with the intensity maximum at about 330 nm arise from the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ transition of Bi^{3+} ions. All other bands detected in reflectance spectra are assigned to the f - f transitions from Nd^{3+} ions. The bands at about

515 and 530 nm are related to the ($^4\text{G}_{7/2} + ^4\text{G}_{9/2}$) $\rightarrow ^4\text{I}_{9/2}$ and $^2\text{K}_{13/2} \rightarrow ^4\text{I}_{9/2}$ transitions, respectively. The most intensive peaks located in range 570–610 nm were assigned to the ($^4\text{G}_{5/2} + ^2\text{G}_{7/2}$) $\rightarrow ^4\text{I}_{9/2}$ transitions. The weak bands in the spectral range 670–700 nm correspond to the $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{9/2}$ transitions. The bands in the spectral range 730–775 nm and 780–835 nm are present due to the ($^4\text{F}_{7/2} + ^4\text{S}_{3/2}$) $\rightarrow ^4\text{I}_{9/2}$ and ($^4\text{F}_{5/2} + ^2\text{H}_{9/2}$) $\rightarrow ^4\text{I}_{9/2}$ transitions, respectively, and the peaks located in the spectral range 850–890 nm are attributed to the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions.

The excitation spectra of BTBO: Nd^{3+} powders were recorded at 300 K in the spectral range 250–900 nm by monitoring the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition of Nd^{3+} ions at 1064 nm (Fig. 7).

As follows from Fig. 7, numerous bands were detected in the excitation spectra of BTBO: Nd^{3+} powders in the range from about 250 nm to about 900 nm. Moreover, the intensity of the bands in the spectra depends on Nd^{3+} concentration. The highest intensity excitation bands were detected in the spectrum of BTBO: Nd^{3+} powder doped with Nd^{3+} ions at the lowest concentration (0.5 at.%). The corresponding bands in the excitation spectra of BTBO: Nd^{3+} powders were detected almost in the same positions for all Nd^{3+} concentrations. In particular, the bands recorded in the range 270–370 nm with the intensity maximum at about 330 nm arise from the $^4\text{D}_{3/2} \leftarrow ^4\text{I}_{9/2}$ transitions. Moreover, the broadening of the excitation bands in this spectral range results from the interference of the mentioned above Nd^{3+} excitation bands and the excitation bands assigned to the $^1\text{S}_0 \leftarrow ^3\text{P}_1$ transition of Bi^{3+} ions. Very weak peaks at

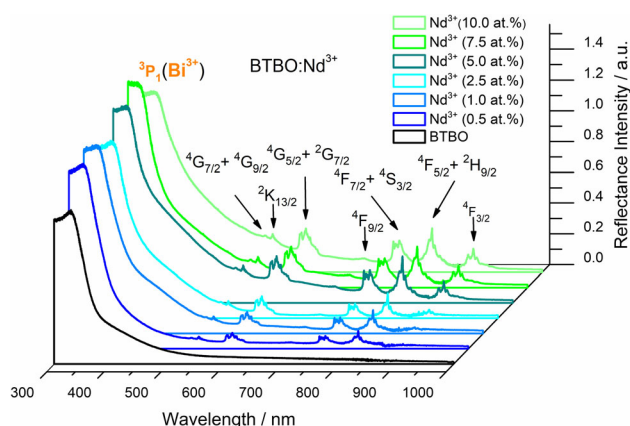


Figure 6 The reflectance spectra of undoped BTBO and BTBO: Nd^{3+} powders detected at 300 K.

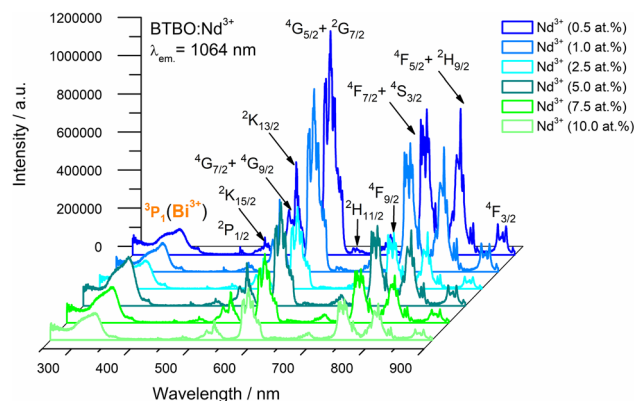


Figure 7 Excitation spectra of BTBO: Nd^{3+} powders recorded by monitoring the emission of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition in Nd^{3+} ions at 1064 nm, detected at 300 K.

about 430 nm correspond to the $^2P_{1/2} \leftarrow ^4I_{9/2}$ transitions. The weak bands in the range from 450 to 490 nm can be assigned to the $^2K_{15/2} \leftarrow ^4I_{9/2}$ transitions. The strong bands at about 515 nm are related to the $(^4G_{7/2} + ^4G_{9/2}) \leftarrow ^4I_{9/2}$ transitions, while the strong peaks centered at about 530 nm arise from the $^2K_{13/2} \leftarrow ^4I_{9/2}$ transitions. The most intensive peaks located in range 570–610 nm were assigned to the $(^4G_{5/2} + ^2G_{7/2}) \leftarrow ^4I_{9/2}$ transitions. Moreover, the bands in the spectral range 620–640 nm (very weak) and 670–700 nm (weak) correspond to the $^2H_{11/2} \leftarrow ^4I_{9/2}$ and $^4F_{9/2} \leftarrow ^4I_{9/2}$ transitions, respectively. The very strong bands in the spectral range of 730–775 nm and 780–835 nm are due to the $(^4F_{7/2} + ^4S_{3/2}) \leftarrow ^4I_{9/2}$ and $(^4F_{5/2} + ^2H_{9/2}) \leftarrow ^4I_{9/2}$ transitions, respectively. The strong peaks located in the spectral range 850–890 nm were attributed to the $^4F_{3/2} \leftarrow ^4I_{9/2}$ transitions. It should be noted that the excitation spectra of BTBO:Nd³⁺ powders (Fig. 7) correspond well with the reflectance spectra (Fig. 6). However, the difference in the transitions intensity observed in the UV excitation and reflectance spectra is a result of different sensitivities of the detectors in the used equipment. It can be also observed that in NIR range, in which PbS detector is used with much lower sensitivity than R928 PMT, with decreasing Nd³⁺ concentration, the transition peaks intensity almost disappears. In the visible and UV range, the changes are less pronounced.

The emission spectra of BTBO:Nd³⁺ powders were investigated upon 327 and 586.4 nm excitation in the 800–1200 nm spectral range (Fig. 8).

The emission spectra of BTBO:Nd³⁺ powders show broad and intense bands in the range of 865–925 nm and 1035–1100 nm. The broad multi-structure bands detected in the range of 865–925 nm are related to the $^4F_{3/2} \rightarrow ^4I_{9/2}$ transitions. The shape of these bands is a result of the Stark effect, which describes the shifting and splitting of spectral lines of active ions due to the presence of an external electric crystal field. As a result, the $^4F_{3/2}$ energy level of Nd³⁺ splits into several Stark components [34]. The strong bands in the range 1035–1110 nm with a maximum at 1064 nm were attributed to the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions. The shape of these bands also suggests the influence of the crystal field on the electronic level $^4F_{3/2}$, which consists of Stark-levels, as mentioned above [35]. Interestingly, the highest intensity emission bands in NIR upon the excitation in UV were detected in the spectra of BTBO:Nd³⁺ powders

doped with the higher concentrations of Nd³⁺ ions (5.0, 7.5 and 10 at.%), with the maximum at 5.0 at.% concentration (Fig. 8a). Upon the excitation in VIS, the highest intensity emission bands in NIR were detected in the spectra of BTBO:Nd³⁺ powders doped with the lower concentrations of Nd³⁺ ions (0.5, 1.0 and 2.5 at.%) with the maximum at 0.5 at.% concentration (Fig. 8b). The observed phenomena result from the different energy transfer mechanisms upon the excitation in UV (by Bi³⁺ ions) and excitation in VIS spectral range (by Nd³⁺ ions).

In Fig. 9, the excitation and emission spectra registered in UV and VIS spectral range for undoped BTBO matrix are presented. In the excitation spectrum, only one band centered at about 327 nm assigned to the $^1S_0 \rightarrow ^3P_1$ transition of Bi³⁺ ions was detected. It shows that Bi³⁺ ions present in BTBO

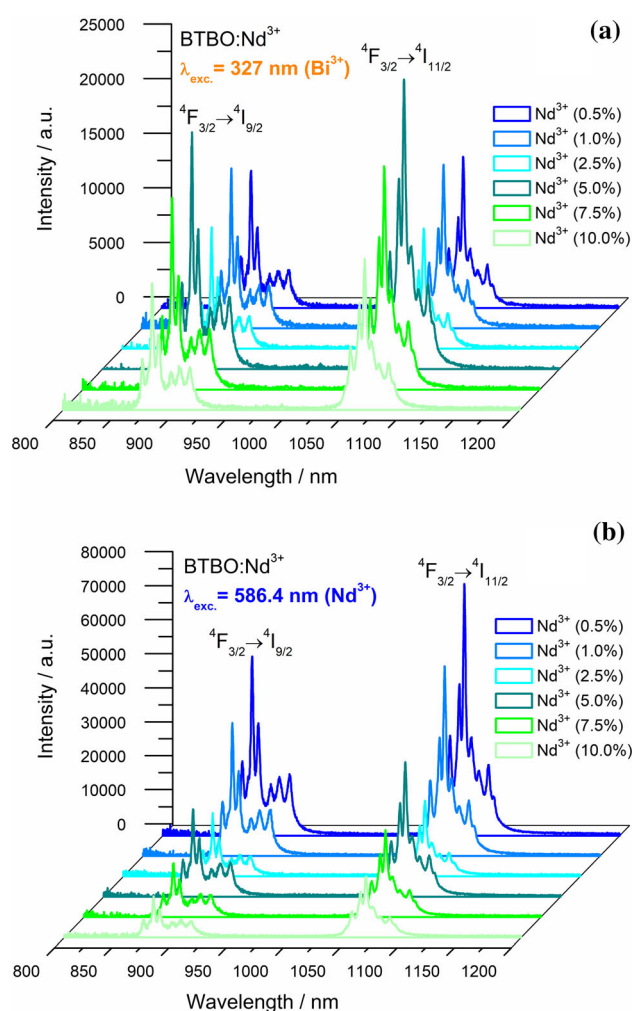


Figure 8 Emission spectra of BTBO:Nd³⁺ powders upon the excitation at 327 nm (a) and 586.4 nm (b), recorded at 300 K.

matrix can be used as a UV absorption sensitizer for Nd^{3+} ions in $\text{BTBO}:\text{Nd}^{3+}$ samples. Moreover, the emission spectrum shows the broad emission band in the 450–650 nm with the maximum at 560 nm (yellow emission) related to the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition of Bi^{3+} ions.

The possible mechanisms of energy relaxation after UV or VIS excitation are illustrated schematically in Fig. 10.

Due to the close positions of electronic levels of the excited states of Bi^{3+} and Nd^{3+} ions, the energy transfer process from Bi^{3+} to Nd^{3+} ions is possible. In particular, after the excitation in UV (at 327 nm), Bi^{3+} ions are excited from the $^1\text{S}_0$ ground states to the $^3\text{P}_1$ excited states, and next, after phonon-assisted non-radiative relaxation, they relax to the $^3\text{P}_0$ excited levels and next Bi^{3+} ions can relax to the $^1\text{S}_0$ ground states by emitting photons in the yellow region or through the resonance energy transfer to the nearest Bi^{3+} or Nd^{3+} ions. The energy of excited Bi^{3+} ions can be also transferred by the energy migration process to the unexcited neighboring Bi^{3+} ions, which leads to LCQ of Bi^{3+} ions. The other possible energy transfer processes from $^3\text{P}_1$ level of Bi^{3+} ions are the relaxations to the lower-lying excited levels of Nd^{3+} ions: $^2\text{P}_{1/2}$, $^2\text{K}_{15/2}$, $^4\text{G}_{7/2} + ^4\text{G}_{9/2}$, $^2\text{K}_{13/2}$, $^4\text{G}_{5/2} + ^2\text{G}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{F}_{9/2}$, $^4\text{F}_{7/2} + ^4\text{S}_{3/2}$, $^4\text{F}_{5/2} + ^2\text{H}_{9/2}$. The excited Nd^{3+} ions after non-radiative relaxation to $^4\text{F}_{3/2}$ level can relax through the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions with NIR emission near 878 nm and 1064 nm, respectively. The phenomena in which one

photon of high energy can convert energy into two photons of lower energy is known as the quantum cutting process [36, 37]. The above-described energy transfer process from Bi^{3+} to Nd^{3+} leads to enhancement of Nd^{3+} emission in the NIR region. It should be noted that for lower concentrations of Nd^{3+} ions (0.5, 1.0 and 2.5 at.%), the mentioned energy transfer process is not effective enough because all Bi^{3+} ions are excited, but they can transfer energy only to the selected neighboring Nd^{3+} ions. The optimal Nd^{3+} concentration for the quantum cutting process to be realized by Bi^{3+} - Nd^{3+} pairs in the $\text{BTBO}:\text{Nd}^{3+}$ system is 5.0 at.%. For higher concentration of Nd^{3+} (7.5 and 10.0 at.%) we observe the LCQ effect.

After the excitation in VIS (at 586.4 nm), the Nd^{3+} ions are excited from the ground state $^4\text{I}_{9/2}$ to the excited states $^4\text{G}_{5/2} + ^2\text{G}_{7/2}$ (the most intensive bands detected in the excitation spectra of $\text{BTBO}:\text{Nd}^{3+}$ powders recorded by monitoring the emission of the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transition in Nd^{3+} ions at 1064 nm). These excited Nd^{3+} ions can relax to the $^4\text{F}_{3/2}$ level through non-radiative relaxation and next the NIR emission can be observed at about 878 nm and 1064 nm by the $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ and $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{11/2}$ transitions, respectively. Moreover, the highest intensity NIR emission was observed for 0.5 at.% Nd^{3+} concentration. For higher concentrations of Nd^{3+} ions (1.0, 2.5, 5.0, 7.5 and 10.0 at. %), we observed a decrease in the NIR emission as a result of

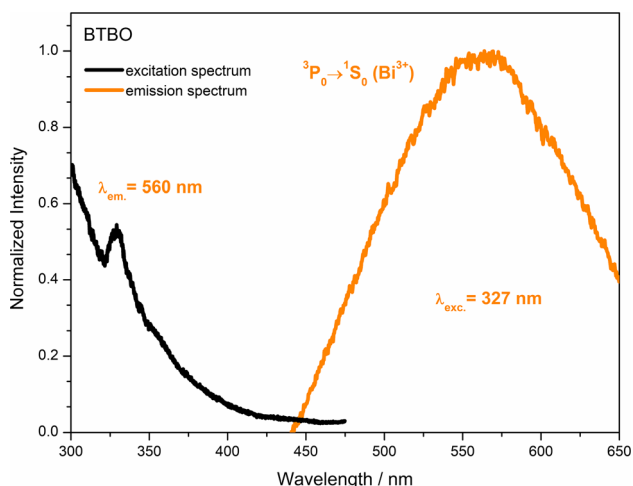


Figure 9 The excitation and emission spectra of BTBO powder for the emission observed at 560 nm assigned to Bi^{3+} ions upon the excitation at 327 nm, recorded at 300 K.

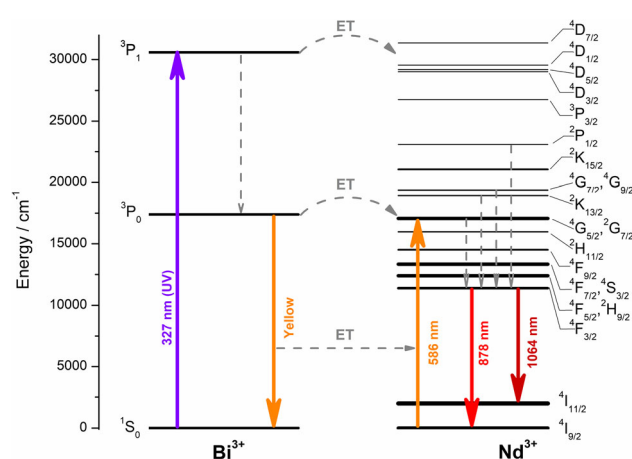


Figure 10 Schematic diagram of the possible ET between active ions in the $\text{BTBO}:\text{Nd}^{3+}$ system upon the excitation at 327 and 586.4 nm.

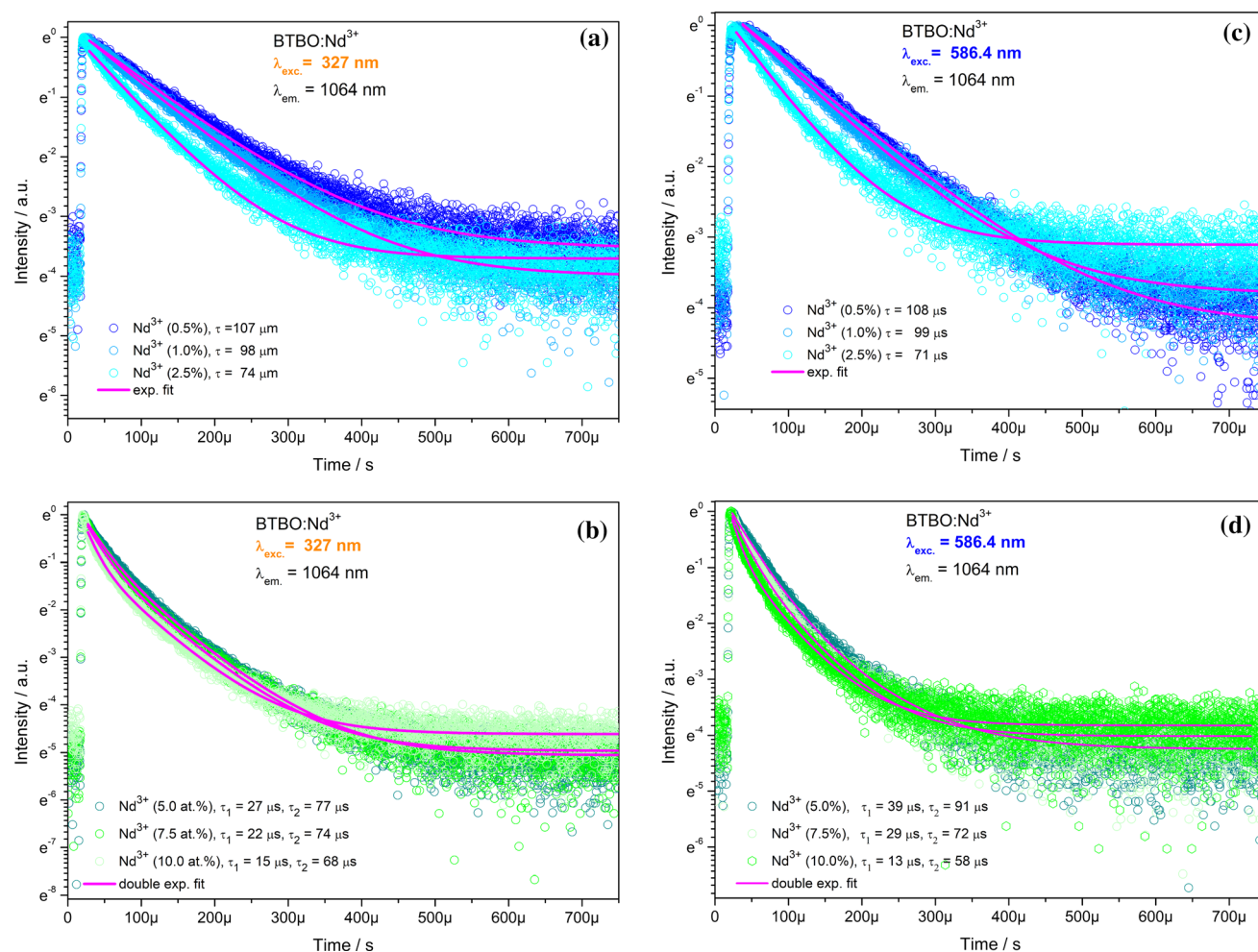


Figure 11 The luminescence decay time curves of BTBO:Nd³⁺ powders recorded by monitoring the emission of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition in Nd³⁺ ions at 1064 nm, upon the excitation at 327 nm (a)(b) and 586.4 nm (c)(d), detected at 300 K.

LCQ effect due to short distances between the active Nd³⁺ ions.

The luminescence decay curves of BTBO:Nd³⁺ powders monitored for the emission at 1064 nm upon the excitation at 327 and 586.4 nm are presented in Fig. 11.

To determine the decay times, the experimental decay curves of BTBO:Nd³⁺ powders were fitted to the exponential function according to the following formula:

$$I = I_1 \exp\left(-\frac{t}{\tau_1}\right) + I_2 \exp\left(-\frac{t}{\tau_2}\right) \quad (5)$$

where I_1 and I_2 are the intensities of different luminescence processes at the initial time and τ_1 and τ_2 are their lifetimes, respectively [37]. For BTBO:Nd³⁺ powders doped with higher Nd³⁺ concentrations (5.0, 7.5 and 10.0 at.%), a good fit was obtained with a

double exponential function, while only one exponential function was needed for lower doped powders (0.5, 1.0 and 2.5 at.%). The decay time determined by the spontaneous emission from the excited Nd³⁺ levels and the time calculated from the fit of the decay curves show the influence of the dopant concentration on the energy transfer process. The presence of two components in the decay fit is due to the different location and environment of Nd³⁺ ions incorporated into the BTBO lattice either in the volume or on the surface of the microcrystals, where Bi³⁺ ions are substituted by Nd³⁺ ions. Moreover, for higher concentrations of Nd³⁺, the surface-related effect is stronger due to higher surface to volume ratio, which results in a double exponential decay time character. The determined lifetimes monitored for the emission at 1064 nm under the excitation at 327 and 586.4 nm are given in Table 5.

Table 5 The lifetimes monitored for emission at 1064 nm upon the excitation at 327 and 586.4 nm

Compound	$\lambda_{\text{exc.}} = 327/\text{nm}$		$\lambda_{\text{exc.}} = 586.4/\text{nm}$	
	$\tau/\mu\text{s}$		$\tau/\mu\text{s}$	
BTBO Nd ³⁺ (0.5 at%)	107		108	
BTBO Nd ³⁺ (1.0 at%)	98		99	
BTBO Nd ³⁺ (2.5 at%)	74		71	
	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$	$\tau_1/\mu\text{s}$	$\tau_2/\mu\text{s}$
BTBO Nd ³⁺ (5.0 at%)	27	77	39	91
BTBO Nd ³⁺ (7.5 at%)	22	74	29	72
BTBO Nd ³⁺ (10.0 at%)	15	68	13	58

As follows from Table 5, the maximum lifetimes τ equal 107 and 108 μs were obtained for the BTBO:Nd³⁺ samples with the lowest concentration of Nd³⁺ (0.5 at.%), both under the excitation at 327 and 586.4 nm. For the other samples (1.0 and 2.5 at.% concentration of Nd³⁺), the lifetimes τ were shorter due to a weak Nd³⁺–Nd³⁺ interaction resulting in the LCQ effect. For the BTBO:Nd³⁺ samples with higher concentration of Nd³⁺ ions (5.0, 7.5 and 10.0 at.%), the lifetimes τ_1 and τ_2 related to the above-mentioned different location of Nd³⁺ ions (in the surface and in the volume of microcrystals, respectively) were determined. Moreover, as presented in Table 2, we observed the lifetimes to decrease with increasing Nd³⁺ concentration, both for τ_1 and τ_2 .

Additionally, the presented experimental results for BTBO:Nd³⁺ powders were supported by the following analysis and calculations. As mentioned above, the LCQ effect and shortening of the lifetime τ for BTBO:Nd³⁺ powders strongly depend on the concentration N_A of active Nd³⁺ ions, which can be calculated using the following equation:

$$N_A = \frac{3Zx}{V} \quad (6)$$

where V is the unit-cell volume, x is the dopant concentration and Z is the number of formula units in the unit cell [35]. The calculated N_A values for BTBO:Nd³⁺ powders are equal 7.68, 15.36, 38.38, 76.89, 115.62 and 154.29 ($\times 10^{25}$ ions/m³) for $x = 0.005$, 0.010, 0.025, 0.050, 0.075 and 0.100, respectively. The effective energy transfer process from the excited (donors D) to the unexcited (acceptors A) Nd³⁺ ions depends on the distance between

them. The average distance R_{DA} between the D and A ions can be calculated from the following formula:

$$R_{DA} \approx 2 \left(\frac{3V}{4\pi xZ} \right)^{1/3} \quad (7)$$

where V is the unit-cell volume, x is the dopant concentration and Z is the number of formula units in the unit cell [35]. The average distance R_{DA} for the investigated BTBO:Nd³⁺ powders calculated using Eq. 7 is equal 42.1, 33.4, 24.6, 19.5, 17.1, 15.5 Å for $x = 0.005$, 0.010, 0.025, 0.050, 0.075 and 0.100, respectively. The relatively high values of R_{DA} in the investigated BTBO:Nd³⁺ powders indicate that the main energy transfer mechanism responsible for the LCQ effect and shortening of the lifetime τ is the electric interaction [35].

Furthermore, for BTBO:Nd³⁺ powder with the lowest concentration of Nd³⁺ ions (0.5 at.%), the decay curve was analyzed using the Inokuti–Hirayama (IH) model [38]. In the IH model, the kinetics of the fluorescence intensity was described by the following equation:

$$I(t) = I_0 \exp \left[-\frac{t}{\tau_0} - Q \left(\frac{t}{\tau_0} \right)^{\frac{3}{s}} \right] + b \quad (8)$$

where τ_0 is the intrinsic decay time of D ions in the absence of A ions; b is the fitting offset; Q is the energy transfer parameter. The decay curve of BTBO:Nd³⁺ (0.5 at.%) powder was well fitted to the IH models for the measured fluorescence lifetime $\tau_0 = 108 \mu\text{s}$ (of the $^4F_{3/2} \rightarrow ^4I_{11/2}$ transition upon the excitation with 586.4 nm) and $s = 6$. The value of $s = 6$, which was used during the fitting procedure, suggests the dipole–dipole interaction as the main mechanism of the energy transfer in the BTBO:Nd³⁺ (0.5 at.%) powder [35]. Moreover, the energy transfer parameter Q can be determined from the fitting procedure using the following formula:

$$Q = \frac{4}{3} \pi \Gamma \left(1 - \frac{3}{s} \right) N_A R_0^3 \quad (9)$$

where Γ is the function taking the values of 1.77 for the dipole–dipole interaction [35], R_0 is the critical distance and N_A is the concentration of A ions.

Assuming the IH model, the energy transfer rate W_{ET} was calculated using the following equation:

$$W_{ET}(R_{DA}) = \frac{C_{DA}^{(s)}}{R_{DA}^{(s)}} \quad (10)$$

where R_{DA} is the average distance between D and A ions, the value of s is equal to 6 for the dipole–dipole interaction [35] and C_{DA} is the energy transfer micro-parameter estimated by analyzing the decay profile using the following relation [39]:

$$C_{DA} = R_o^s \tau_o^{-1} \quad (11)$$

where the value of $R_o = 3.48 \text{ \AA}$ was calculated from the transformed Eq. 9.

Finally, according to the IH model, the following energy transfer parameters for BTBO:Nd³⁺ (0.5 at.%) powder were determined: $Q = 0.12$, the energy transfer micro-parameter $C_{DA} = (1.60 \times 10^{-53}) \text{ m}^6/\text{s}$ and the energy transfer rate $W_{ET} = 0.003 \text{ s}^{-1}$. Moreover, for BTBO:Nd³⁺ powders with the higher Nd³⁺ concentrations (1.0, 2.5, 5.0, 7.5 and 10.0 at.%), the decay curves were not well fitted to the IH model and the observed shortening of the lifetime τ indicates some other energy transfer processes between the D and A ions such as the resonant energy migration or cross-relaxation [40].

Conclusions

The investigated BTBO:Nd³⁺ microcrystalline powders doped with Nd³⁺ ions in various concentrations (0.5, 1.0, 2.5, 5.0, 7.5 and 10.0 at. %) were synthesized by means of the modified Pechini method. Their phase uniformity (hexagonal structure of $P6_3$ space group) was confirmed by XRD. On the basis of the Raman spectra of BTBO:Nd³⁺ powders, the phonon energy of BTBO matrix associated with vibrations of the characteristic BO₃ and TeO₆ molecular groups was determined. The relatively low phonon energy of BTBO matrix allows effective phonon assisted energy transfer between Bi³⁺ and Nd³⁺ active ions. The excitation spectrum of BTBO for Bi³⁺ ions emission in VIS (with maximum intensity at about 560 nm) shows the band at 327 nm. The excitation spectra of BTBO:Nd³⁺ for Nd³⁺ ions emission at 1064 nm show the bands related to the f - f optical transitions of Nd³⁺ ions as well as the bands related to the $^1S_0 \rightarrow ^3P_1$ transition of Bi³⁺ ions at about 327 nm. The emission spectra of BTBO:Nd³⁺ powders excited at 327 nm (by Bi³⁺ ions) and at 586.4 nm (by Nd³⁺ ions) show relatively strong luminescence at about 878 and

1064 nm arising from the $^4F_{3/2} \rightarrow ^4I_{9/2}$ and $^4F_{3/2} \rightarrow ^4I_{11/2}$ transitions of Nd³⁺ ions, respectively. The higher intensity emission bands in NIR for the excitation in UV (by Bi³⁺ ions) were detected in the spectra of the BTBO:Nd³⁺ powders doped with higher concentrations of Nd³⁺ ions (5.0, 7.5 and 10 at.%), with the maximum for 5.0 at.% concentration. So, the optimal Nd³⁺ concentration for the quantum cutting process to be realized by Bi³⁺-Nd³⁺ pairs in the BTBO:Nd³⁺ system is 5.0 at.%. for the excitation in UV (by Bi³⁺ ions). For higher concentration of Nd³⁺ (7.5 and 10.0 at.%), we observe the LCQ effect. For the excitation in VIS (by Nd³⁺ ions), higher intensity of emission bands in NIR was detected in the spectra of BTBO:Nd³⁺ powders doped with lower concentrations of Nd³⁺ ions (0.5, 1.0 and 2.5 at.%) with the maximum for 0.5 at.% concentration. For higher concentrations of Nd³⁺ ions (1.0, 2.5, 5.0, 7.5 and 10.0 at. %), we observed a decrease in the NIR emission as a result of LCQ effect due to short distances between the active Nd³⁺ ions. Moreover, the longest fluorescence decay lifetimes monitored at 1064 nm are equal 107 and 108 μs for the BTBO:Nd³⁺ sample with the lowest concentration of Nd³⁺ (0.5 at.%), upon the excitation at 327 and 586.4 nm, respectively. For BTBO:Nd³⁺ powders with higher concentration of Nd³⁺ ions, the fluorescence decay lifetimes change character and decrease due to the increasing significance of the surface-related effect. Moreover, the observed phenomena result from different energy transfer mechanisms upon the excitation in UV (by Bi³⁺ ions) and excitation in VIS spectral range (by Nd³⁺ ions). Due to the energy transfer process from Bi³⁺ to Nd³⁺, the enhancement of Nd³⁺ emission in the NIR region is observed in BTBO:Nd³⁺ systems. As a result, due to good optical and luminescence properties, the BTBO:Nd³⁺ microcrystalline powders can be potentially used as an efficient UV/VIS to NIR spectral converters for new generation c-Si solar cells.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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Full Length Article

Enhanced near-infrared emission of Er^{3+} as a synergistic effect of energy transfers in $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ phosphorsT. Zhezhera^a, P. Gluchowski^b, M. Nowicki^{a,c}, M. Chrunik^d, A. Majchrowski^d, D. Kasprowicz^{a,*}^a Faculty of Materials Science and Technical Physics, Poznan University of Technology, Piotrowo 3, 60-965, Poznan, Poland^b Institute of Low Temperature and Structure Research of Polish Academy of Sciences, Okólna 2, 50-422, Wrocław, Poland^c Center for Advanced Technology, Adam Mickiewicz University, Uniwersytetu Poznańskiego 10, 61-614, Poznan, Poland^d Institute of Applied Physics, Military University of Technology, Kaliskiego 2, 00-908, Warsaw, Poland

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ABSTRACT

Enhanced near-infrared emission at 1531 nm of Er^{3+} ions excited by Bi^{3+} and/or Yb^{3+} ions was revealed in $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ phosphors. The microcrystalline powders investigated: $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$ and $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ were synthesized by means of the modified Pechini method. Their hexagonal structure with P63 space group was confirmed by XRD measurements. The morphology of the above-mentioned samples was analyzed using SEM technique. The results of μ -Raman investigations showed low phonon energy of Bi_3TeBO_9 matrix. The characteristic Er^{3+} emission at 1531 nm assigned to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition in $\text{Bi}_3\text{TeBO}_9:\text{Er}^{3+}$ and $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ powders was excited by Bi^{3+} or Yb^{3+} ions (the $^1\text{S}_0 \rightarrow ^3\text{P}_1$ or $^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transitions) upon their excitation at 327 or 975 nm, respectively. It was revealed that the effective energy transfer from the excited Bi^{3+} ions (at 327 nm) directly to Er^{3+} ions or indirectly to Er^{3+} ions both via the excitation of Bi^{3+} ions in VIS range or excitation of Yb^{3+} ions in the NIR range results in synergistic effect, which produces enhanced emission at 1531 nm of Er^{3+} ions in $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ system. Moreover, it was found that the effective energy transfer from the excited Yb^{3+} ions (at 975 nm) directly to Er^{3+} ions results in the efficient emission at 1531 nm of Er^{3+} ions. Furthermore, the calculations of energy transfer efficiency and quantum efficiency proved the effective energy transfer from Bi^{3+} to Yb^{3+} and from Yb^{3+} to Er^{3+} ions. The corresponding mechanisms of energy transfer processes in the investigated materials were discussed on the basis of reflectance, excitation and emission spectra and measured decay times. The results indicate a potential of the use of $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$ powders as spectral converters in new generation of photovoltaic devices.

1. Introduction

Nowadays, one of the most crucial ecological challenges is development of new strategies and new technologies for production environmentally safe energy. To do that it is necessary to explore the potential natural sources of green energy. From among natural sources of energy, the Sun provides the cleanest and relatively easily harvested energy [1]. In recent years high dynamics in modification of conventional solar cells technology to improve efficiency in conversion of the natural solar energy into electric energy by the photovoltaic effect was observed [2,3]. The main issue that limits the solar energy conversion efficiency is the spectral mismatch between the incident sunlight and the band gap of semiconductor materials used in solar cell devices [4]. At present, there are several kinds of solar cells such as: single-junction

crystalline silicon c-Si, single- or polycrystalline silicon, non-crystalline (amorphous) silicon, germanium, perovskite, and single- or multi-junction III-V semiconductor solar cells [4–6].

Up to now conventional c-Si type solar cells, the first-generation solar conversion devices, have been most popular and occupy the major photovoltaic market due to their established production technology and low price compared to the others [4,7]. However, in conventional c-Si solar cells only a small range of the solar spectrum, namely 900–1100 nm range (corresponding to the Si band gap of about 1.1 eV) can be fully utilized and converted into electricity. The photons of lower energy than the Si band gap energy cannot be absorbed, while the excess energy of higher energy photons is lost due to charge carriers thermalization or electron–hole recombination effects [4,7]. Moreover, the conventional c-Si solar cells show low energy conversion efficiencies

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of around 22% and 25% for industrial application and laboratory research, respectively [8,9]. A possible solution to improve the efficiency of conventional c-Si is to use some spectral converting materials in their structure that would concentrate the solar spectrum (from UV via VIS up to NIR range) into the spectral response region for c-Si semiconductor materials in the up- or down-conversion processes, and improve the solar spectral utilization efficiency. Among others, rare earth (RE) ions doped luminescent materials are attractive for this task, because of their characteristic structure of electronic energy levels with possible transitions in absorption process as well as effective energy transfer between RE^{3+} active ions, which allow conversion of solar radiation into the required spectral range of 900–1100 nm and consequently improve the photovoltaic efficiency in conventional c-Si solar cells [10,11]. Moreover, there are many reports on RE^{3+} ions such Eu^{3+} , Nd^{3+} , Tm^{3+} , Pr^{3+} , Tb^{3+} , Er^{3+} , and Ho^{3+} [11–14] or other ions such as Cr^{3+} , Ce^{3+} or Bi^{3+} [9,14–16] with broadband absorption bands, which were used as the sensitizers of Yb^{3+} ions (the ions whose spectral range of absorption matches the Si band gap energy) to realize spectral conversion mainly through the up- and down-conversion or quantum cutting processes.

New generation photovoltaic semiconducting solar cells, providing the highest efficiency of solar energy conversion into electricity, are the III-V semiconductor based single- or multi-junction photovoltaic devices [4–6,17]. The III-V semiconductors are characterized with the tunable bandgaps (E_g) depending on the used elements of III and/or V group, which allow effective utilization of the solar spectrum [17]. The range of optical activity of III-V semiconductors covers the UV, VIS and NIR wavelengths offering the possibility to efficiently absorb the broad solar spectrum radiation [4]. In particular, GaAs ($E_g = 1.42$ eV), InP ($E_g = 1.35$ eV) GaInP ($E_g = 1.81$ eV) single-junction solar cells show the 29.1, 22.1 and 20.8% efficiency under solar radiation (for the AM1.5 standard solar spectrum), respectively [4]. Recently, a short-circuit current density of 15.2 mA/cm^2 (for standard AM1.5D illumination at 1000 W/m^2) of the low-bandgap GaInNAsSb single junction solar cells has been reported, which corresponds to the highest external quantum efficiency ever reached by dilute nitride solar cells with energy bandgaps below 0.8 eV [17]. Because the limiting efficiency of single-junction solar cells is 30–32%, multi-junction solar cells have been intensively developed and modified [6]. Moreover, the III-V compounds single-junction solar cells such as GaAs, InP, AlGaAs, GaInAs or GaInP are important as sub-cells for multi-junction solar cells [4,6,18–20]. For multi-junction photovoltaic devices the efficiencies exceeding 40% were reported for example for: an upright metamorphic triple-junction (3 J) cell (42%) [20], wafer bonded four-junction (4 J) cell (46%) [21] or six-junction (6 J) solar cell (39.2% under AM1.5 solar radiation and 47.1% under light concentration) [6]. Moreover, many RE^{3+} ions such as: Yb^{3+} , Er^{3+} , Pr^{3+} or Tb^{3+} are considered as an active luminescent ions for new generation/type multi-component semiconductor solar cells [11–14].

In this paper we present the studies of a complex borate Bi_3TeBO_9 (BTBO) crystalline powders doped with Yb^{3+} and/or Er^{3+} ions, which could be considered as effective spectral converters used in solar cells technology for concentration of solar radiation in the required spectral ranges: for c-Si solar cells (ranges about 980 nm) and/or multi-components semiconductor solar cells (ranges about 1531 nm). BTBO was used as host lattice due to its excellent structure and optical properties as well as a relatively easy possibility of doping with RE^{3+} ions [22–25]. The structure, luminescence and vibrational properties of BTBO micro-powders, pure and doped with Nd^{3+} ions, have been already reported by us [26,27]. In particular, the sensitization of Yb^{3+} ions by Bi^{3+} ions as well as sensitization of Er^{3+} ions by Bi^{3+} or Yb^{3+} ions were studied for BTBO: Er^{3+} , BTBO: Yb^{3+} and BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ powders. As we reported in our previous paper, the Bi^{3+} ions present in BTBO matrix excited in the UV range can efficiently transfer their energy to the other RE^{3+} ions present in the doped BTBO powders [27]. The electronic energy levels of Bi^{3+} ions include the ground state $^1\text{S}_0$ and the excited states $^1\text{P}_1$, $^3\text{P}_2$, $^3\text{P}_1$ and $^3\text{P}_0$. The transition from $^1\text{P}_1$ to the ground state

occurs in the UV short wavelengths region, while the location of the emission band originating from $^3\text{P}_1$ and $^3\text{P}_0$ can be observed in the UV or VIS range, depending on the host lattice. The structure of the energy levels of Bi^{3+} ions may change depending on the host material and a lowering of the excited states energy is typically observed, relative to that of the electronic levels of isolated Bi^{3+} ions [28–30]. The structure of electronic levels of Yb^{3+} ions permits the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition (at about 975 nm) corresponding to the spectral range of absorption of Si solar cells, which is of great interest for photovoltaic application. Er^{3+} ions can be considered as an active luminescent ions for new generation/type multi-component semiconductor solar cells, owing to their rich structure of electronic levels: the ground state $^4\text{I}_{15/2}$ and many excited levels $^2\text{K}_{15/2} + ^4\text{G}_{7/2}$, $^4\text{G}_{11/2}$, $9/2$, $^2\text{H}_{9/2}$, $^4\text{F}_{5/2}$, $3/2$, $^4\text{F}_{7/2}$, $^2\text{H}_{11/2}$, $^4\text{S}_{3/2}$, $^4\text{F}_{9/2}$, $^4\text{I}_{11/2}$, $^4\text{I}_{13/2}$, and possible transitions in NIR spectral range (associated with the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{9/2}$ transitions) or in VIS spectral range (due to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions), which are within the spectral response of the low-bandgap semiconductor materials for solar cells [31–35]. Moreover, because of broad absorption cross section of Yb^{3+} ion, as well as its wide absorption bandwidth, the effective resonant energy transfer from Yb^{3+} to Er^{3+} ions was observed in the investigated BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ systems. Additionally, based on the basis of the measured luminescence lifetimes of the analyzed emissions, the energy transfer efficiency and quantum efficiency were calculated.

2. Experimental

XRD measurements of BTBO: Er^{3+} , BTBO: Yb^{3+} and BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ powders were made using the BRUKER D8 Discover diffractometer with $\text{CuK}\alpha$ radiation ($\lambda_{\text{K}\alpha 1} = 1.54056 \text{ \AA}$, $\lambda_{\text{K}\alpha 2} = 1.54443 \text{ \AA}$, Siemens KFL CU 2 K, 40 kV and 40 mA) equipped with the Göbel FGM2 mirror. The Bragg–Brentano diffraction geometry was applied. The diffraction angle was $2\theta_B$ ranged from 18 to 70° with a step of 0.01° and acquisition time of 2 s per step. The measurements were carried out at 299 K in the temperature-stabilized Anton Paar HTK 1200 N chamber. The DIFFRAC. SUITE EVA application (provided by diffractometer producer) was applied for data processing. The phase analysis was performed with the support of the ICDD PDF-2 & COD databases in Match program by Crystal Impact. The FullPROF ver. 3.0 program with EdPCR were used for Rietveld refinement and calculations of precise experimental diffraction profile, unit cell parameters and crystallite sizes.

SEM measurements were performed with the FEI Quanta 250 FEG microscope, the images obtained for secondary electrons are presented in this paper. The microscope was operated in high vacuum mode at an accelerating voltage of 5 kV.

The Raman investigations were performed in the back-scattering geometry using the Renishaw InVia Raman spectrometer equipped with confocal DM 2500 Leica optical microscope and CCD detector. The Raman spectra were excited with the Ar laser emitting light of 488 nm wavelength and recorded in single scan with 30 s exposure time and 1 mW of the applied power. The position of the Raman peaks was calibrated before data collection using the Si reference sample as an internal standard with the peak position at 520.3 cm^{-1} . The diffraction-limited optical spatial resolution depended on the excitation wavelength and for the used $50\times$ LWD objective it was approximately equal to $1.5 \text{ }\mu\text{m}$. The instrumental resolution of the spectrometer was better than 2 cm^{-1} . Spectral analysis was performed with the software packages WiRE3.1/ Renishaw.

The reflectance spectra were measured with the Varian Model 5 E UV-VIS-NIR spectrophotometer equipped with two excitation sources: the tungsten halide lamp in NIR/VIS and the deuterium arc UV range. As detectors the Hamamatsu R928 PMT in UV/VIS and Peltier-cooled PbS photocell in NIR range were used. All spectra were corrected for sources, detectors and gratings characteristics. The excitation and emission spectra as well as decay kinetics and quantum yield measurements of BTBO crystalline powders doped with Yb^{3+} and/or Er^{3+} ions were

recorded using the FLS980 Fluorescence Spectrometer (Edinburgh Instruments) equipped with the holographic grating of 1800 lines/mm, blazed at 300 mm focal length monochromators in the Czerny-Turner configuration. The excitation and emission spectra were obtained using a 450 W Xenon lamp. For decay times measurements, the 450 W excitation source was replaced with the 150 W lamp (μ F2) with external triggering. The uncertainties for measured lifetimes were lower than 0.01 ms. The emission spectra and decay times in the visible range were recorded on the Hammamatsu C5680 streak camera with time resolution below 50 ps and effective spectral range from 200 to 1000 nm. The excitation source was the Coherent Libra-S-laser (femtosecond laser, wavelength 800 nm, pulse width of less than 100 fs and energy of 1 mJ at 1 kHz repetition rate) paired with the Coherent OPerA Solo Optical Parametric Oscillator (two-stage amplifier of white continuum) that allows generation of pulses in the range of wavelengths from 230 to 2800 nm.

3. Results and discussion

3.1. Crystal structure

BTBO:Er³⁺, BTBO:Yb³⁺ and BTBO:Yb³⁺/Er³⁺ crystalline powders were synthesized by means of the modified Pechini method, based on the procedure developed and described in detail in our previous work [33]. The doping concentrations of RE³⁺ ions in the BTBO matrix used for the investigated samples BTBO:Er³⁺, BTBO:Yb³⁺ and BTBO:Yb³⁺/Er³⁺ were 1.0 at.%, 5.0 at.% and 5.0/1.0 at.%, respectively. The Er³⁺ ions content of investigated samples was kept at 1 at.% to avoid luminescence quenching. Moreover, to overcome low pump absorption achievable with Er³⁺ alone, co-doping with Yb³⁺ ions was used. The Yb³⁺ ions act as a sensitizer due to the much higher absorption cross section than Er³⁺ ions. Typically used molar ratio of Yb³⁺/Er³⁺ in systems for effective down- or up-conversion emission of Er³⁺ ions is chosen as 5:1 to improve the efficiency of pump absorption [36]. The XRD data obtained for the above-mentioned powders are presented in Fig. 1.

All obtained diffraction patterns of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders are in good agreement with the reference COD card (No. 96-412-5286), what means all of them have hexagonal structure with noncentrosymmetric P63 (no. 173) space group ($Z = 2$) and correspond to that obtained for the undoped BTBO powder [27]. The results for BTBO:Er³⁺, BTBO:Yb³⁺ and co-doped BTBO:Yb³⁺/Er³⁺ show that the crystal structure with the hexagonal symmetry remains undisturbed when the mentioned RE³⁺ ions in the above-specified concentrations are incorporated into the BTBO matrix. The unit cell parameters of BTBO:Er³⁺, BTBO:Yb³⁺ and BTBO:Yb³⁺/Er³⁺ samples are presented in Table 1.

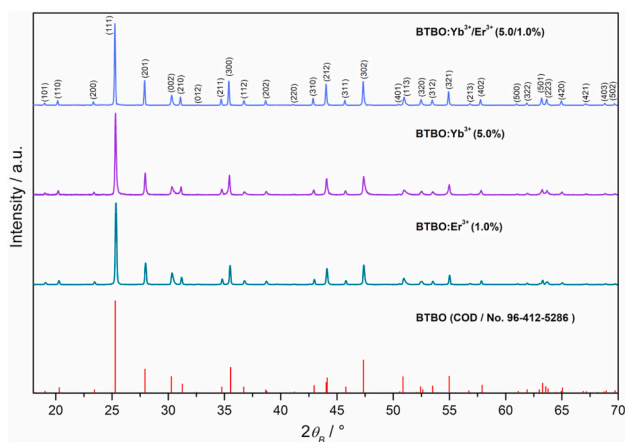


Fig. 1. A set of XRD patterns of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders.

Table 1

Calculated unit cell parameters of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders.

Compound	Unit cell parameters			V [Å ³]	D [nm]
	a[Å]	c[Å]	a/c		
BTBO:Yb ³⁺ /Er ³⁺ (5/1%)	8.7338 (2)	5.8641 (3)	1.4894	387.38	45
BTBO:Yb ³⁺ (5%)	8.7508 (2)	5.8595 (3)	1.4934	388.59	39
BTBO:Er ³⁺ (1%)	8.7556 (2)	5.8893 (3)	1.4867	390.99	58
BTBO[27]	8.7505 (2)	5.8871 (2)	1.4864	390.39	–

The results given above show a direct connection between the content of Er³⁺, Yb³⁺ and Yb³⁺/Er³⁺ ions in BTBO host and the changes in its unit cell volume. The values of effective ionic radius of Bi³⁺, Er³⁺ and Yb³⁺ are 1.030, 1.004 and 0.985 Å, respectively [37]. This may suggest that the isovalent substitution of Bi³⁺ with Er³⁺ or Yb³⁺ ions (as well as both) occurs, leading to shrinkage of the unit cell volume, which was observed in this study. This allows the conclusion that the unit cell geometry is only slightly changed upon BTBO doping, without any changes in the symmetry. The a/c ratio remains commensurable in each case and was estimated as 1.49. For BTBO:Er³⁺ with a small amount of dopant (1 at.%), the change in unit cell geometry is just so subtle so that the geometry is comparable to that of undoped BTBO. With increasing amount of the mentioned dopants, the effect of unit cell compression is more noticeable. Average crystallite sizes D , calculated using the Debye-Scherrer method, are less than 60 nm and these results are typical of polycrystalline powders obtained via wet-chemical methods.

3.2. Morphological analysis

Microscopic observation of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ samples using the scanning electron microscopy (SEM) technique revealed their morphology. All of the investigated materials had different irregular microstructures (Fig. 2). BTBO:Yb³⁺/Er³⁺ sample (Fig. 2a) was composed of large grains ranging in size from a few to hundreds of micrometres decorated with smaller grains of sub-micrometric size. The large number of grain boundaries were sharp edged. For BTBO:Yb³⁺ sample (Fig. 2b) smaller grains with sizes of 1 μ m and less were typical. Individual larger grains with diameters less than 20 μ m could be observed. This sample had the finest grain size of the materials analyzed in this work. BTBO:Er³⁺ powder (Fig. 2c) contained sizable grains with sizes of 1–20 μ m, they had more rounded edge shapes and were more homogeneous than BTBO:Yb³⁺/Er³⁺.

3.3. μ -Raman investigation

The unpolarized Raman spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders excited with 488 nm laser radiation were recorded at room temperature and are presented in the 100–1000 cm⁻¹ spectral range (Fig. 3). In this spectral range the Raman active bands related with the external and internal vibrations of the investigated crystals were detected. Because of the strong luminescence of Er³⁺ ions detected in the spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ powders above 1000 cm⁻¹ it was not possible to detect in this spectral range some Raman active modes typical of the vibrations of BO₃ groups, present in BTBO crystals [26].

Most of the bands in the Raman spectra presented in Fig. 3 originated from the vibrations of the characteristic BO₃ or TeO₆ molecular groups. In particular, the very weak modes detected at 924 and 816 cm⁻¹ originate from internal stretching vibration of BO₃ complex. The most intensive modes recorded at 690 cm⁻¹ and the medium-intensity modes occurring at 650 cm⁻¹ were assigned to the stretching vibrations of TeO₆ groups. The weak modes at 620 cm⁻¹, medium-intensity modes at 605

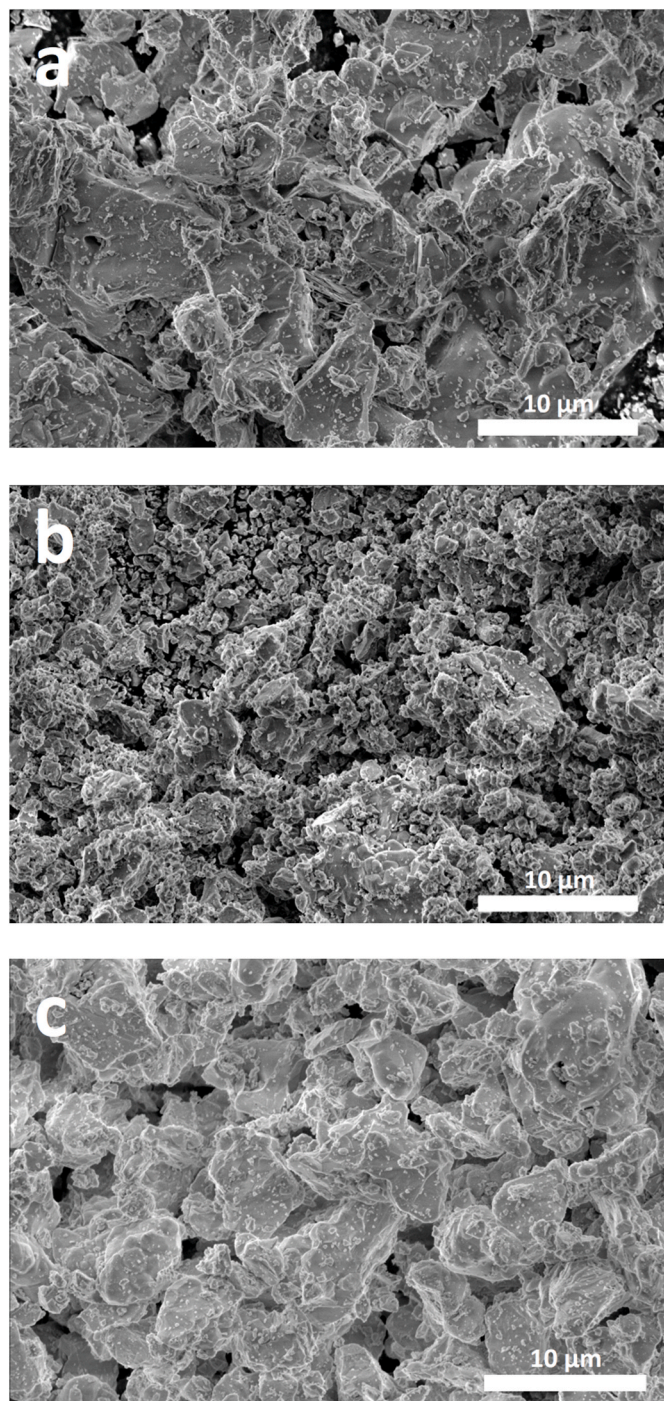


Fig. 2. SEM micrographs of BTBO:Yb³⁺/Er³⁺ (a), BTBO:Yb³⁺ (b) and BTBO:Er³⁺ (c). Magnification 10 000x.

and 596 cm⁻¹ detected in the spectra were attributed to the bending vibrations of BO₃ groups. The weak modes at 564 and 538 cm⁻¹, very strong modes centered at 494 cm⁻¹, the shoulder at 418 cm⁻¹ and broad medium-intensity modes at 401 cm⁻¹, registered in the spectra, can be assigned to the bending vibrations of TeO₆ groups. The modes below 350 cm⁻¹ originate from the external lattice vibrations of Bi (Er, Yb) or Te atoms and TeO₆ and BO₃ groups and correspond to the librational or translational motions of these molecular groups. The wavenumbers of the Raman active bands mentioned above are given for BTBO:Yb³⁺/Er³⁺ powders, while the assignment of the Raman bands of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ composite is presented in Table 2.

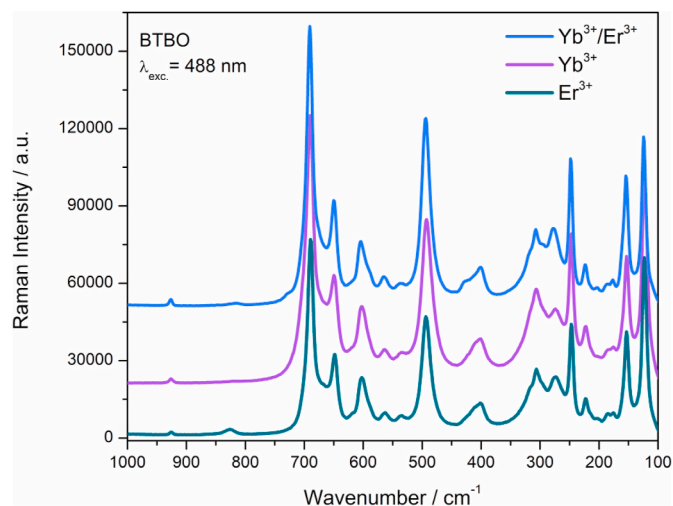


Fig. 3. Unpolarized Raman spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders, detected upon 488 nm excitation.

Table 2

Assignment of the Raman bands of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders.

BTBO:RE ³⁺			Assignment
powders			
Yb ³⁺ /Er ³⁺	Er ³⁺	Yb ³⁺	
925 vw	925 vw	926 vw	stretching vibrations of BO ₃
816 vw	827 vw	821 vw	
690 vs	689 vs	690 vs	
650 s	648 s	649 s	stretching vibrations of TeO ₆
620 vw	619 vw	621 vw	
605 m	603 m	604 m	
596 m/sh	594 m/sh	596 m/sh	bending vibrations of BO ₃
564 w	563 w	563 w	
538 w	536 w	536 w	
494 s	493 s	492 s	bending vibrations of TeO ₆
418 m/sh	419 m/sh	419 m/sh	
401 m	400 m	401 m	
315 m/sh	316 m/sh	316 m/sh	librations and translations of BO ₃ and TeO ₆
307 m	306 m	306 m	
276 m	274 m	273 m	
248 s	248 s	247 s	
223 m	223 m	223 m	
203 w	202 w	204 w	
185 w	186 w	187 w	
177 w	175 w	177 w	
161 m/sh	161 m/sh	162 m/sh	
154 s	153 s	153 s	
124 vs	124 vs	123 vs	

Vs – very strong; s – strong; m – medium; w – weak; vw – very weak; sh – shoulder.

3.4. Luminescent properties

The reflectance, excitation and emission spectra were measured for BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ in order to study their luminescent properties. The bands present in the spectra were assigned to the energy levels of Yb³⁺ and Er³⁺ active ions according to the Dieke's diagram [31]. Moreover, the kinetics of the luminescent processes was analyzed on the basis of the fluorescence decay time measurements.

The reflectance spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders were recorded in the spectral range 250–2500 nm at room temperature (Fig. 4).

As shown in Fig. 4, the strong and broad bands in the range 210–460 nm with the intensity maximum at about 260/326 nm, that arise from

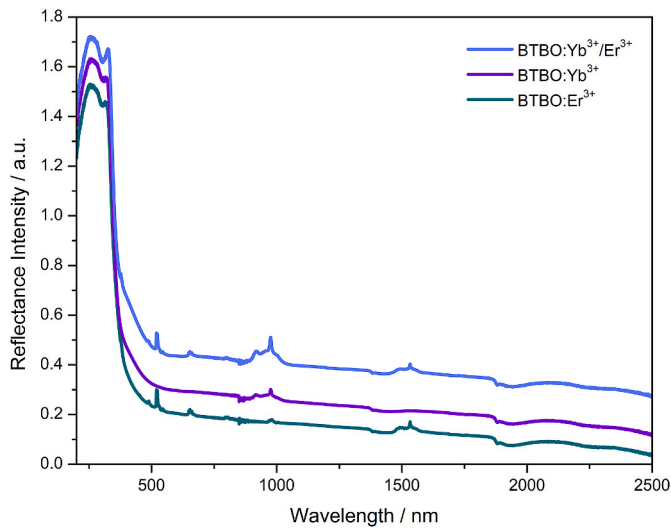


Fig. 4. The reflectance spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders.

the $^1S_0 \rightarrow ^3P_1$ transition of Bi³⁺ ions, were detected in the reflectance spectra of all samples. The bands detected in the spectral ranges 460–560, 620–690 and 1420–1600 nm in the reflectance spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ powders were assigned to the transitions of Er³⁺ ions. Moreover, the low intensity band detected in the spectral range 940–1020 nm for BTBO:Yb³⁺ sample was assigned to the transitions of Yb³⁺ ions, while those appearing in the spectral range 890–1040 nm in the spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ samples were assigned to the transitions of Yb³⁺ and Er³⁺ ions. Very weak peaks at 490 and 546 nm can be assigned to the $^4I_{15/2} \rightarrow ^4F_{7/2}$ and $^4I_{15/2} \rightarrow ^4S_{3/2}$ transitions of Er³⁺ ions, respectively. The bands at around 525 and 655 nm are due to the $^4I_{15/2} \rightarrow ^2H_{11/2}$ and $^4I_{15/2} \rightarrow ^4F_{9/2}$ transitions of Er³⁺ ions, respectively. A weak band assigned to Er³⁺ ions at about 975 nm in the spectrum of BTBO:Er³⁺ powders originated from the $^4I_{15/2} \rightarrow ^4I_{11/2}$ transitions. The broad band with a maxima at 921 and 975 nm appearing in the spectrum of BTBO:Yb³⁺ was assigned to the $^2F_{7/2} \rightarrow ^2F_{5/2}$ transition of Yb³⁺ ions, while for BTBO:Yb³⁺/Er³⁺ the bands detected in this spectral range are the result of the overlapping of the bands assigned to the above-mentioned transitions of Yb³⁺ and Er³⁺ ions. The bands at around 1531 nm can be assigned to the $^4I_{15/2} \rightarrow ^4I_{13/2}$ transitions of Er³⁺ ions.

On the basis of the diffuse reflectance spectrum of BTBO:Yb³⁺/Er³⁺ powder the value of the energy band gap E_g of BTBO:Yb³⁺/Er³⁺ was evaluated according to the Kubelka–Munk model [38] and using the Tauc method [39]. The procedure of E_g calculation using mentioned above method was described in the Supplementary Material. The determined value of the energy band gap E_g for BTBO:Yb³⁺/Er³⁺ sample is equal to 2.98 eV (Fig. S1), which corresponds to the values E_g determined using the theoretical methods 2.96 and 3.21 eV (calculated using DFT–LDA and DFT–GGA functionals) [25], respectively and 2.70 and 3.23 eV calculated and obtained experimentally, respectively, by other authors [22].

The excitation spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders were recorded at 300 K in the spectral range 250–700 nm by monitoring the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition of Yb³⁺ ions at 975 nm (Fig. 5a) and the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ ions at 1531 nm (Fig. 5b).

As follows from Fig. 5a, only the broad and intensive bands in the range 285–370 nm with the intensity maximum at about 333 nm were observed in the excitation spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Yb³⁺. These excitation bands, monitored for the $^2F_{5/2} \rightarrow ^2F_{7/2}$ emission of Yb³⁺ ions at 975 nm, were assigned to the $^1S_0 \leftarrow ^3P_1$ transition of Bi³⁺ ions. The excitation spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ recorded by

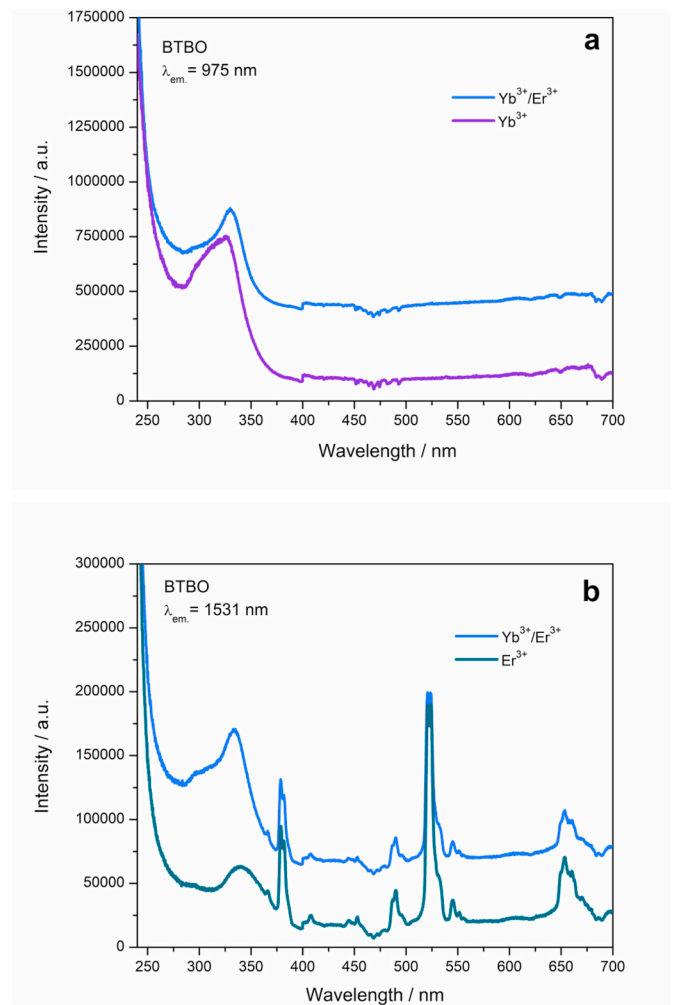


Fig. 5. Excitation spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ powders recorded for the emission of Yb³⁺ ions at 975 nm (the $^2F_{5/2} \rightarrow ^2F_{7/2}$ transition) (a) and the emission of Er³⁺ ions at 1531 nm (the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition) of BTBO:Yb³⁺/Er³⁺, BTBO:Er³⁺ powders (b).

monitoring the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition of Er³⁺ ions at 1531 nm are presented in Fig. 5b. The broad and intensive bands in the range 285–374 nm with the intensity maximum at about 333 nm were assigned to the $^1S_0 \leftarrow ^3P_1$ transition of Bi³⁺ ions. The other bands in the excitation spectra were assigned to the transitions of Er³⁺ ions. In particular, the intense bands at 364 nm correspond to the $(^2K_{15/2} + ^4G_{7/2}) \leftarrow ^4I_{15/2}$ transitions. The strong bands at 379/391 nm are related to the $^4G_{11/2; 9/2} \leftarrow ^4I_{15/2}$ transitions. The weak bands centered at 407 and 453 nm were assigned to the $^2H_{9/2} \leftarrow ^4I_{15/2}$ and $^4F_{5/2; 3/2} \leftarrow ^4I_{15/2}$ transitions, respectively. The medium intense broad bands centered at 489 nm correspond to the $^4F_{7/2} \leftarrow ^4I_{15/2}$ transitions. The most intense peaks assigned to the $^2H_{11/2} \leftarrow ^4I_{15/2}$ transition are located in the 505–540 nm spectral range with maxima at 521/524 nm. The medium intense bands centered at 546 nm are attributed to the $^4S_{3/2} \leftarrow ^4I_{15/2}$ transition. The bands in the spectral range of 623–690 nm are assigned to the $^4F_{9/2} \leftarrow ^4I_{15/2}$ transition.

The emission spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ be, BTBO:Er³⁺ and undoped BTBO [27] powders were recorded upon the excitation of Bi³⁺ ions at 327 nm (Figs. 6 and 7). Moreover, the emission spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ powders were detected also upon the excitation at 975 nm (Fig. 8).

Fig. 6 shows the emission spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ and undoped BTBO powders recorded in the range 430–650 nm upon the excitation at 327 nm. For all samples the broad

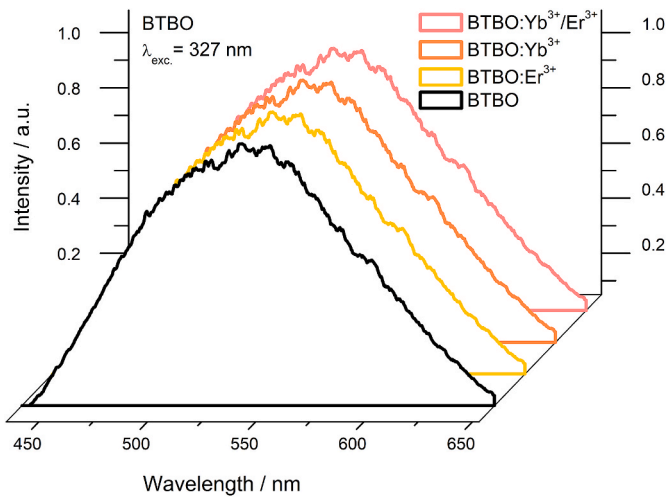


Fig. 6. Emission spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺, BTBO:Er³⁺ and undoped BTBO [27] powders recorded upon the excitation at 327 nm for the ³P₀ → ¹S₀ transition of Bi³⁺ ions.

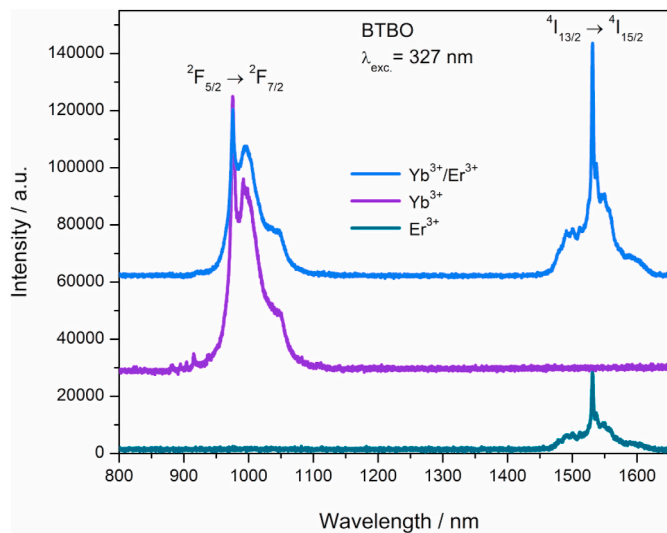


Fig. 7. Emission spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders recorded upon the excitation at 327 nm.

emission bands with the maximum at about 560 nm, assigned to the ³P₀ → ¹S₀ transition of Bi³⁺ ions were recorded, which suggests that Bi³⁺ ions present in BTBO matrix can be used as a UV absorption sensitizer for Yb³⁺ and Er³⁺ ions in the considered systems.

The emission spectra of BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and BTBO:Er³⁺ powders recorded in the spectral range of 800–1650 nm upon the excitation at 327 nm are presented in Fig. 7. As shown in this figure, the typical emissions around 1531 nm of Er³⁺ ions (⁴I_{13/2} → ⁴I_{15/2} transition) and around 975 nm of Yb³⁺ ions (²F_{5/2} → ²F_{7/2} transition) were detected in the emission spectra of BTBO:Er³⁺ and BTBO:Yb³⁺, respectively, while, for BTBO:Yb³⁺/Er³⁺ we observed the emission of Yb³⁺ and Er³⁺ ions at 975 and 1531 nm, respectively.

It should be noted that the intensity of the emission bands at 975 nm is higher for the Yb³⁺-doped compound (BTBO:Yb³⁺) than for Er³⁺-co-doped one (BTBO:Yb³⁺/Er³⁺). For BTBO:Yb³⁺ the total energy from the excited Bi³⁺ ions is transferred to Yb³⁺ ions, while for BTBO:Yb³⁺/Er³⁺, part of the energy from the excited Bi³⁺ ions is transferred directly to Er³⁺ ions. Moreover, the emission bands at 1531 nm observed in the spectrum of BTBO:Yb³⁺/Er³⁺ were of higher intensity than that detected for BTBO:Er³⁺, which is a result of the energy transfer from the excited

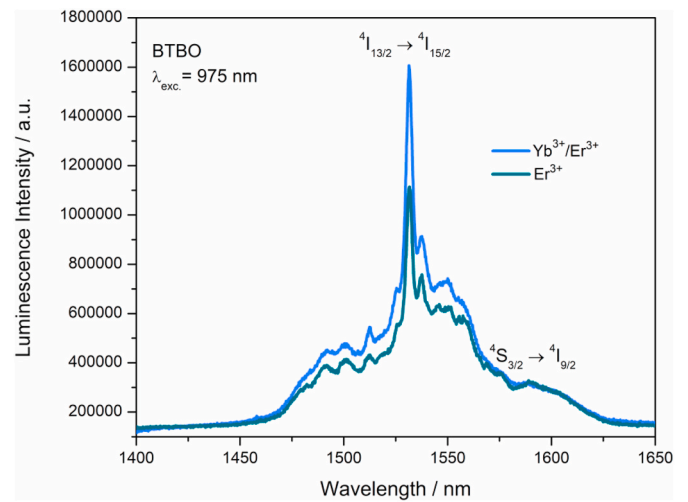


Fig. 8. The emission spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ recorded upon the excitation at 975 nm.

Bi³⁺ ions directly to Er³⁺ ions as well as the energy transfer from Yb³⁺ ions (excited by Bi³⁺ ions) to Er³⁺ ions. This synergistic effect of energy transfer between Bi³⁺, Yb³⁺ and Er³⁺ active ions produced enhanced emission in the NIR range of Er³⁺ ions in BTBO:Yb³⁺/Er³⁺ powders.

Fig. 8 presents the emission spectra of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺, recorded in the spectral range of 1400–1650 nm, upon the excitation at 975 nm. The spectra show the broad bands with maximum intensity at around 1531 nm, assigned to the ⁴I_{13/2} → ⁴I_{15/2} transition of Er³⁺ ions. The shape of these bands is a result of the Stark effect, which describes the shifting and splitting of spectral lines of active Er³⁺ ions due to the presence of an external electric crystal field. As a result, the ⁴I_{13/2} energy level of Er³⁺ splits into several Stark components. Moreover, some additional bands appearing on the shoulder at about 1600 nm of these broad emission bands were assigned to the ⁴S_{3/2} → ⁴I_{9/2} transitions.

As follows from the spectra in Fig. 8, the intensity of the emission at 1531 nm (⁴I_{13/2} → ⁴I_{15/2} transition) is higher for the co-doped BTBO:Yb³⁺/Er³⁺ systems than for BTBO:Er³⁺. The observed enhanced emission of Er³⁺ ions is due to the additional energy transfer process from the excited Yb³⁺ ions to the excited levels of Er³⁺ ions. The processes of energy transfer from Bi³⁺ to Yb³⁺ or Er³⁺ ions and from Yb³⁺ to Er³⁺ ions were discussed on the basis of the scheme presented in Fig. 11.

3.5. The luminescence decay times for 1531 nm emission

The luminescence decay curves of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ powders monitored for the emission at 1531 nm (the ⁴I_{13/2} → ⁴I_{15/2} transition of Er³⁺ ions) upon the excitation at 327 or 975 nm are presented in Fig. 9.

The decay curves for the ⁴I_{13/2} → ⁴I_{15/2} emission of Er³⁺ ions are single-exponential (Fig. 9). To determine the decay times, the experimental decay curves of the investigated samples were fitted to the exponential function according to the following formula:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (1)$$

where I_0 is the intensity of the luminescence process at the initial time and τ is its lifetime.

As follows from Fig. 9, the decay profiles in BTBO:Yb³⁺/Er³⁺ powders exhibit an initial rise followed by exponential decay. The observed initial rise time can be due to the sensitization of Er³⁺ emission by Yb³⁺ ions. The initial rise time τ_r and following decay times τ_d are equal to 17 μ s and 1.44 ms (for 327 nm excitation/Figs. 9a) and 23 μ s and 1.40 ms (for 975 nm excitation/Fig. 9b). The decay times of Er³⁺ emission at

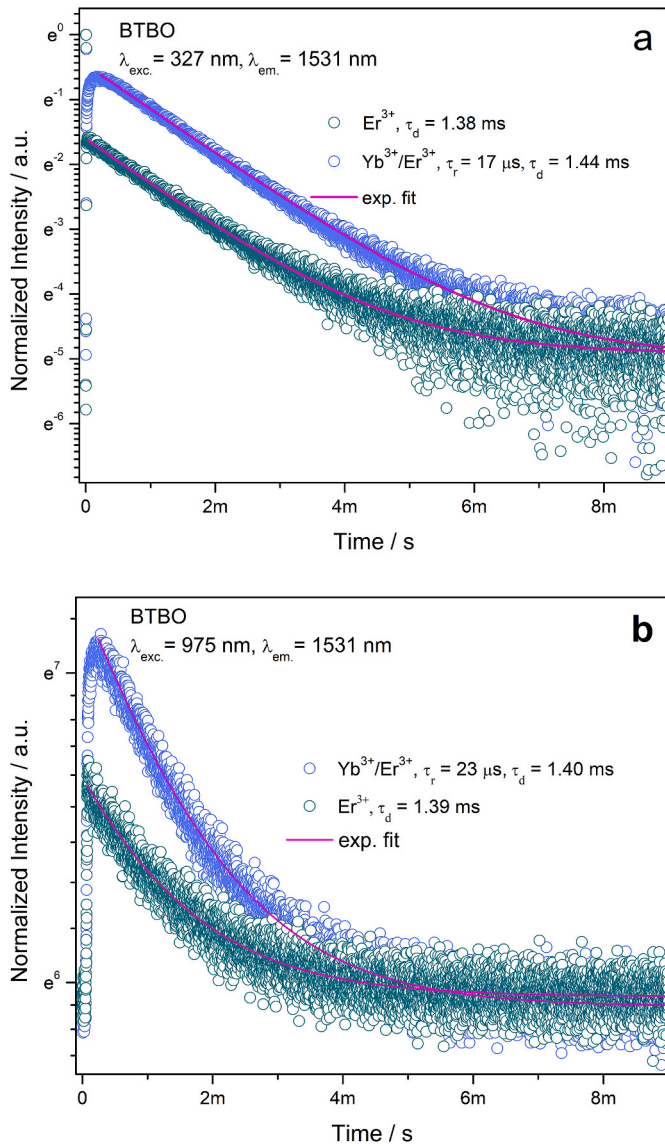


Fig. 9. The luminescence decay time curves of BTBO:Yb³⁺/Er³⁺ and BTBO:Er³⁺ powders recorded by monitoring the emission at 1531 nm upon the excitation with 327 nm (a) and 975 nm (b) laser radiation.

1531 nm, determined for BTBO:Er³⁺ upon the excitation at 327 and 975 nm, are equal to 1.38 and 1.39 ms, respectively. Moreover, the decay time of Er³⁺ emission at 1531 nm is comparable, for the excitation at both 327 and 975 nm, for BTBO:Er³⁺ as well as Yb³⁺ co-doped BTBO:Yb³⁺/Er³⁺ powder.

Energy transfer between Bi³⁺, Yb³⁺ and Er³⁺ ions.

To determine the Energy Transfer Efficiency (ETE) and Quantum Efficiency (QE) of the energy transfer from Bi³⁺ to Yb³⁺ ions and from Yb³⁺ to Er³⁺ ions, the luminescence decay times for the emissions related to the ³P₀ → ¹S₀ transitions of Bi³⁺ ions, the ²F_{5/2} → ²F_{7/2} transitions of Yb³⁺ ions were measured for BTBO:Yb³⁺/Er³⁺, BTBO:Yb³⁺ and undoped BTBO powders upon the excitation at 327/330 nm (Fig. 10).

From the decay curves shown in Fig. 10, the average lifetimes were calculated by the following formula:

$$\langle \tau \rangle = \frac{\int_0^{\infty} I(t) dt}{I(0)} \quad (2)$$

where $\langle \tau \rangle$ is the average lifetime, $I(t)$ denotes the measured intensity of

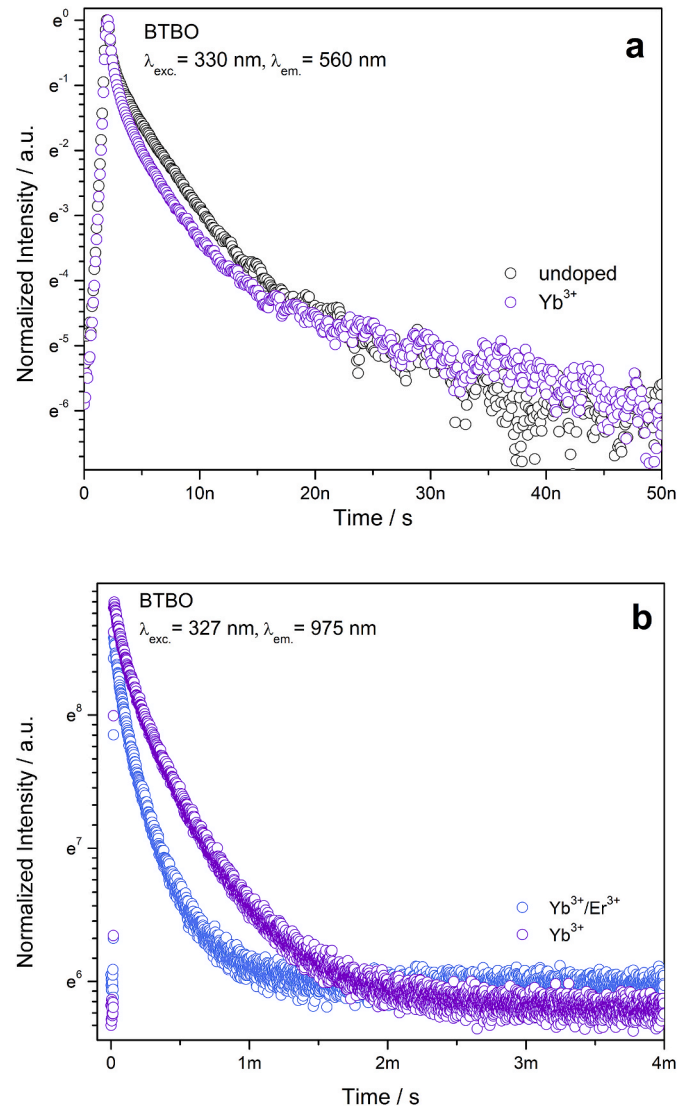


Fig. 10. The luminescence decay time curves of undoped BTBO (a), BTBO:Yb³⁺ (a, b) and BTBO:Yb³⁺/Er³⁺ (b) powders recorded by monitoring the emission of Bi³⁺ and Yb³⁺ ions upon the excitation at 330 nm (a) and 327 nm (b).

photoluminescence decay curve as a function of time and $I(0)$ is the initial intensity (at $t = 0$ s) [40]. Using formula (2), the following average lifetime values were determined: 1.55 ns (BTBO:Yb³⁺), 2.00 ns (BTBO) for the ³P₀ → ¹S₀ transitions of Bi³⁺ ions (Figs. 10a) and 298 μs (BTBO:Yb³⁺) and 186 μs (BTBO:Yb³⁺/Er³⁺) for the ²F_{5/2} → ²F_{7/2} transitions of Yb³⁺ ions (Fig. 10b). The determined decay time curves presented in Fig. 10a correspond to the emission of Bi³⁺ ions, detected for BTBO:Yb³⁺ and undoped BTBO powders (broad emission bands in the VIS spectral range with maximum intensity at about 560 nm presented in Fig. 6). Moreover, the short lifetime of the ³P₀ → ¹S₀ transition of Bi³⁺ ions can be a result of a complex energy transfer mechanisms between Bi³⁺ and two other active ions (Yb³⁺ and Er³⁺) in considered systems. It should be noticed that the decay time measured for the emission of Yb³⁺ ions at 975 nm upon the excitation at 327 nm of BTBO:Yb³⁺ powder (298 μs) is significantly longer than that for BTBO:Yb³⁺/Er³⁺ powder (186 μs) (Fig. 10b). This result corresponds to the emission spectra presented in Fig. 7; after excitation at 327 nm of BTBO:Yb³⁺ sample, Yb³⁺ ions relax for a long time with relatively high intensity, while for BTBO:Yb³⁺/Er³⁺ sample, the excited Yb³⁺ ions, after a relatively short time, transfer part of their energy to Er³⁺ ions (which relax through the emission at 1531 nm), which results also in a lower intensity of the Yb³⁺

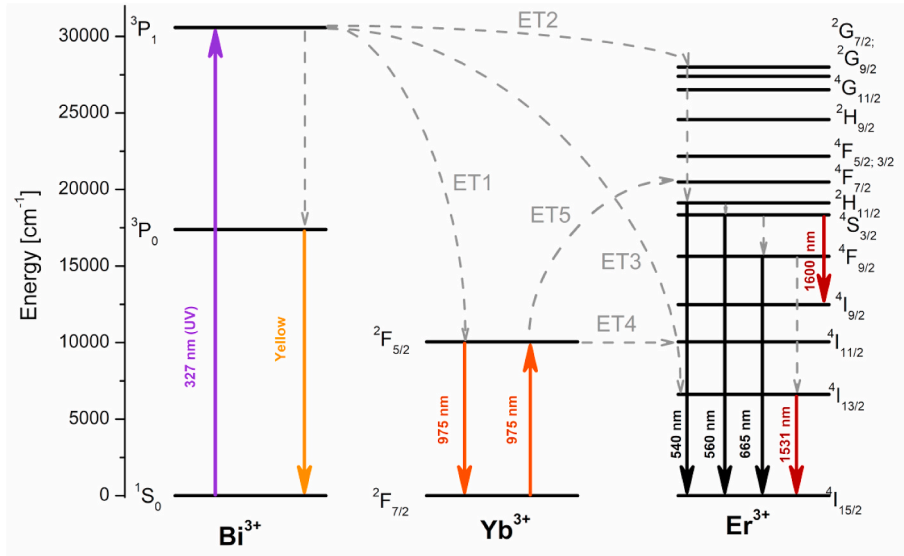


Fig. 11. Schematic energy level diagram showing the possible energy transfer between Bi^{3+} , Yb^{3+} and Er^{3+} active ions in BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ systems upon the excitation at 327 and/or 975 nm, for the NIR luminescence at 975 or 1531 nm (ET1 - energy transfer from Bi^{3+} to Yb^{3+} ions; ET2, ET3 - energy transfer from Bi^{3+} to Er^{3+} ions and ET4, ET5 - energy transfer from Yb^{3+} to Er^{3+} ions).

emission band at 975 nm. As mentioned, for Er^{3+} co-doped BTBO: Yb^{3+} the energy transfer from Yb^{3+} ions (excited by Bi^{3+} ions) to Er^{3+} ions was observed (Fig. 7), which results in shorter living time of excited Yb^{3+} ions in Er^{3+} co-doped BTBO: Yb^{3+} in comparison to those in BTBO: Yb^{3+} . The possible mechanisms of energy relaxation after excitation at 327 nm are illustrated schematically in Fig. 11.

3.6. The luminescence decay times for 1531 nm emission

Based on the luminescence decay curves shown in Fig. 10, the ETE determined by the η_{ET} coefficient and the total theoretical QE determined by the η_{QE} coefficient, can be calculated [41,42]. As mentioned above, the ETE and QE were calculated for two situations: energy transfer from Bi^{3+} to Yb^{3+} ions, where Bi^{3+} is a donor (D) and Yb^{3+} is an acceptor (A) of energy and from Yb^{3+} to Er^{3+} ions, where Yb^{3+} is an energy D and Er^{3+} is an energy A. The ETE can be obtained by dividing the integrated intensity of the experimentally measured luminescence decay curves of A and D ions co-doping phosphors by that of the luminescence decay curves of the materials containing D ions. The η_{ET} and η_{QE} coefficients for the mentioned above energy transfer were calculated from the following equation:

$$\eta_{ET} = 1 - \frac{\langle \tau \rangle_{D/A}}{\langle \tau \rangle_D} \quad (3)$$

where $\langle \tau \rangle_{D/A}$ is the average lifetime of decay curves recorded for the powders containing D and A ions (BTBO: Yb^{3+} and BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ samples), $\langle \tau \rangle_D$ is the average lifetime of decay curves for the powders that only have D ions (BTBO and BTBO: Yb^{3+} samples). Consequently, the ETE coefficients were found as follows: $\eta_{ET} = 22.65$ and 37.37% for ET from Bi^{3+} to Yb^{3+} and Yb^{3+} to Er^{3+} , respectively.

The corresponding η_{QE} coefficients were calculated using the following equation.

$$\eta_{QE} = \eta_D(1 - \eta_{ET}) + 2\eta_A\eta_{ET} \quad (4)$$

where η_D and η_A stand for the luminescent quantum efficiency of the A and D ions, respectively. Assuming that all the excited D ions and the residual excited A ions decay radiatively we have $\eta_D = \eta_A = 1$ [41]. Consequently, the upper limited values of the total QE for BTBO powder doped with Yb^{3+} (5%) and Er^{3+} (1%) were calculated to be $\eta_{QE} = 122.65$ and 137.37% for Bi^{3+} to Yb^{3+} and Yb^{3+} to Er^{3+} ET, respectively. The

determined total QE values for Bi^{3+} to Yb^{3+} ET expressed by η_{QE} coefficients were reported for many various crystalline materials containing Bi^{3+} and Yb^{3+} ions. Some examples were collected in Table 3.

In Fig. 11 schematic energy level diagram showing the possible energy transfer between Bi^{3+} , Yb^{3+} and Er^{3+} active ions in BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ systems is presented.

The energy level diagram for the BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ system was made on the basis of the excitation and emission spectra. After the absorption of UV energy (at 327 nm) Bi^{3+} ions are excited from the $^1\text{S}_0$ ground to the $^3\text{P}_1$ excited state. Part of the energy from the excited state of Bi^{3+} ions can relax to the $^1\text{S}_0$ ground state by emitting photons in the VIS spectral range (wide bands in the 450–650 nm spectral range with maximum intensity at about 560 nm corresponding to yellow emission presented in Fig. 6) and the remaining energy from the $^3\text{P}_1$ excited state can be transferred to the nearest Bi^{3+} , Yb^{3+} or Er^{3+} ions. In particular, the energy of the excited Bi^{3+} ions can be transferred by energy migration process to the un-excited Bi^{3+} ions. This leads to quenching of luminescence of Bi^{3+} ions and it is very possible for undoped and Yb^{3+} and/or Er^{3+} co-doped BTBO systems due to the short distance between the nearest Bi^{3+} ions in the BTBO matrix. The other possible mechanism is the energy transfer process (ET1) from $^3\text{P}_1$ level of Bi^{3+} ions to the excited levels of Yb^{3+} ions. Since the $^3\text{P}_1$ level of Bi^{3+} ions is located at higher energy level than the $^2\text{F}_{5/2}$ level of Yb^{3+} ions, the ET1 process from excited Bi^{3+} to two Yb^{3+} ions can be realized to achieve the NIR emission of Yb^{3+} (at 975 nm), according to the following formula: $\text{Bi}^{3+}(^3\text{P}_1) \rightarrow 2 \text{Yb}^{3+}(^2\text{F}_{5/2})$, which expresses that two NIR photons, corresponding to the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transitions of Yb^{3+} ions are obtained

Table 3

The total QE calculated for Bi^{3+} to Yb^{3+} ions energy transfer in %.

samples	η_{QE}
$\text{Gd}_2\text{O}_3:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(5\%)$ [42]	134.47
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(0.5\%)$ [43]	109.05
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(1\%)$ [43]	118.85
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(3\%)$ [43]	129.67
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(5\%)$ [43]	158.49
$\text{YNbO}_4:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(2\%)$ [44]	109
$\text{YNbO}_4:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(8\%)$ [44]	121
$\text{YNbO}_4:\text{Bi}^{3+}(1\%)/\text{Yb}^{3+}(16\%)$ [44]	120
$\text{YVO}_4:\text{Bi}^{3+}(5\%)/\text{Yb}^{3+}(2\%)$ [45]	106.9
$\text{YVO}_4:\text{Bi}^{3+}(5\%)/\text{Yb}^{3+}(5\%)$ [45]	141.5
BTBO: $\text{Yb}^{3+}(5\%)/\text{Er}^{3+}(1\%)$ this work	122.65

after absorption of a single UV photon from the excited Bi^{3+} ion. This corresponds to the observed high intensity emission of Yb^{3+} for BTBO: Yb^{3+} samples presented in Fig. 7. The energy transfer processes from $^3\text{P}_1$ level of Bi^{3+} ions to the excited levels of Er^{3+} ions located close in energy (ET2) or to the lower-lying levels of Er^{3+} ions (ET3) are also possible. The ET2 process to the close-lying (in energy) levels of Er^{3+} ions occurs according to the following formula: $\text{Bi}^{3+}(^3\text{P}_1) \rightarrow \text{Er}^{3+}(^2\text{G}_{7/2})$, which can result in up-conversion emission accompanied by the green and red color emission of Er^{3+} ions [46], which was not investigated in this study. The ET3 process to the lower-lying levels of Er^{3+} ions can lead to the emission of Er^{3+} in the NIR region (with a maximum intensity at 1531 nm), according to the following formula: $\text{Bi}^{3+}(^3\text{P}_1) \rightarrow 2 \text{Er}^{3+}(^2\text{H}_{11/2})$, which corresponds to the observed emission of Er^{3+} for BTBO: Er^{3+} presented in Fig. 7. Moreover, the NIR emission of Er^{3+} ions in the BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ system at around 1531 nm (Fig. 7) can be enhanced additionally as a result of sensitization of Er^{3+} emission by Yb^{3+} ions. In the considered system, Yb^{3+} plays a role of a sensitizer due to a broad absorption band (875–1000 nm) and large overlap between the Yb^{3+} emission and Er^{3+} absorption. This large overlap allows a resonant energy transfer (ET4) from the absorbing Yb^{3+} to the emitting Er^{3+} ion with energy losses, which can be described as: $\text{Yb}^{3+}(^2\text{F}_{5/2}) \rightarrow \text{Er}^{3+}(^4\text{I}_{11/2})$. The depopulation of the $^4\text{I}_{11/2}$ level takes place as a result of a multi-phonon relaxation from $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$ of Er^{3+} ions. In BTBO the maximum phonon energy involved in the nonradiative relaxation process is 690 cm^{-1} , and therefore only 4 phonons are necessary for non-radiative relaxation from the $^4\text{I}_{11/2}$ to $^4\text{I}_{13/2}$ and next we observe the NIR emission of Er^{3+} ions at 1531 nm corresponding to the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition. Moreover, the emission at 1531 nm is more intensive for co-doped BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ than BTBO: Er^{3+} powders, at the excitation wavelength of 975 nm (Fig. 8). The energy transfer (ET5) from the excited Yb^{3+} ions to the higher-lying (in energy) levels of Er^{3+} ions is also possible, according to the following formula: $2 \text{Yb}^{3+}(^2\text{F}_{5/2}) \rightarrow \text{Er}^{3+}(^4\text{F}_{7/2})$ by the up-conversion process, which produces the green and red color emission of Er^{3+} ions [46], not investigated in this study.

4. Conclusions

Efficient BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ phosphor, which is a promising luminescent down-conversion material for low-band gap semiconductor solar cells was synthesized and characterized. The microcrystalline powders BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$, BTBO: Yb^{3+} and BTBO: Er^{3+} synthesized by means of the modified Pechini method, crystallized in the hexagonal structure of P63 space group. The low doping concentrations of Er^{3+} , Yb^{3+} and $\text{Yb}^{3+}/\text{Er}^{3+}$ ions in BTBO matrix used for the mentioned above samples (1.0 at.%, 5.0 at.% and 5.0/1.0 at.%, respectively) were proved not to change their symmetry. Average crystallite sizes D , calculated using the Debye-Scherrer method, are lower than 60 nm. Results of μ -Raman investigation show a low phonon energy of BTBO matrix, which allows effective phonon assisted energy transfers between the active Bi^{3+} , Yb^{3+} and/or Er^{3+} ions. The emission spectra of BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$, BTBO: Yb^{3+} and BTBO: Er^{3+} powders excited at 327 nm (by Bi^{3+} ions) and 975 nm (by Yb^{3+} ions) show the emission of Bi^{3+} ions in the VIS spectral range with a maximum intensity at about 560 nm (the $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transition) as well as the NIR emission of Yb^{3+} ions at 975 nm (the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transition) and/or of Er^{3+} ions at 1531 nm (the $^4\text{I}_{13/2} \rightarrow ^4\text{I}_{15/2}$ transition). Moreover, upon the excitation at 327 nm (by Bi^{3+} ions), the intensity of the emission bands at 975 nm is higher for BTBO: Yb^{3+} than for BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ powder. The higher intensity emission bands at 1531 nm were detected for BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ than for BTBO: Er^{3+} , which is due to the energy transfer from the excited Bi^{3+} ions directly to Er^{3+} ions as well as the energy transfer from Yb^{3+} ions (excited by Bi^{3+} ions) to Er^{3+} ions. This synergistic effect of the energy transfer between Bi^{3+} , Yb^{3+} and Er^{3+} active ions produce enhanced NIR emission of Er^{3+} ions in BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ powders. Moreover, the characteristic emission of Er^{3+} ions at 1531 nm was also measured for BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ and BTBO: Er^{3+} systems upon the excitation at 975 nm (by Yb^{3+} ions) and higher

intensity of the emission at 1531 nm was observed for co-doped BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ systems than for BTBO: Er^{3+} ones. The observed enhanced emission of Er^{3+} ions in BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ systems is due to the additional energy transfer process from the excited Yb^{3+} ions to the excited levels of Er^{3+} ions. Moreover, the decay lifetimes (described by the single-exponential function) measured for the emission of Er^{3+} ions at 1531 nm are equal to 1.38 and 1.39 ms for BTBO: Er^{3+} and 1.44 and 1.40 ms for BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$, upon the excitation at 327 and 975 nm, respectively. The calculated ETE coefficients η_{ET} for BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ system are equal to 22.65 and 37.37% for ET from Bi^{3+} to Yb^{3+} and Yb^{3+} to Er^{3+} , respectively. Furthermore, the total QE η_{QE} were calculated to be 122.65 and 137.37% for Bi^{3+} to Yb^{3+} and Yb^{3+} to Er^{3+} energy transfer, respectively. As a result, due to the effective energy transfer from Bi^{3+} to Yb^{3+} or Er^{3+} ions and from Yb^{3+} to Er^{3+} ions, the BTBO: $\text{Yb}^{3+}/\text{Er}^{3+}$ phosphor is a very promising material for the solar radiation concentration in the required absorption range in new generation low-band gap semiconductor based solar cells.

Credit author statement

T. Zhezhera: Investigation of spectroscopic properties, calculations, interpretation of results, writing, P. Gluchowski: Investigation of luminescence properties, M. Nowicki: SEM measurements, M. Chronik: synthesis of materials and XRD measurements, A. Majchrowski: interpretation of results D. Kaspricz: Conceptualization, interpretation of results, writing and draft preparation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2023.119774>.

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Enhanced near-infrared emission of Er³⁺ as a synergistic effect of energy transfers in Bi₃TeBO₉:Yb³⁺/Er³⁺ phosphors

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On the basis of the diffuse reflectance spectrum of BTBO:Yb³⁺/Er³⁺ powder the value of the energy band gap E_g was evaluated according to the Kubelka–Munk model [38] and using the Tauc method [39]. The modified Tauc equation for the diffuse reflectance spectrum is given by:

$$F(R_\infty)h\nu = C_1(h\nu - E_g)^n$$

where: h is a Planck constant, ν is frequency of reflected light, n is a coefficient related to the nature of the electronic transitions. Since BTBO is an indirect band gap semiconductor [22], so in this case $n = 2$, and $F(R_\infty)$ is reemission function calculating using the following equation:

$$F(R_\infty) = \frac{k}{s} = \frac{(1 - R_\infty)^2}{2R_\infty}$$

where R_∞ is the reflectance of the sample, k and s are the absorption and scattering Kubelka–Munk coefficients, respectively and C_1 is proportionality constant. The value of E_g can be determined from the Tauc plot $(F(R_\infty)h\nu)^{1/n}$ vs $h\nu$ at the intersection of the extrapolated straight fitting line (obtained for the straight-linear fitting of the linear range of the Tauc plot) and the $h\nu$ axis (Figure S1)

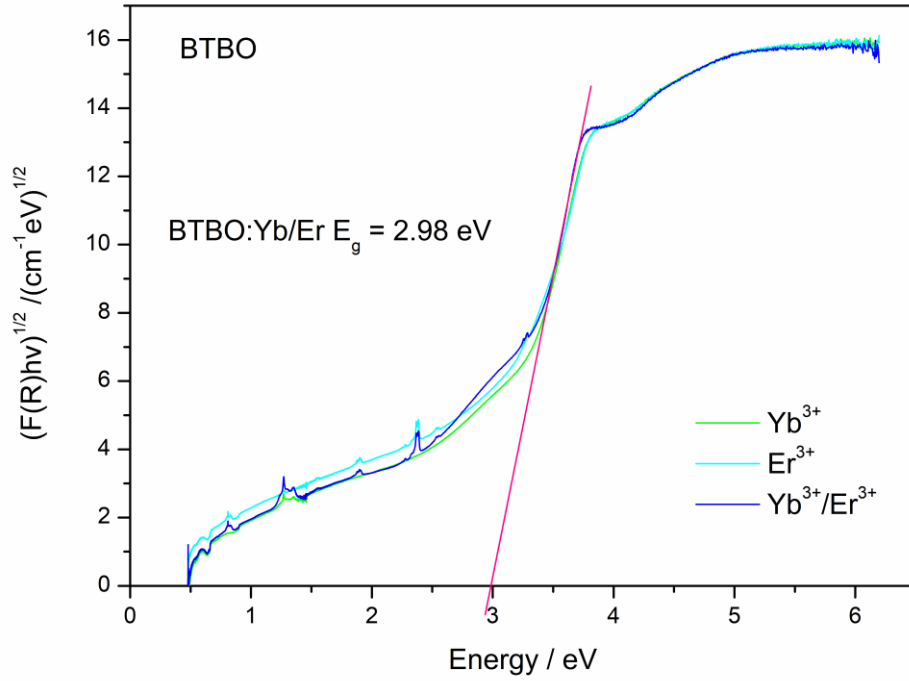


Figure S1. Tauc plots $(F(R_{\infty})hv)^{1/n}$ vs $h\nu$ of BTBO:Yb³⁺, BTBO:Er³⁺ and BTBO:Yb³⁺/Er³⁺ samples and straight-linear fitting lines of the linear range of the Tauc plot of BTBO:Yb³⁺/Er³⁺ sample.

The determined value of the energy band gap E_g of BTBO:Yb³⁺/Er³⁺ sample is equal to 2.98 eV, which correspond to the values determined using the theoretical method 2.96 and 3.21 eV (calculations using DFT–LDA and DFT–GGA functionals) [25], respectively and 2.70 and 3.23 eV calculated and obtained experimentally, respectively, by other authors [22].

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Pressure modified upconversion luminescence of Yb³⁺ and Er³⁺-doped Bi₃TeBO₉ ceramics

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ABSTRACT

Yb³⁺ and Er³⁺-doped Bi₃TeBO₉ ceramics exhibit efficient upconversion luminescence in the visible spectral range upon laser diode excitation at 975 nm. Bi₃TeBO₉:Yb³⁺/Er³⁺ powder was prepared by means of the modified Pechini method. A series of Bi₃TeBO₉:Yb³⁺/Er³⁺ ceramic samples was fabricated using the high-pressure low-temperature technique, by sintering Bi₃TeBO₉:Yb³⁺/Er³⁺ powder under different pressures (2, 4, 6 or 8 GPa). The structure and morphology of the above-mentioned samples were analyzed using XRD, SEM and EDX measurements. The phonon energy of Bi₃TeBO₉ matrix associated with the vibrations of TeO₆ and BO₃ molecular groups was revealed using μ -Raman spectroscopy. The low phonon energy of Bi₃TeBO₉ matrix allows the effective energy transfer between Yb³⁺ and Er³⁺ ions as well as the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions from the excited to ground states of Er³⁺ ions, resulting in efficient upconversion emission at 523, 540 and 653 nm, respectively. The decay times determined for all analyzed emissions were longer for Bi₃TeBO₉:Yb³⁺/Er³⁺ ceramics than for the powder sample. The highest values of decay times were detected for the ceramics obtained under a pressure of 8 GPa and were equal to 174, 172 and 175 μ s for the emissions at 523, 540 and 653 nm, respectively. The obtained results suggest that Bi₃TeBO₉:Yb³⁺/Er³⁺ ceramics can be proposed as efficient spectral converters in the new type solar cells enhancing the efficiency of the photovoltaic effect.

1. Introduction

Nowadays, the solar cells are gaining increasing interest due to the global demand for green and cheap energy. The efficiency of conventional crystalline silicon solar cells cannot exceed a level of about 30 % according to the Shockley-Queisser detailed-balance model [1]. Silicon (Si) solar cells are the most popular among all produced types of solar cells, due to their low costs and well known fabrication process [2,3]. It should be noted that conventional Si solar cell materials have the energy bandgap (E_g) equal 1.12 or 1.75 eV for crystalline or amorphous Si solar cells, which corresponds to the absorption of the solar radiation wavelengths at about 1107 and 708 nm, respectively [2,4]. The new generation semiconductor single- or multi-junction solar cells modified with the luminescence active ions may lead to concentration of the solar radiation spectrum into a required spectral range by the down- or upconversion or downshifting processes and thus increase the efficiency of solar energy conversion into electric energy [5–7]. The losses in

currently used semiconductor solar cells are related to surface reflection and spectral mismatch between the solar spectrum and the solar cells spectral response/absorption, which corresponds to their E_g . Spectral mismatch means that photons with energies corresponding to E_g create the electron-hole pairs and take part in photovoltaic process. The photons of energies lower than E_g are unable to pass E_g and their energy is lost, while the photons with energies higher than E_g are lost due to charge carriers thermalization process [2,8]. On the other hand, the absorption limit of the solar radiation corresponding to E_g of semiconducting materials, can be reduced by using new generation semiconducting materials with E_g dedicated to the absorption of solar radiation in a wide spectral range from ultraviolet (UV) via visible (VIS) up to near infrared (NIR) spectral ranges.

Currently, there are several semiconductors used in solar cells with E_g in the VIS spectral range such as: InN (1.8–1.9 eV) [9], GaInP (1.8–1.9 eV) [10], AlGaInP (1.9–2.2 eV) [11], AlGaAs (1.42–2.16 eV for various Al contents) [12], GaP (2.27 eV) [9], AlP (2.45 eV) [9]. Moreover, a large group of

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semiconductor materials attractive for photovoltaic application are chalcopyrite compounds I-III-VI₂ (I=Cu, Ag, III=Al, Ga, In, VI=S, Se, or Te), composed of three or more elements. Recently, chalcopyrite compounds such as: CuInSe₂, CuGaSe₂, Cu(Ga,In)Se₂ or (Cu,Ag)(In,Ga)Se₂ have been considered as the most promising absorbers for polycrystalline thin-film solar cells, because their bandgap energies cover a wide spectral range suitable for high absorption of solar radiation. Unfortunately, the conversion efficiency of these wide bandgap solar cells cannot reach 20 % [13,14].

One of the possibilities to improve such semiconductor solar cells efficiency, proposed in this study, is to modify the technology of their production by introduction of some rare earth (RE) ions doped materials, which concentrate the solar radiation in the VIS range through the upconversion process.

The RE³⁺ doped upconversion materials have been extensively studied because of their luminescence properties and potential applications as optical converters [5,15] or concentrators in photovoltaic cells [16,17]. The matrices for RE³⁺ ions doping were often selected from crystalline materials such as: fluorides, oxides, borates or phosphates thanks to their transparency windows in a wide spectral range [18–21]. The luminescence properties of RE³⁺ ions result from their characteristic electronic energy levels structure [22]. RE³⁺ ions have a partially filled 4f shell, which is shielded from the external environment (for example the crystalline host) by the outer filled 5s² and 5p⁶ electron shells. The partially filled 4f shell allows the inner shell 4f–4f transitions and their optical activity, depending on the selected ions, can cover the wide spectral range from VUV via VIS up to NIR spectral range [23]. The systems created from the mentioned above crystalline materials doped with some selected RE³⁺ ions, exhibit the luminescence properties with emissions in the required spectral range thanks to the energy transitions between the electronic energy levels of RE³⁺ ions in the down- or upconversion processes [23,24]. The trivalent Er³⁺ ion is luminescence active with rich energy levels structure and possible optical transitions between the ⁴I_{15/2} ground state and/or the excited states: ⁴I_{13/2}, ⁴I_{11/2}, ⁴I_{9/2}, ⁴F_{9/2}, ⁴S_{3/2}, ²H_{11/2}, ⁴F_{7/2}, ⁴F_{5/2}, ⁴F_{3/2}, ²H_{9/2}, ²G_{9/2}, ⁴G_{11/2}, ²P_{3/2}, ⁴D_{5/2}, ²I_{11/2}, ²I_{13/2}, ²D_{5/2} and ⁴D_{1/2} [22]. In particular, the efficient NIR emissions at about 1.5 and 2.9 μm are linked with the ⁴I_{13/2} → ⁴I_{15/2} and ⁴I_{11/2} → ⁴I_{13/2} transitions, respectively, or the emissions in the VIS spectral range of the green and red color are associated with the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions, respectively [25]. The Er³⁺-doped materials are very often co-doped with Yb³⁺ ions to enhance the characteristic upconversion of Er³⁺ ions emission in VIS spectral range [26–30]. The Yb³⁺ ions have two electronic level structure and the excitation of Yb³⁺ ions corresponds to the ²F_{7/2} → ²F_{5/2} transition generating emission at about 980 nm [22]. In the Er³⁺ and Yb³⁺ co-doped upconversion systems, Yb³⁺ ions are sensitizers, which activate Er³⁺ ions due to the energy transfer process from the excited Yb³⁺ ions into the unexcited Er³⁺ ions. Moreover, due to the overlapping of the emission/absorption bands of Yb³⁺ and Er³⁺ ions at about 980 nm, the enhanced upconversion emission of Er³⁺ ions can be observed in the VIS spectral range in Yb³⁺ and Er³⁺-doped in comparison to single Er³⁺-doped system after excitation at 980 nm [31].

Most of investigated materials exhibiting luminescent properties are single crystals or crystalline powders [32,33]. Powders mostly show a bit worse properties compared to those of single crystals, however, obtaining of the latter ones is often very difficult and expensive. Consequently, new technological methods are searched for luminescent materials in a different form that can be used in a wide range of applications. One of the possible alternatives are the materials in the form of ceramics. By pressing and simultaneously sintering powders, transparent ceramics can be obtained. As a result of the temperature influence during the ceramics fabrication, the grains of the powders can grow and the applied pressure prevents their further growth, thereby reducing the pores and increasing the density and transparency of the ceramic [34]. These effects result in changed physical properties, for example in changes in decay times relative to those of the single crystal or powder samples [35].

In this paper we present the results of investigation of the structural, spectroscopic and upconversion luminescent properties of Bi₃TeBO₉:Yb³⁺/Er³⁺ (BTBO:Yb³⁺/Er³⁺) powder and ceramic samples. The structures of BTBO:Yb³⁺/Er³⁺ samples were analyzed on the basis of XRD measurements and morphology of samples was examined using SEM and EDX methods. The vibrational properties were studied using Raman spectroscopy measurements. The upconversion luminescence of BTBO:Yb³⁺/Er³⁺ samples was analyzed on the basis of emission spectra and lifetimes measurements. Some structural and spectroscopic properties of BTBO, BTBO:Nd³⁺ and BTBO:Yb³⁺/Er³⁺ powders have been already reported in our previous papers [32,36,37].

2. Materials and experimental methods

2.1. Synthesis of powders and preparation of ceramics

BTBO:Yb³⁺/Er³⁺ microcrystalline powder was synthesized by means of a modified Pechini method [38] with doping concentration 5.0/1.0 % of Yb³⁺/Er³⁺ ions [37]. The mentioned above powder was used to make ceramics by means of high-pressure low-temperature (HPLT) method. For this purpose, firstly pellets with a diameter of about 5 mm and at around 2 mm in height were prepared from the powder under pressure of 0.2 GPa at room temperature (RT) using a cylindrical cell. After that, the pellets were placed in a specially shaped container with the ceramic made of CaCO₃ (pressure medium) and internal graphite heater located inside. Then the samples were placed in solid-state high-pressure cell of toroid-type to be sintered. Finally, all samples were sintered by hot-pressing at a temperature at about 500 °C for 1 min at pressures of 2, 4, 6 or 8 GPa. After completion of the pressing and cooling process, the ceramics were sanded using a sandpaper with different grit sizes for further experiments. As a result, four ceramic samples were obtained under different pressures and labelled as 2 GPa, 4 GPa, 6 GPa and 8 GPa samples. Detailed description of the HPLT method is available in Ref. [39].

2.2. Experimental methods

The XRD diffraction patterns of synthesized BTBO:Yb³⁺/Er³⁺ materials were obtained with using the Panalytical Empyrean equipment with a copper anode (CuK_α, λ_{Kα} = 1.541874 Å) with Bragg–Brentano reflection mode configuration working at 45 kV and 40 mA. The diffraction angle 2θ_B varied from 18° to 70° with a step of 0.0334° and acquisition time of 45 s per step. The measurements were made at RT.

The surface analysis of the investigated BTBO:Yb³⁺/Er³⁺ ceramics was carried out using the scanning electron microscope (SEM) FEI Quanta 250FEG. All investigated ceramics were measured in high vacuum at pressure 1.29–1.48 mPa in secondary electron mode at an accelerating voltage of 5 kV. Moreover, to determine the elements content for BTBO:Yb³⁺/Er³⁺ ceramics the energy dispersive X-ray (EDX) measurements and microchemical analysis were applied using the Edax Octane SDD system at an accelerating voltage of 30 kV.

Unpolarized spectra of BTBO:Yb³⁺/Er³⁺ ceramics at RT were recorded using the Renishaw inVia Raman spectrometer equipped with the CCD detector and Ar⁺-ion laser. The Raman spectra were excited with 488 nm wavelength and recorded in single scan with 30 s exposure time and 1 mW of the applied power. Before recording the spectra, the system was calibrated using the Si reference sample with the peak position of 520.3 cm⁻¹. All spectra were recorded with a spectral resolution better than 2 cm⁻¹. The power of the laser beam was focused on the samples with the 50× LWD objective. Spectral analysis was done with the software packages WiRE3.4/Renishaw.

The upconversion emission spectra of BTBO:Yb³⁺/Er³⁺ powder and ceramics were measured at RT after NIR laser diode irradiation with a 975 nm wavelength using the SilverNova CCD spectrometer (StellarNet Inc., Tampa, FL, USA) with 200 μm slit and 1 s integration time. The decay kinetics of BTBO:Yb³⁺/Er³⁺ samples were recorded using the

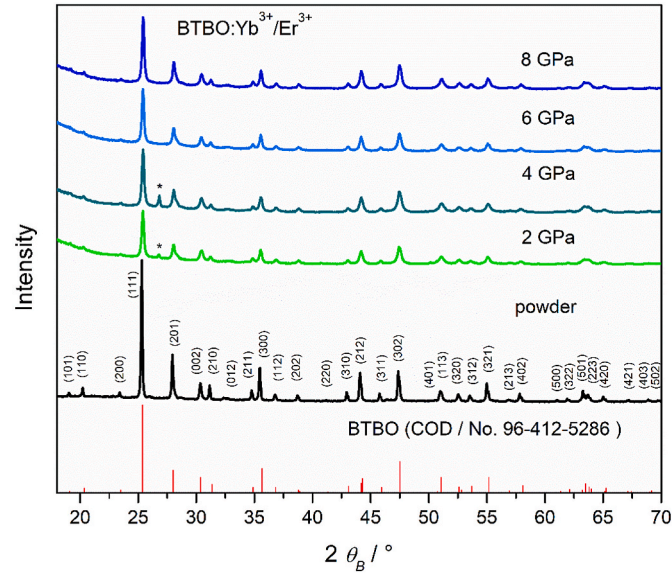


Fig. 1. A set of XRD patterns of BTBO:Yb³⁺/Er³⁺ powder and 2 GPa, 4 GPa, 6 GPa and 8 GPa ceramic samples. The positions marked with (*) come from h-BN, which was used during sintering of ceramics as an insulating material and was not completely removed from the ceramic surface during polishing ceramics.

Table 1

Calculated unit cell parameters of BTBO:Yb³⁺/Er³⁺ powder and ceramics with Rietveld refinement parameters.

BTBO: Yb ³⁺ /Er ³⁺	unit cell parameters			V [Å ³]	D [nm]	χ^2	R_{bragg}
	a [Å]	c [Å]	a/c				
powder	8.7474 (4)	5.8720 (4)	1.490	389.11	97	0.22	1.67
2 GPa	8.7543 (4)	5.8763 (4)	1.490	390.01	38	2.78	0.98
4 GPa	8.7537 (3)	5.8781 (3)	1.489	390.08	31	3.05	0.85
6 GPa	8.7534 (3)	5.8783 (3)	1.489	390.06	36	2.51	0.86
8 GPa	8.7526 (3)	5.8759 (3)	1.490	389.83	32	3.18	0.68

FLS980 Fluorescence Spectrometer (Edinburgh Instruments) equipped with the holographic grating of 1800 lines/mm, blazed at 300 mm focal length monochromators in the Czerny-Turner configuration. For measurements the Hammamatsu C5680 streak camera with time resolution below 50 ps and effective spectral range from 200 to 1000 nm was used.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of BTBO:Yb³⁺/Er³⁺ powder and ceramics (2 GPa, 4 GPa, 6 GPa and 8 GPa samples) recorded at RT are presented in Fig. 1.

The data presented in Fig. 1 could be assigned to the reference COD card (No. 96-412-5286), which means that all samples have hexagonal structure with noncentrosymmetric P6₃ (No. 173) space group (Z = 2) and correspond to the earlier obtained results for undoped BTBO powder [36]. Moreover, as shown in Fig. 1, the diffractions peaks detected for the ceramics are slightly broader and approximately twofold lower in intensity in comparison to those of the powder samples. Moreover, the observed differences between the diffraction peaks of the powder and ceramics, are due to the decrease in the grain size and increase in the strains in the ceramic samples pressed at a relatively high pressure as well as sintered at a relatively high temperature (500 °C) during the preparing process. It is important to note that there were no significant changes in the diffractograms of all ceramic samples excluding peak

originating from hexagonal boron nitride (h-BN) used during sintering process observed for 2 GPa and 4 GPa samples about 26 2 θ_B degree.

The unit cell parameters of the investigated samples were estimated on the basis of XRD patterns by means of the Rietveld refinement [40] and are presented in Table 1. The basic assumption and goal of the Rietveld refinement was to strive to achieve the minimum value of the function χ^2 (so-called chi-squared) in form: $\chi^2 = \sum_i \omega_i [y_{i,d} - y_{i,t}]^2$, where i – current number of the diffraction line, $y_{i,d}$ – intensity of the experimental (observed) diffraction i -line, $y_{i,t}$ – intensity of the calculated (real) diffraction i -line and ω_i – the reciprocal variance of $y_{i,d}$ intensity. After defining the polynomial representing the measurement background, the initial adjustment of the experimental profile to the reference model (included in the database COD/No. 96-412-5286) based on the reflections half-widths β_i was proceeded. The profile parameters were refined until the χ^2 value was reduced to the limit value given in Table 1. The results of the analysis were supplemented with statistical parameter of Bragg correlation coefficient (R_{bragg}). The Rietveld refinement was performed using the FullPROF ver. 3.0 program with EdPCR.

Comparing the values of the unit cell parameters for the powder and ceramic samples, slight differences in the values of the lattice constants can be observed. The lattice constants a and c are lower for the powder than for the ceramic samples. However, the a/c ratio as well as the cell volume parameter V remain commensurate in the range of experimental error for all investigated samples. The observed phenomenon is due to the simultaneous use of relatively high pressure and temperature in the technological process of ceramics preparation. The high temperature used in the process of the ceramics production resulted in the greater values of a and c parameters of the ceramic samples relative to those of the powder sample, while the high pressure limited the space for the unit cell expansion, which resulted in a stable a/c ratio and V parameters for all ceramic samples. The similar behavior of ceramics fabricated in the corresponding conditions was observed by other authors [41,42].

The calculated average crystallite size D decreased from 97 nm for the powder sample to below 40 nm (40 % of the initial dimension) for the ceramic samples (Table 1). The observed decrease in D parameter can be associated with fragmentation of crystallites in the ceramic samples caused by the high pressure applied during sintering and pressing of μ -crystals during preparation of the ceramic samples. It should be mentioned that the parameters for BTBO:Yb³⁺/Er³⁺ powder sample have been already determined by us using another experimental XRD setup [37].

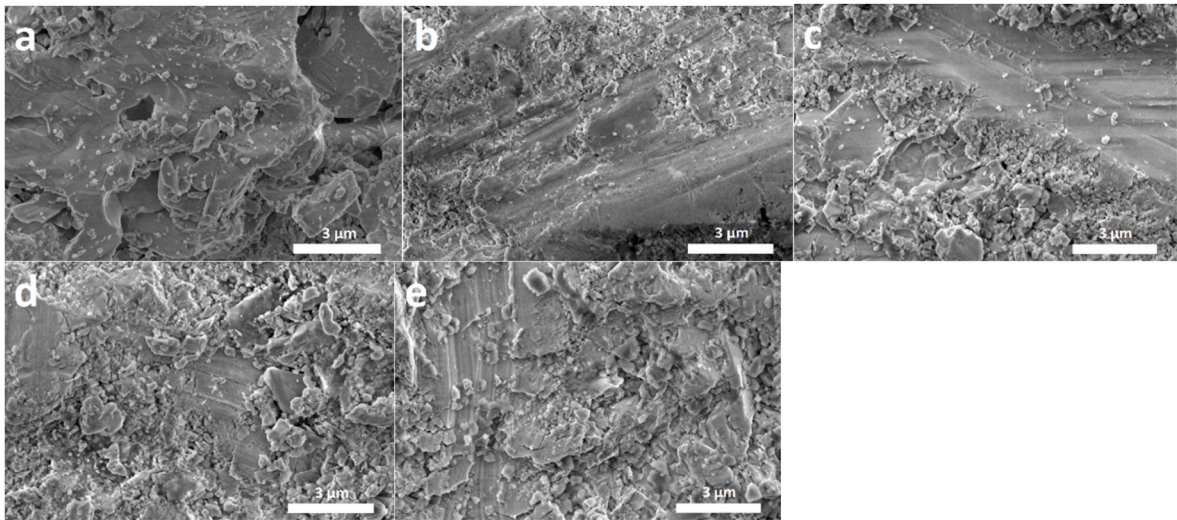


Fig. 2. SEM images of BTBO:Yb³⁺/Er³⁺ powder (a) and ceramic samples 2 GPa (b), 4 GPa (c), 6 GPa (d) and 8 GPa (e).

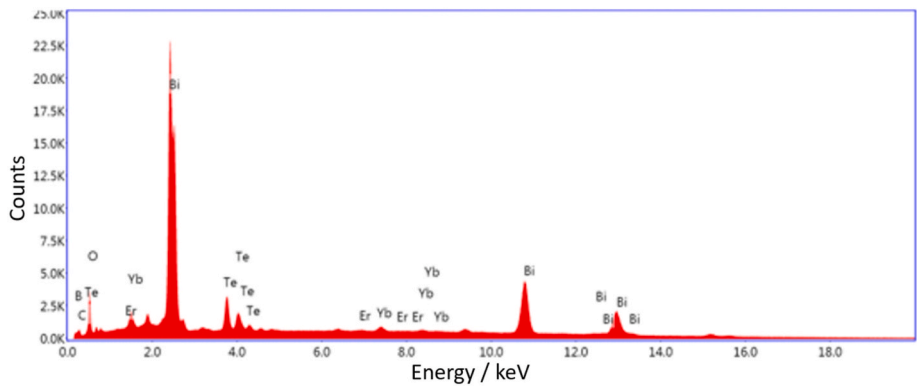


Fig. 3. The EDX spectrum of BTBO:Yb³⁺/Er³⁺ powder.

Table 2

The elements content in BTBO:Yb³⁺/Er³⁺ powder.

	BTBO:Yb ³⁺ /Er ³⁺						
Element	B	C	O	Te	Er	Yb	Bi
Weight %	2.40	1.46	15.28	11.44	0.29	1.56	67.57
	± 0.16	± 0.14	± 1.49	± 0.82	± 0.16	± 0.33	± 2.41

The data presented in Table 2 confirmed the elemental content of the investigated material. The presence of carbon in the EDX spectrum of BTBO:Yb³⁺/Er³⁺ powder comes from the substrate used during SEM/EDX measurements.

3.2. SEM and EDX analysis

Measurements using SEM technique revealed the morphology of BTBO:Yb³⁺/Er³⁺ powder and ceramic samples (Fig. 2). For the powder sample (Fig. 2a) it could be seen that the microcrystal sizes are in the range from a few to 10 μm. Moreover, many smaller sharp-edged grains of sub-micrometric size may be also observed. Results of SEM investigation of BTBO:Yb³⁺/Er³⁺ powder have been also discussed in our previous paper [37].

For the ceramic samples (2 GPa, 4 GPa, 6 GPa and 8 GPa), it can be observed that the pressing and sintering processes effected reduction in size of the empty space between the micro-powder grains as well as fragmentation of large grains. For all samples both, large grains of sizes more than 10 μm and numerous smaller grains of sizes between 1 and 5 μm are visible in SEM images (Fig. 2b–e). Most of the small grains of the

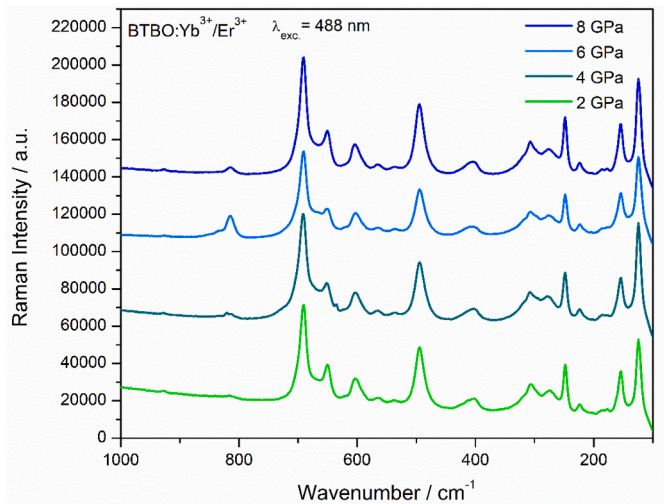


Fig. 4. The unpolarized Raman spectra of BTBO:Yb³⁺/Er³⁺ ceramics, recorded at RT.

ceramic samples retained their sharp-edge shapes. It can be also observed that large grains are fragmented to smaller ones as a result of the above mentioned pressing and sintering processes. Moreover, EDX analysis confirmed that all samples contain the same elements. The EDX

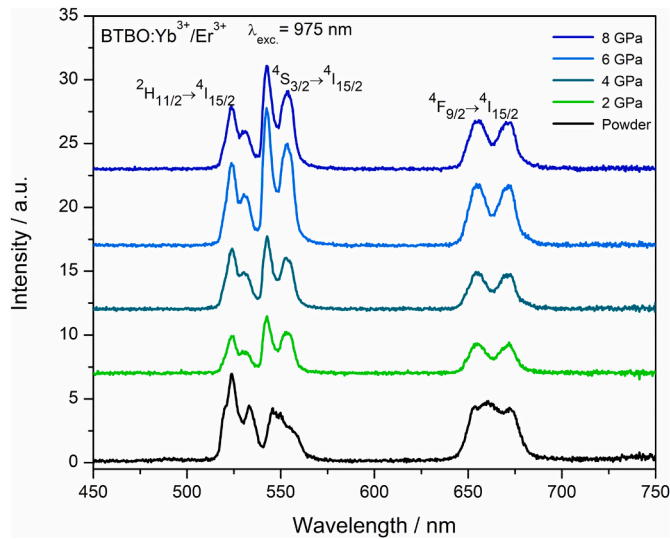


Fig. 5. The upconversion spectra of BTBO:Yb³⁺/Er³⁺ samples upon excitation at 975 nm recorded at RT.

spectrum of the selected BTBO:Yb³⁺/Er³⁺ powder sample is presented in Fig. 3.

It should be mentioned that EDX analysis provides very local information due to the inhomogeneous morphology of the investigated materials. In particular, the weight percent concentration of the elements occurring in low amounts is determined with relatively large measurement (especially apparatus) uncertainty. The weight contents of the individual elements (relative to the structural unit BTBO) in the selected BTBO:Yb³⁺/Er³⁺ powder sample are given in Table 2.

3.3. μ -Raman investigations

BTBO:Yb³⁺/Er³⁺ powder and ceramic samples crystallize in the hexagonal structure of $P6_3$ space group with two formula units in the unit cell. The detail description all of vibrations investigated for

undoped and some RE³⁺ doped BTBO powders using Raman spectroscopy have been presented in our previous papers [32,36,37].

The unpolarized Raman spectra of BTBO:Yb³⁺/Er³⁺ ceramics (2 GPa, 4 GPa, 6 GPa and 8 GPa samples) recorded at RT are presented in Fig. 4. It should be noted that it was not possible to detect Raman bands (observed for undoped BTBO powders [36]) above 1000 cm⁻¹ in the Raman spectra of BTBO:Yb³⁺/Er³⁺ ceramics due to the high intensity luminescence bands of Er³⁺ ions, which overlap the Raman bands of BTBO matrix in this spectral range.

In particular, the bands recorded at around 927 and 815 cm⁻¹ correspond to the internal stretching vibrations of the BO₃ groups. It should be noted that for the samples 2 GPa, 4 GPa and 8 GPa these bands have a very weak intensity, while for the sample 6 GPa the band at 815 cm⁻¹ has medium intensity. This may be a result of random orientations of the micro-crystals in the ceramics and recording of the unpolarized Raman spectra. One of the dominant peaks located at around 691 cm⁻¹ and a strong band at 651 cm⁻¹ in the spectra originate from the stretching vibrations of the TeO₆ groups. The observed modes: a very weak at 622 cm⁻¹, medium at 602 cm⁻¹ and the shoulder at 590 cm⁻¹ in the Raman spectra were assigned to the bending vibrations of BO₃ groups. The weak modes at 565 and 537 cm⁻¹, strong peak at 494 cm⁻¹ and two medium modes at 415 and 403 cm⁻¹ correspond to the bending vibrations of TeO₆ groups. Moreover, the low-frequency modes (from 100 to 350 cm⁻¹) were related to the external lattice vibrations: the librational or translational motions of TeO₆ and BO₃ molecular groups and Te or Bi atoms. All active modes detected in the Raman spectra and their assignment for the investigated BTBO:Yb³⁺/Er³⁺ ceramics are presented in Table S1.

3.4. Luminescence properties

The RT upconversion luminescence spectra of BTBO:Yb³⁺/Er³⁺, recorded in the range 450–750 nm upon 975 nm excitation for the powder and ceramics (2 GPa, 4 GPa, 6 GPa and 8 GPa samples), are presented in Fig. 5.

As presented in Fig. 5, the upconversion spectra of the investigated samples show the bands associated with green and red emission, which originated from the energy transfers between Yb³⁺ and Er³⁺ and the

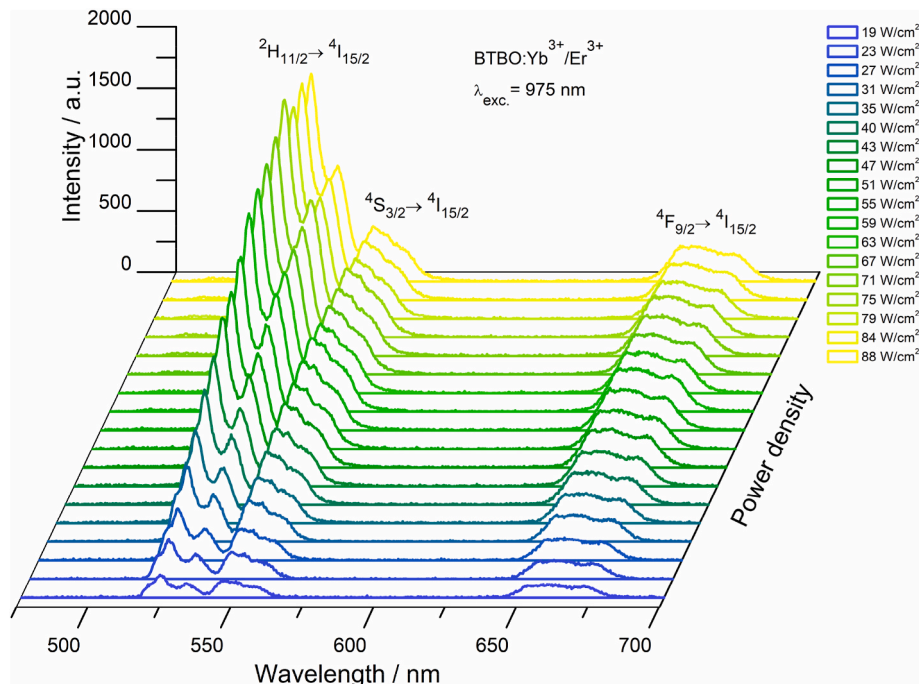


Fig. 6. The upconversion spectra of BTBO:Yb³⁺/Er³⁺ powder upon the excitation at 975 nm recorded with varying power density.

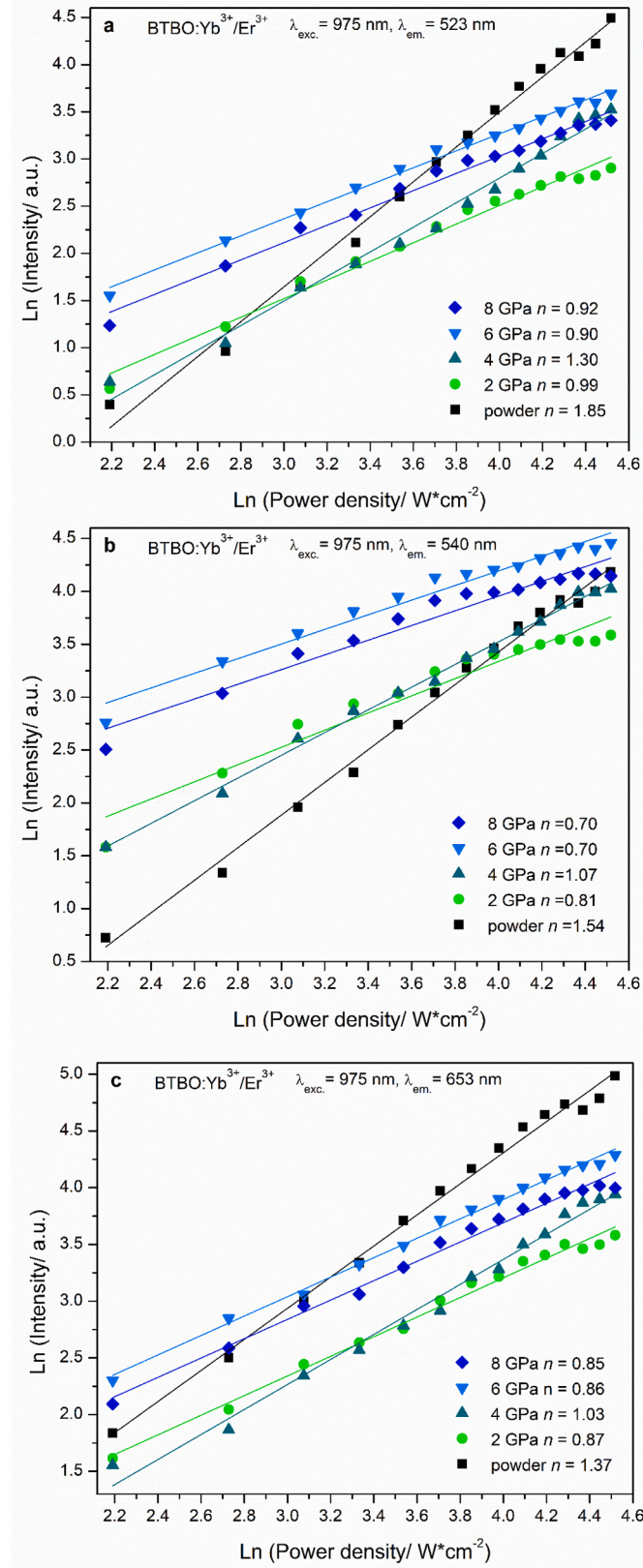


Fig. 7. Dependences of the logarithm of integral intensity of the upconversion emission bands at 523 (a), 540 (b) and 653 (c) nm on the logarithm of power density at 975 nm for BTBO:Yb³⁺/Er³⁺ samples.

Table 3

The slope coefficients of the dependences of the logarithm of integral intensity of the upconversion emission bands on the logarithm of power density at 975 nm for BTBO:Yb³⁺/Er³⁺ samples.

sample BTBO:Yb ³⁺ /Er ³⁺	the slope coefficient n		
	$^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$	$^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$	$^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$
powder	1.85	1.54	1.37
2 GPa	0.99	0.81	0.87
4 GPa	1.30	1.07	1.03
6 GPa	0.90	0.70	0.86
8 GPa	0.92	0.70	0.85

transitions between excited and ground levels of Er³⁺ ions. In particular, the bands with maximum intensity at about 523, 540 and 653 nm, corresponding to the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er³⁺ ions, were detected. The bands consist of several lines associated with the electronic transitions between the Stark sublevels of excited and ground states of Er³⁺ ions. The upconversion spectra of BTBO:Yb³⁺/Er³⁺ samples were analyzed on the basis of the Dieke's diagram of energy levels of trivalent lanthanides [22] and the following upconversion luminescence mechanism was proposed. The excited Yb³⁺ ions ($^2\text{F}_{7/2} \rightarrow ^2\text{F}_{5/2}$ transition) in BTBO:Yb³⁺/Er³⁺ systems can transfer energy to the excited states of Er³⁺ ions and then, after a series of the Excited State Absorption (ESA) processes in Er³⁺ ions, the transitions from the excited to ground states of Er³⁺ ions (the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions) occur, giving the green and red upconversion luminescence, respectively. The energy level diagram of Yb³⁺ and Er³⁺ ions and the possible mechanisms of energy relaxations after excitation at 975 nm were presented previously by us for BTBO:Yb³⁺/Er³⁺ systems [37].

Additionally, to determine the mechanism of photon activation during the upconversion process, the upconversion spectra of BTBO:Yb³⁺/Er³⁺ powder and ceramic samples were measured as a function of the density of the excitation power P of laser diode emitted at 975 nm (Fig. 6).

The dependences of the logarithm of integral intensity I of the emission bands on the logarithm of density of the laser excitation power P , calculated for the emission at 523, 540 and 653 nm (the $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$, $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{F}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions) for the investigated BTBO:Yb³⁺/Er³⁺ powder and ceramic samples, are presented in Fig. 7.

The integral intensity of the upconversion emission band I can be expressed as $I \sim P^n$, where P is the pump intensity and n is the number of photons involved in the upconversion process [43]. The slope coefficient of the corresponding linear fit is equal to the number of photons n participating in the upconversion processes *i.e.* to the number of absorbed low energy infrared photons required for the emission of one photon with higher energy (in VIS spectral range). The slope coefficients determined for the mentioned above emissions for BTBO:Yb³⁺/Er³⁺ powder and ceramics are collected in Table 3.

Considering the results presented in Table 3 for the BTBO:Yb³⁺/Er³⁺ powder sample (n equals to 1.85, 1.54 and 1.37 for the emission bands at 523, 540 and 653, respectively) we can conclude that the upconversion process involves two pumped photons, which produce photons in VIS spectral range, by the energy transfer from the excited Yb³⁺ ions to the excited states of Er³⁺ ions. In particular, two excited Yb³⁺ ions (Yb³⁺-Yb³⁺ pairs) transfer their energy to the excited states of Er³⁺ ions. The upconversion process for the BTBO:Yb³⁺/Er³⁺ ceramics is also related to generation of one photon in the VIS spectral range produced by two lower energy NIR photons. However, it should be noted that the lower values of n for the corresponding upconversion emission bands of BTBO:Yb³⁺/Er³⁺ ceramic samples result from their lower integral intensity of upconversion emission bands due to heating of the samples by the laser (with increasing power), with less heat dissipation in comparison to the process for the BTBO:Yb³⁺/Er³⁺ powder samples.

Kinetics of the upconversion luminescence of BTBO:Yb³⁺/Er³⁺

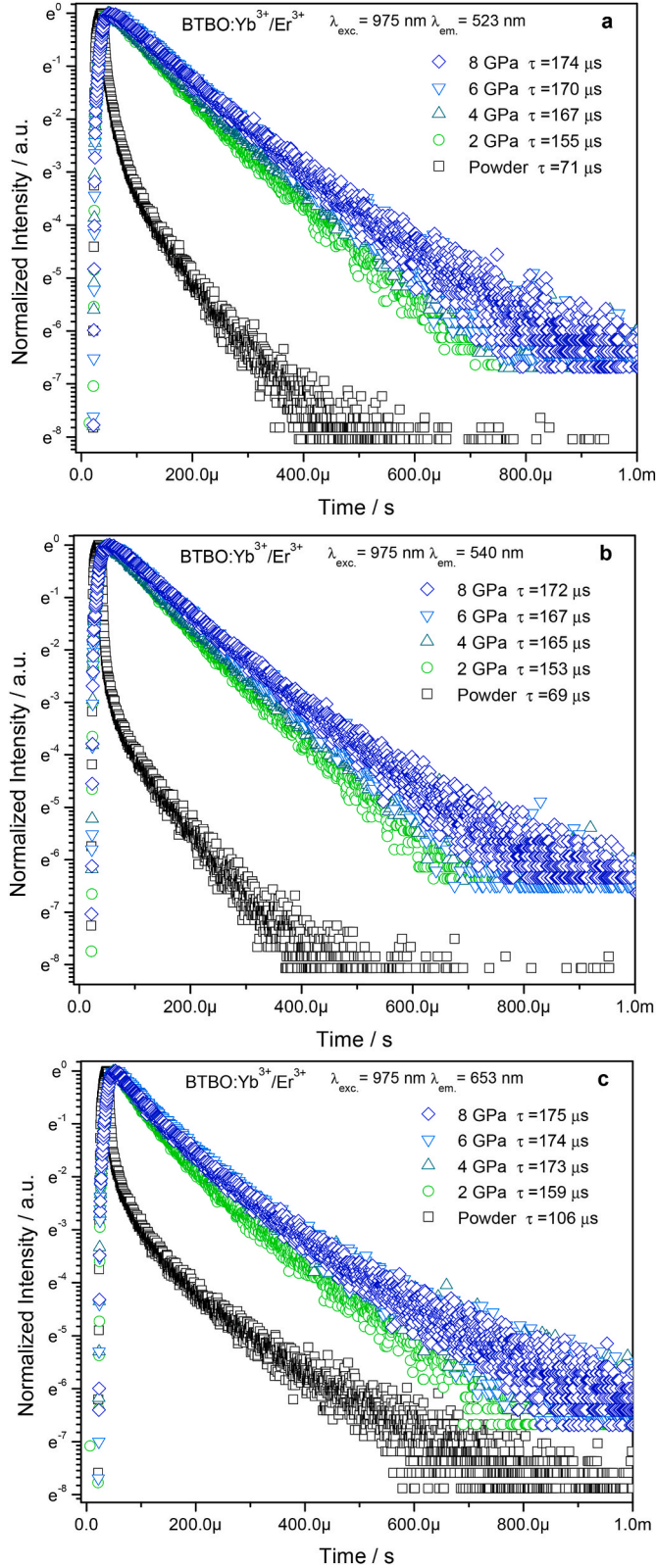


Fig. 8. The decay curves for 523 (a), 540 (b) and 653 (c) nm emissions of BTBO:Yb³⁺/Er³⁺ samples measured upon excitation at 975 nm at room temperature.

Table 4

The lifetimes monitored for 523, 540 and 653 nm upconversion emissions of BTBO:Yb³⁺/Er³⁺ samples and some other crystalline materials.

sample BTBO:Yb ³⁺ /Er ³⁺ (5/1 %)	average decay lifetime ⟨τ⟩/μs		
	² H _{11/2} → ⁴ I _{15/2}	⁴ S _{3/2} → ⁴ I _{15/2}	⁴ F _{9/2} → ⁴ I _{15/2}
powder	71	69	106
2 GPa	155	153	159
4 GPa	167	165	173
6 GPa	170	167	174
8 GPa	174	172	175
sample	average decay lifetime ⟨τ⟩/μs		
	² H _{11/2} → ⁴ I _{15/2}	⁴ S _{3/2} → ⁴ I _{15/2}	⁴ F _{9/2} → ⁴ I _{15/2}
KMgF ₃ :Yb ³⁺ /Er ³⁺ (1.0/0.5 %) [45]			135.6
Sr ₃ Y(PO ₄) ₃ :Yb ³⁺ /Er ³⁺ (10/2 %) [46]	52 ± 2		
LaNbO ₄ :Yb ³⁺ /Er ³⁺ (10/2 %) [47]		171.62	233.66
Gd ₂ ZnTiO ₆ :Yb ³⁺ /Er ³⁺ (5/4 %) [48]		240	
Gd ₂ ZnTiO ₆ :Yb ³⁺ /Er ³⁺ (20/4 %) [48]		31	
La ₂ O ₂ S:Yb ³⁺ /Er ³⁺ (9.0/1 %) [49]		120	160

powder and ceramics was analyzed based on the decay time measurements for the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions of Er³⁺ ions, which correspond to the upconversion emission at 523, 540 and 653 nm, respectively, upon excitation at 975 nm (Fig. 8).

The average lifetimes of the particular emissions were calculated from the measured decay time curves, using the following equation:

$$\langle\tau\rangle = \int_0^{\infty} \frac{I(t)}{I(0)} dt \quad (1)$$

where ⟨τ⟩ is the average lifetime, *I*(*t*) denotes the measured intensity of photoluminescence decay curve as a function of time and *I*(0) is the initial intensity (at *t* = 0 s) [44]. The average lifetime ⟨τ⟩ values determined for all samples monitored for the emission at 523, 540 and 653 nm after the excitation at 975 nm, calculated from Eq. (1), are presented in Table 4.

As follows from the data given in Table 4, the lifetimes of the above-mentioned emissions/transitions are shorter for BTBO:Yb³⁺/Er³⁺ powder sample than those of BTBO:Yb³⁺/Er³⁺ ceramics. Moreover, it should be noted, that BTBO:Yb³⁺/Er³⁺ ceramics obtained under increased pressure, show longer lifetimes of the emissions at 523, 540 and 653 nm. The longest lifetimes were detected for the ceramics obtained under 8 GPa and were equal to 174, 172 and 175 μs for emissions at 523, 540 and 653 nm, respectively. Moreover, additional analysis of particular decay time curves revealed the single or double exponential character of the decay of the considered upconversion emissions of BTBO:Yb³⁺/Er³⁺ ceramic samples sintered under different pressures (2, 4, 6 and 8 GPa), while the three-exponential function was the best fit for the decay time curves of the powder sample. The three decay times determined for BTBO:Yb³⁺/Er³⁺ powder sample can be a result of the presence of Er³⁺ active ions in the bulk (in well-coordinated positions) and surface of micro-crystals as well as the presence of some nano-crystals in BTBO:Yb³⁺/Er³⁺ powder sample, along with the presence of some surface molecules (H₂O, CO₂, etc.). For BTBO:Yb³⁺/Er³⁺ ceramic samples sintered under different pressures (2, 4, 6 or 8 GPa) the decay times are related only to the bulk and surface positions of Er³⁺ active ions, which show a higher crystallinity of BTBO:Yb³⁺/Er³⁺ ceramics in comparison to powder sample. Moreover, the lifetime of above-mentioned emissions of Er³⁺ ions were reported for many various crystalline materials containing Yb³⁺ and Er³⁺ ions. Some examples were collected in Table 4.

4. Conclusions

The structural, vibrational and upconversion luminescence properties of BTBO:Yb³⁺/Er³⁺ ceramics are presented for the first time. BTBO:Yb³⁺/Er³⁺ ceramics were prepared using the HPLT technique by sintering BTBO:Yb³⁺/Er³⁺ powder under different pressures (2, 4, 6 and 8 GPa). The hexagonal structure of P6₃ space group of BTBO:Yb³⁺/Er³⁺ ceramic and powder samples was confirmed by XRD measurements. Moreover, analysis of XRD data of BTBO:Yb³⁺/Er³⁺ samples revealed differences in the intensity, width and position of the diffraction peaks as well as the small differences in unit cell parameters between BTBO:Yb³⁺/Er³⁺ powder and ceramic samples. The mentioned differences were generated due to the simultaneous application of high pressure and temperature in the technological process of obtaining the ceramics. These structural modifications have proved to be crucial for the reported improved luminescence properties of prepared ceramics in comparison to as-synthesized BTBO:Yb³⁺/Er³⁺ powder sample.

The μ -Raman spectroscopy measurements confirmed that the doping concentration as well as the sintering processes during the production of the ceramics do not cause changes in the vibrational properties of BTBO:Yb³⁺/Er³⁺ samples. Moreover, the low phonon energy of BTBO matrix allows efficient energy transfer between active Yb³⁺ and Er³⁺ ions.

The emission spectra of BTBO:Yb³⁺/Er³⁺ powder and ceramic samples excited at 975 nm (by Yb³⁺ ions absorption) show relatively strong upconversion luminescence associated with green and red emission at about 523, 540 and 653 nm arising from the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions of Er³⁺ ions, respectively. Furthermore, calculations of the number of photons responsible for the upconversion emission for the above-mentioned transitions of Er³⁺ ions indicate that the upconversion process in BTBO:Yb³⁺/Er³⁺ powder and ceramic samples involves two pumped NIR photons that produce photons in the VIS spectral range by transferring energy from the excited Yb³⁺ ions to the excited states of the Er³⁺ ions. The upconversion luminescence lifetimes of particular emissions at about 523, 540 and 653 nm assigned to the ²H_{11/2} → ⁴I_{15/2}, ⁴S_{3/2} → ⁴I_{15/2} and ⁴F_{9/2} → ⁴I_{15/2} transitions of Er³⁺ ions were calculated from the measured decay time curves upon excitation BTBO:Yb³⁺/Er³⁺ powder and ceramic samples at 975 nm. The determined lifetimes of these emissions are shorter for BTBO:Yb³⁺/Er³⁺ powder sample in comparison to those for BTBO:Yb³⁺/Er³⁺ ceramics. Moreover, it should be noted, that BTBO:Yb³⁺/Er³⁺ ceramics obtained under increased pressure, show the increasing lifetimes of the emissions at 523, 540 and 653 nm. The longest lifetimes were detected for the ceramics obtained under 8 GPa and are equal to 174, 172 and 175 μ s for the emissions at 523, 540 and 653 nm, respectively.

As a result, we obtained very promising BTBO:Yb³⁺/Er³⁺ ceramics with effective upconversion emission in the VIS spectral range, which can be potentially used as optical converters in new generation semiconductor solar cells.

Credit author statement

Marek Nowicki: Investigation. Pawel Gluchowski: Investigation. Taras Zhezhera: Data curation, Formal analysis, Investigation, Methodology, Writing – original draft. Dobrosława Kasprowicz: Conceptualization, Data curation, Methodology, Writing – original draft, Writing – review & editing. Andrzej Miklaszewski: Investigation. Maciej Chrunik: Formal analysis, Investigation.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jlumin.2023.120401>.

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Enhancement of Yb³⁺ Emission in Bi₃TeBO₉ through Efficient Energy Transfer from Bi³⁺ Ions

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Supporting Information

ABSTRACT: An efficient near-infrared emission of Yb³⁺ ions sensitized by Bi³⁺ ions was revealed in Bi₃TeBO₉:Yb³⁺ microcrystalline powders. Bi₃TeBO₉:Yb³⁺ doped with different concentrations of Yb³⁺ ions (0.5, 1.0, 2.5, 4.0, and 7.5 at %) were synthesized by means of the modified Pechini method. The structure, morphology, and elemental composition of samples were investigated using X-ray diffraction, scanning electron microscopy, and energy-dispersive X-ray spectroscopy techniques. The μ -Raman spectroscopic measurements of Bi₃TeBO₉:Yb³⁺ allowed us to determine the energy vibrations of characteristic molecular groups BO₃ and TeO₆ present in the Bi₃TeBO₉ matrix. Emissions of Bi₃TeBO₉:Yb³⁺ powders were measured upon excitation at 330 nm by Bi³⁺ ions (the ¹S₀ → ³P₁ transition) in VIS (Bi³⁺ ions emission assigned to the ³P₀ → ¹S₀ transition) and NIR (Yb³⁺ ions emission assigned to the ²F_{5/2} → ²F_{7/2}) spectral ranges. In particular, the strongest emission band of Yb³⁺ ions at 975 nm was observed in the spectrum of Bi₃TeBO₉:Yb³⁺ doped with 4.0 at % of Yb³⁺ ions. This suggests that Bi³⁺ ions present in the Bi₃TeBO₉ matrix can be used as a UV absorption sensitizer for Yb³⁺ ions in the considered systems. Moreover, the decay times of ³P₀ → ¹S₀ transitions of Bi³⁺ ions (emission in VIS with maximum at 550 nm) and ²F_{5/2} → ²F_{7/2} transitions of Yb³⁺ ions (emission in NIR at 975 nm) upon excitation at 330 nm were measured. The calculated energy transfer efficiency and quantum efficiency coefficients confirmed the effective energy transfer from Bi³⁺ to Yb³⁺ ions in the Bi₃TeBO₉:Yb³⁺ system. The obtained results show that Bi₃TeBO₉:Yb³⁺ powders, as efficient UV to NIR spectral converters, can be potentially used in c-Si solar cell technology, enhancing the photovoltaic effect.



1. INTRODUCTION

Besides many nonconventional sources of energies, such as tides, wind, or biomass, the sun is one of the most important sources of sustainable energy that can be repeatedly obtained and easily converted into electric energy. The sun provides large amounts of energy in the form of solar radiation, generated in the fusion of hydrogen nuclei.¹ Although solar energy is available all over the world, its use is limited by many factors, in particular, geographical location, which determines the time of potential use of solar energy as it is available during the day, not at night. Solar energy is available without any costs and can be easily converted into electric energy by using photovoltaic solar cells. The efficiency of solar energy conversion into electric energy strongly depends on the type of solar cells. Nowadays, much effort is directed to improving the efficiency of different types of photovoltaic solar cells to make solar energy harvesting more efficient.^{2–4} The first generation solar cells were based on single crystalline silicon c-Si (wafers) or polycrystalline silicon mc-Si (wafers).^{1–5} The second generation solar cells are the thin-film solar cells based on the following materials: c-Si, amorphous silicon a-Si:H, copper indium gallium diselenide Cu(In,Ga)(Se)₂ (CIGS), cadmium telluride (CdTe), copper zinc tin sulfide Cu(Zn,Sn)-(S)₂ (CZTS), or compounds of groups III–V (for example, GaAs, InP, or GaInP), which permit creating multijunction

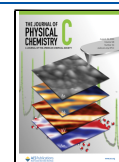
solar cells consisting of more than one junction, to achieve higher efficiency.^{1–5} The third generation solar cell technology provides the possibility of making the following types of multijunction solar cells: CZTS solar cells, dye sensitized solar cells, organic and polymeric solar cells, quantum dot solar cells, or perovskite solar cells.^{1–5} The fourth generation photovoltaic solar cells are combinations of those based on the previous generations of materials with, e.g., graphene as a potentially very promising component to enhance solar cells efficiency.⁵ Nowadays, the solar cell market is based on c-Si solar cells (about 80%), which are used all over the world with the highest commercial efficiency,¹ related to their low cost, relatively high photovoltaic efficiency, low toxicity, well-known fabrication process, and long lifetime (more than 20 years).⁵ However, according to the Shockley–Queisser detailed-balance model, the efficiency of c-Si solar cells cannot exceed a limit of 32–33%.^{1–5} An important parameter of photovoltaic semiconductors used in solar cells is the energy band gap,

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which corresponds to the selected wavelength range of solar radiation absorbed and converted into the electric energy. The major problem with efficiency loss in c-Si solar cells is the mismatch between the solar spectral range and the energy corresponding to the band gap energy of Si (1.12 eV).² One of the possible ways to enhance the efficiency of c-Si solar cells is to use optical converters in solar cell technology, which concentrate the solar radiation into the spectral range corresponding to the energy band gap of Si. Such optical converters can concentrate the solar radiation into the required spectral range by the quantum cutting (QC) process, in which one photon with high energy is cut into two ones with lower energies,⁵ from which solar energy can be easily absorbed and next converted into electric energy by the photovoltaic effect.² Moreover, the QC process effectively minimizes the energy losses due to the thermalization of electron–hole pairs in semiconductors.² It is possible to increase the maximum theoretical conversion efficiency from 30.9 to 39.6% for a c-Si solar cell by the QC process.² Crystalline materials doped with rare earth (RE) elements are often used as optical/spectral converters due to their unique structure of electronic energy levels, which allows easy absorption or emission of radiation in ultraviolet (UV), visible (VIS), or near-infrared (NIR) range and energy transfer (ET) processes between active RE ions by up- or down-conversion processes.^{6–10} Moreover, to enhance the photovoltaic efficiency in conventional solar cells, spectrally converted layers obtained from such RE-doped crystalline materials can be placed on the upper surface of a solar panel/cell, enabling more efficient utilization of solar radiation.⁶

Among other RE ions, Yb³⁺ ions are particularly attractive due to their characteristic two-quantum-level structure (the ground ²F_{7/2} and excited ²F_{5/2} states), which allows using them as optically active ions. The energy absorption by Yb³⁺ ions, through the ²F_{5/2} → ²F_{7/2} transition, at about 975 nm (equivalent to 1.26 eV) perfectly matches the band gap of c-Si solar cells (1.12 eV).² Recently, the pair of optically active ions Bi³⁺–Yb³⁺ has been reported as a good candidate for the QC process, possibly applicable for solar spectrum modification.^{11–18} In many crystalline materials, Bi³⁺ ion acts as an energy donor and Yb³⁺ ion as an energy acceptor.^{11–18} The Bi³⁺ ion has the outer electronic configuration of 6s² with the ground state of ¹S₀, while its excited state features a 6s6p electronic configuration, split into the ³P₀, ³P₁, ³P₂, and ¹S₁ energy states.¹⁴ Typically, Bi³⁺ ions exhibit a transition from ¹P₁ to the ground state in the vacuum ultraviolet region, while the emissions from ³P₁ and ³P₀ states are observed in the UV or VIS range, depending on the host matrix.¹⁶ Consequently, with the use of a Bi³⁺–Yb³⁺ system, the solar energy from the shorter wavelength range UV could be efficiently converted into the NIR spectral range, from which it could be absorbed by c-Si solar cells.

This work continues our research on the Bi₃TeBO₉ (BTBO) matrix, which is doped and codoped with rare earth ions.^{19–22} The nonlinear properties of the matrix and the efficient energy transfers between its constituent ions suggest a wide range of potential applications. Therefore, in this work, we focused on using these matrix ions to enhance the emission of luminescent ions. Our study revealed a novel effect: enhancing the infrared emission of Yb³⁺ ions through ultraviolet (UV) excitation, facilitated by efficient energy transfer from Bi³⁺ ions within the Bi₃TeBO₉ matrix. Previous research has typically focused on materials where Bi³⁺ ions function as optically active centers

emitting in the visible range. In contrast, we discovered that the excited states of Bi³⁺ ions can effectively engage in energy transfer, thus efficiently pumping Yb³⁺ ions and enhancing their emission in the infrared range. We measured the emission of Bi₃TeBO₉ powders under 330 nm excitation, corresponding to the Bi³⁺ ions' ¹S₀ → ³P₁ transition, and observed emissions in both the visible range (attributed to the Bi³⁺ ³P₀ → ¹S₀ transition) and the NIR range (attributed to the Yb³⁺ ²F_{5/2} → ²F_{7/2} transition).

Our findings indicate that Bi³⁺ ions within the Bi₃TeBO₉ matrix can serve as effective UV absorbers and sensitizers for Yb³⁺ ions in the system. The calculated energy transfer efficiency and quantum efficiency coefficients confirmed the effective energy transfer from Bi³⁺ to Yb³⁺ ions in the Bi₃TeBO₉ system. Consequently, Bi₃TeBO₉ powders can be used as efficient UV-to-NIR spectral converters, with potential applications in enhancing the photovoltaic effect in c-Si solar cell technology.

2. EXPERIMENTAL METHODS

X-ray diffraction (XRD) measurements of BTBO:Yb³⁺ powders were made using the BRUKER D2 PHASER diffractometer equipped with a CuK_α radiator ($\lambda_{K\alpha 1} = 1.54056$ Å, $\lambda_{K\alpha 2} = 1.54443$ Å, Siemens KFL CU 2 K, 30 kV voltage, and 10 mA current in operating mode) and 1D LYNXEYE detector. The Bragg–Brentano diffraction geometry was applied. The diffraction angle $2\theta_B$ ranged from 10 to 80° with a step of 0.015° and acquisition time of 3 s per step. All the measurements were carried out at room temperature (RT). The DIFFRAC.SUITE EVA application (supported by diffractometer producer) was applied for data processing. The phase analysis was performed with support of the ICDD PDF-2 and COD databases in Match! program by Crystal Impact. The FullPROF ver. 3.0 program managed with EdPCR editor was used for Rietveld refinement and precise calculations of entire diffraction profiles along with refined unit cell parameters. The crystallite sizes of as-prepared powders were estimated by means of the Debye–Scherrer method.

The scanning electron microscopy (SEM) analysis of BTBO:Yb³⁺ powders was performed with a SEM/FEI Quanta 250FEG microscope. The samples were analyzed in the low-vacuum mode at a pressure of 70 Pa. The images were recorded in the secondary electron mode at an accelerating voltage of 10 kV. The energy-dispersive X-ray spectroscopy (EDX) analysis was performed with the EDAX Octane SDD system at an accelerating voltage of 30 kV.

The Raman investigations were performed in the back-scattering geometry using the Renishaw InVia Raman microscope equipped with the confocal the DM 2500 Leica optical microscope and the CCD detector. The unpolarized Raman spectra were excited with the Ar laser emitting light of 488 nm wavelength and recorded in a single scan with 30 s exposure time and 1 mW of the applied power. The positions of the Raman peaks were calibrated before data collection using the Si reference sample as an internal standard with the peak position at 520.3 cm^{−1}. The diffraction-limited optical spatial resolution depended on the excitation wavelength, and for the used 50× LWD objective, it was approximately equal to 1.5 μm. The instrumental resolution of the spectrometer was better than 2 cm^{−1}. Spectral analysis was performed with the software packages WiRE3.4/Renishaw.

The excitation and emission spectra as well as the decay kinetics of BTBO:Yb³⁺ crystalline powders were recorded

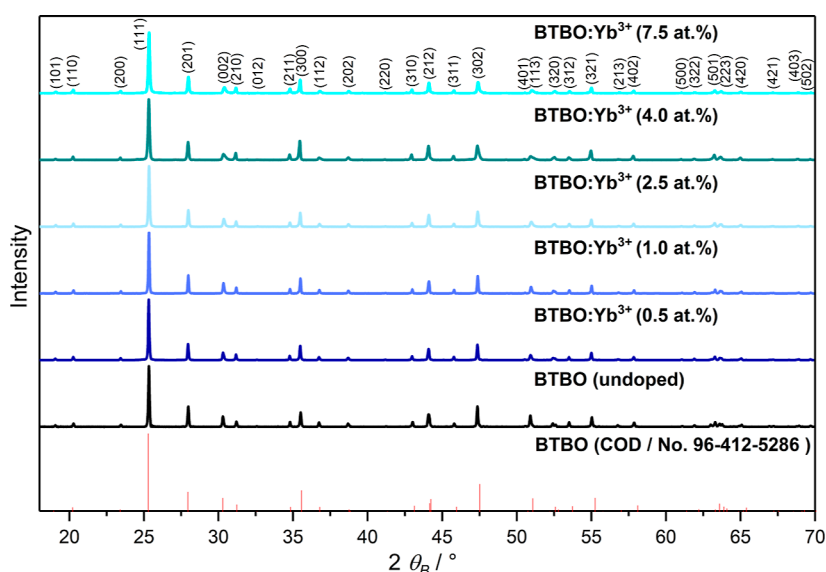


Figure 1. Set of experimental XRD patterns of BTBO:Yb³⁺ powders.

Table 1. Calculated Unit Cell Parameters of BTBO:Yb³⁺ Powders

compound	unit cell parameters [Å]		<i>V</i> [Å ³]	<i>a/c</i>	<i>D</i> [nm]	<i>R</i> _{Bragg}
	<i>a</i>	<i>c</i>				
BTBO ²⁴	8.7510(12)	5.8981(12)	391.16	1.484		
BTBO	8.7538(4)	5.8971(3)	391.35	1.484	170	1.399
BTBO:Yb ³⁺ (0.5 at %)	8.7505(4)	5.8869(3)	390.38	1.486	182	0.997
BTBO:Yb ³⁺ (1.0 at %)	8.7521(1)	5.8863(1)	390.48	1.487	179	1.700
BTBO:Yb ³⁺ (2.5 at %)	8.7542(1)	5.8801(1)	390.25	1.489	135	1.490
BTBO:Yb ³⁺ (4.0 at %)	8.7497(2)	5.8705(2)	389.22	1.490	103	1.681
BTBO:Yb ³⁺ (7.5 at %)	8.7536(1)	5.8687(2)	389.44	1.492	127	1.780

using the FLS980 Fluorescence Spectrometer (Edinburgh Instruments) equipped with the holographic grating of 1800 lines/mm, blazed at 300 nm focal length monochromators in a Czerny Turner configuration. The excitation and emission spectra were obtained using a 450 W xenon lamp. For decay times measurements, the 450 W excitation source was replaced with a 150 W lamp (μ F2) with external triggering. The emission spectra and decay times in the visible range were recorded on the Hamamatsu C5680 streak camera with time resolution below 50 ps and effective spectral range from 200 to 1000 nm. The Coherent Libra-S-laser (femtosecond laser, wavelength 800 nm, pulse width of less than 100 fs, and energy of 1 mJ at 1 kHz repetition rate) paired with the Coherent OPerA Solo Optical Parametric Oscillator (two-stage amplifier of white continuum) was an excitation source that allows the generation of pulses in the range of wavelengths from 230 to 2800 nm.

3. RESULTS AND DISCUSSION

3.1. Synthesis and Crystal Structure. Polycrystalline powders of BTBO:Yb³⁺ were synthesized via the modified Pechini method,²³ described in detail in our previous work.¹⁹ The only difference implemented in this approach was to increase the last stage of annealing temperature to 700 °C to ensure high phase homogeneity. The XRD data of the obtained powders are listed in Figure 1.

All of the presented diffraction patterns of undoped BTBO and BTBO:Yb³⁺ powders are in good correlation with the reference COD card (no. 96-412-5286). They all correspond

to a hexagonal crystal system with a noncentrosymmetric *P*6₃ (no. 173) space group (with the number of formula units per unit cell equal to *Z* = 2). The obtained results showed that the hexagonal crystal structure remains stable when Yb³⁺ ions of the applied concentrations are incorporated into the BTBO host matrix. Each diffraction profile was adjusted by using Rietveld refinement. The unit cell parameters of each sample are presented in Table 1. All the obtained results were provided with a statistical parameter of the Bragg correlation coefficient (*R*_{Bragg}).

The results given in Table 1 show a direct correlation between the Yb³⁺ ion content in the BTBO lattice and the changes in its unit cell volume. The values of effective ionic radius for Bi³⁺ and Yb³⁺ are 1.030 and 0.985 Å, respectively.²⁵ The similarity in their size may indicate that the isovalent substitution of Bi³⁺ ions with Yb³⁺ may occur, causing the compression of BTBO unit cell volume with increasing Yb³⁺ ions concentration. One can then conclude that the unit cell geometry is slightly changed within BTBO doping but does not disturb the original symmetry. The *a/c* ratio increases noticeably with increasing Yb³⁺ dopant concentration (a very similar effect was also observed by us for the Nd³⁺-doped BTBO system).¹⁹ With an increasing amount of Yb³⁺ dopant, the unit cell shrinkage is more pronounced. Average crystallite sizes, calculated using the Debye–Scherrer method, were in the range of 100–200 nm, and their relatively big dimensions were caused by long-term heat treatment during pyrolysis at elevated temperatures.

3.2. SEM and EDX Analysis. Morphology of the BTBO:Yb³⁺ samples was determined by SEM. SEM images revealed that all investigated powders had different irregular microstructures (Figure 2).

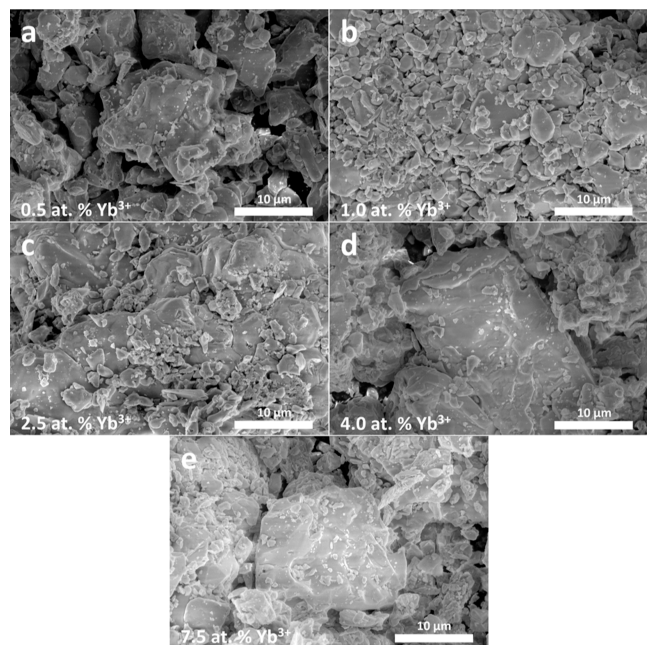


Figure 2. SEM images of BTBO:Yb³⁺ powders doped with different concentrations of Yb³⁺ ions: 0.5 at % (a), 1.0 at % (b), 2.5 at % (c), 4.0 at % (d), and 7.5 at % (e) in a magnification of 10 000 $\times$.

BTBO:Yb³⁺(0.5 at %) sample (Figure 2a) is composed of relatively large-size grains, ranging from a few to several tens of microns. Large grains' sizes range from 5 to 20 μm , while the size of smaller ones ranges between one and a few microns. Moreover, it should be noted that most of the large grains have a monolithic shape, although some agglomerations of much smaller grains were also detected. For the BTBO:Yb³⁺ (1.0 at %) sample (Figure 2b) most of the grains are between 1 and 5 μm in size and have sharp edges. Larger grains are also visible, but comparing to the previous sample, it can be concluded that small grains are predominant. The microstructure of sample BTBO:Yb³⁺(2.5 at %) is slightly different (Figure 2c). On the background of the image, there are large grain agglomerations of 20–30 μm , on whose surface small sharp edges are chaotically distributed. Comparing the SEM image of the

BTBO:Yb³⁺(4.0 at %) sample (Figure 2d) with those of the previously mentioned samples, a large monolithic grain of a few ten microns in size is located in the center of the sample area imaged. In addition, small grains of sizes between one and 10 μm can be observed next to it. Also visible are grains smaller than 1 μm in size. Finally, there is one large grain of the size of about 20 μm in the middle of the SEM image of the BTBO:Yb³⁺(7.5 at %) sample (Figure 2e) and many small grains of sizes of a few micrometers. Nevertheless, smaller grains of nanometer sizes were also observed on the surface of larger ones or in the empty space between large grains for all investigated samples.

For all considered BTBO:Yb³⁺ powders, the EDX analysis was performed. In Figure 3, the EDX spectrum of a selected BTBO:Yb³⁺ (1.0 at %) sample is presented.

The EDX characterization was applied in order to evaluate the element content of BTBO:Yb³⁺ systems and confirm whether their segregation on the grain boundaries had occurred. The weight and atomic contents of individual elements in the selected sample are given in Table 2.

Table 2. Elements Content in the BTBO:Yb³⁺(1.0 at %) Sample

BTBO:Yb ³⁺ (1.0 at %)	element	weight %	atomic %	error %
	B	32.46	75.50	3.19
	O	10.79	16.96	9.41
	Te	8.95	1.76	3.65
	Yb	0.75	0.11	9.18
	Bi	47.04	5.66	2.62

In the investigated BTBO:Yb³⁺ samples, doped with Yb in concentrations of 0.5, 1.0, 2.5, 4.0, or 7.5 at %, the Yb and Bi stoichiometric contents within the Bi_(3-x)Yb_xTeBO₉ formula are as follows: $x = 0.015, 0.030, 0.075, 0.120$, and 0.225 and $(3 - x) = 2.985, 2.970, 2.925, 2.880$, and 2.775 , respectively. The theoretical and experimental (according to EDX data) atomic contents of Yb and Bi elements (with respect to the whole 14 atoms in the BTBO formula) and the atomic ratio Yb/Bi determined for the studied BTBO:Yb³⁺ samples are presented in Table 3.

The theoretical Yb/Bi atomic ratios were determined for all considered samples by comparison of the number of Yb atoms which can occupy the Bi positions to that of Bi atoms in relation to all 14 atoms (3 Bi, 1 Te, 1 B, and 9 O), which are present in the Bi₃TeBO₉ structure unit. The experimental Yb/Bi atomic ratios were calculated from the experimental EDX

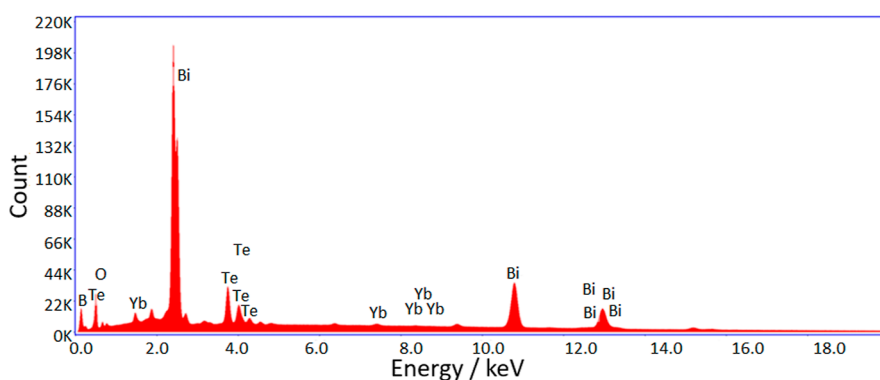
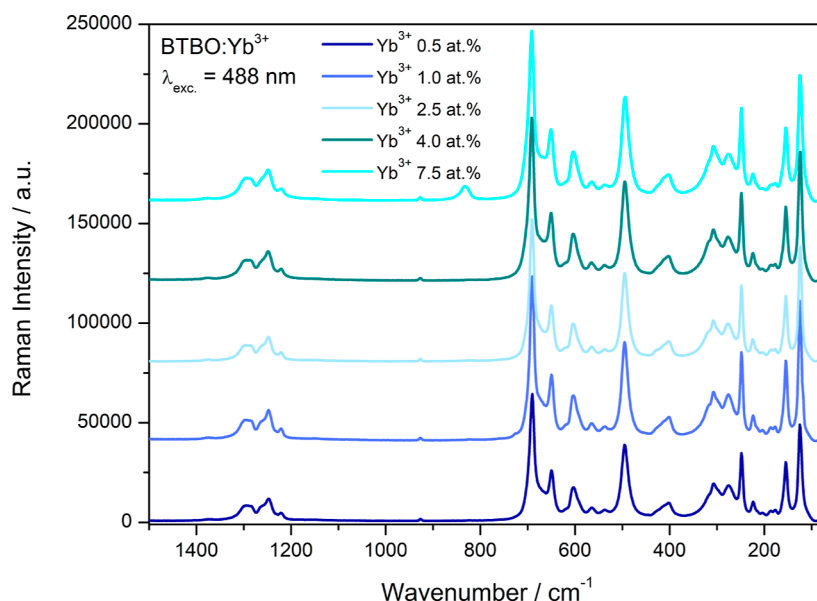


Figure 3. EDX spectrum for the BTBO:Yb³⁺ (1.0 at %) sample.

Table 3. Theoretical and Experimental Atomic Contents of Yb and Bi as well as Their Ratio Yb/Bi

compounds	atomic content theor. [%]		atomic content exp. [%]		Yb/Bi theor.	Yb/Bi exp.
	Yb	Bi	Yb	Bi		
BTBO:Yb ³⁺ (0.5 at %)	0.1071	21.3214	0.05 ± 0.01	6.43 ± 0.17	0.0050	0.0078 ± 0.0012
BTBO:Yb ³⁺ (1.0 at %)	0.2143	21.2143	0.11 ± 0.01	5.66 ± 0.15	0.0101	0.0194 ± 0.0019
BTBO:Yb ³⁺ (2.5 at %)	0.5357	20.8929	0.10 ± 0.02	5.65 ± 0.16	0.0256	0.0177 ± 0.0020
BTBO:Yb ³⁺ (4.0 at %)	0.8571	20.5714	0.24 ± 0.02	5.74 ± 0.15	0.0417	0.0417 ± 0.0027
BTBO:Yb ³⁺ (7.5 at %)	1.6071	19.8214	0.26 ± 0.02	5.76 ± 0.15	0.0811	0.0451 ± 0.0026

**Figure 4.** Unpolarized Raman spectra of BTBO:Yb³⁺ powders, detected at 300 K.

data given in Table 3 for the Yb and Bi atoms for all investigated BTBO:Yb³⁺ samples. Moreover, the analysis of the data presented in Table 3 allows concluding that the contents of individual Yb and Bi elements obtained from experimental data differ significantly compared to the theoretical values. The observed difference can be a result of the typical morphology of the powder materials that is responsible for significant fluctuations in the EDX signal within the area of a single grain, especially when the particle size is characterized by a large dispersion. However, it should be noted that the tendency of increasing Yb and decreasing Bi content as well as increasing atomic Yb/Bi ratio with increasing concentration of Yb from 0.5 to 7.5 at % in BTBO:Yb³⁺ is observed for theoretical as well as experimental values, except for the experimental value of Yb/Bi ratio for the BTBO:Yb³⁺ (2.5 at %) sample. Moreover, the best agreement between the theoretical and experimental values of the Yb/Bi atomic ratio (0.0417) was observed for the BTBO:Yb³⁺ (4.0 at %) sample. As already mentioned, the volume location of Yb³⁺ ions is preferred to the surface one in higher Yb³⁺-doped samples. Finally, the EDX measurements confirmed the presence of the expected elemental composition of the investigated BTBO:Yb³⁺ powder samples.^{26–28}

3.3. μ -Raman Investigation. The unpolarized Raman spectra of BTBO:Yb³⁺ powders were measured in the 100–1500 cm^{−1} spectral range at RT (Figure 4). As shown in Figure 4, the detected Raman spectra of BTBO:Yb³⁺ powders correspond to those recorded by us for pure BTBO microcrystalline powder and those doped with other RE ions (BTBO powders, BTBO:Nd³⁺ powders, and BTBO:Yb³⁺/Er³⁺ powders and ceramics).^{19–22} BTBO has a hexagonal structure

of the P6₃ space group ($Z = 2$). The primitive unit cell of the BTBO crystal contains 28 atoms, which generate 84 fundamental vibrations, from which 28 Raman active bands were detected in the relevant spectra.^{19,20} Most of the Raman active bands arise from stretching and bending vibrations of BO₃ and TeO₆ groups. In the low wavenumber range, the bands assigned to the lattice vibrations of Bi(Yb) or Te atoms and TeO₆ and BO₃ groups were detected.

As follows from the spectra (Figure 4), very weak peaks at 1375 and 927 cm^{−1}, a weak band at 833 cm^{−1}, and medium modes at 1297, 1283, 1263, and 1248 cm^{−1} correspond to the stretching vibrations of the BO₃ group. It should be noted that the peak at 833 cm^{−1} was observed only for the BTBO:Yb³⁺ (7.5 at %) sample, which is probably due to the random orientations of the microcrystals in the powder sample and the local not global homogeneity of the powder sample. One of the most intensive modes recorded at 691 cm^{−1} and a strong peak at 650 cm^{−1} are assigned to the stretching vibrations of the TeO₆ group. In the spectral range of 630–590 cm^{−1}, the bending vibrations of the BO₃ group were observed: in particular, a very weak mode at 620 cm^{−1}, a medium peak at 603 cm^{−1}, and a medium shoulder 594 cm^{−1}. In the spectral range 570–350 cm^{−1}, strong bands at 494 cm^{−1}, two weak modes at 565 and 537 cm^{−1}, and a medium mode/shoulder 410 with medium 401 cm^{−1} peaks, which can be assigned to the bending vibrations of the TeO₆ group, were detected. Finally, below 350 cm^{−1}, a very strong band at 125 cm^{−1}, strong modes at 248 and 154 cm^{−1}, medium intensity peaks at 306, 275, and 224 cm^{−1} with shoulders at 322 and 163 cm^{−1} and also weak peaks at 205, 187, and 177 cm^{−1} appeared,

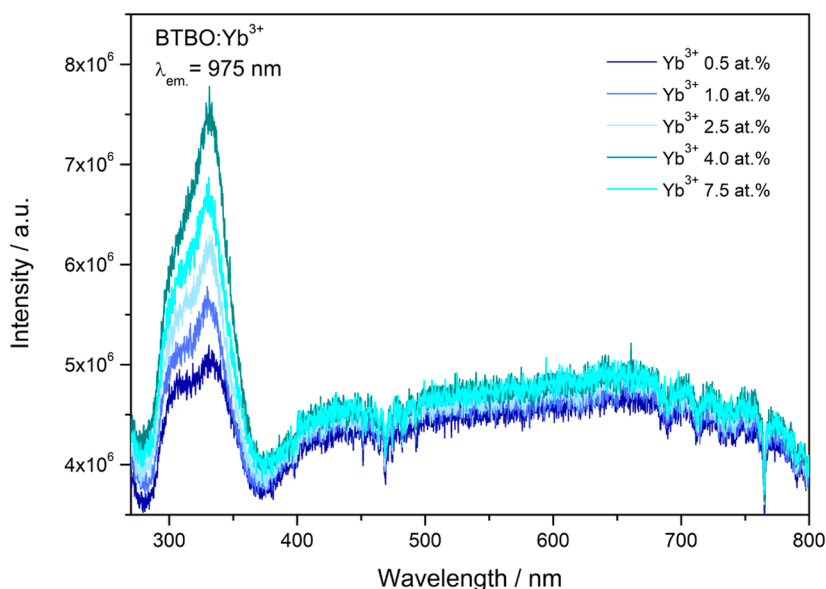


Figure 5. Excitation spectra of BTBO:Yb³⁺ powders recorded by monitoring the emission of the Yb³⁺ ions at 975 nm, detected at 300 K.

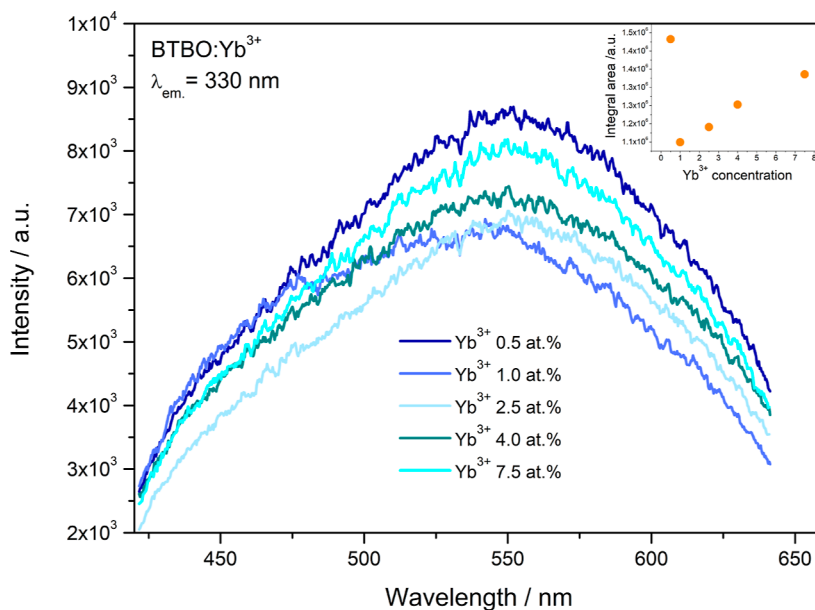


Figure 6. Emission spectra of BTBO:Yb³⁺ powders, assigned to Bi³⁺ ions emission, upon excitation at 330 nm recorded at 300 K and the integral intensity of the emission spectra of BTBO:Yb³⁺ powders determined in the 425–650 nm range (inset).

which correspond to the lattice vibrations of Bi(Yb) or Te atoms and TeO₆ and BO₃ groups (librational or translational motions). A detailed description of the Raman bands and their assignment to individual modes is presented in Table S1 (Supporting Information). Furthermore, spectral analysis of the Raman spectra of BTBO:Yb³⁺ powders and previously investigated pure BTBO powder²⁰ leads to a conclusion that the concentrations of doped Yb³⁺ ions does not affect the vibrational properties of the BTBO matrix. It means that the obtained results indicate a low phonon energy of the BTBO matrix, which is crucial in ET processes between the active Bi³⁺ and Yb³⁺ ions.

3.4. Luminescence Properties. The excitation and emission spectra measured for BTBO:Yb³⁺ powders are presented in Figures 5 to 7. The bands appearing in the spectra were assigned to the energy levels of Yb³⁺ active ions

according to Dieke's diagram.²⁹ In particular, the excitation spectra of BTBO:Yb³⁺ powders recorded in the spectral range 270–800 nm by monitoring the ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ ions are shown in Figure 5.

As follows from Figure 5, the strong and broad bands present in the excitation spectra of BTBO:Yb³⁺ powders in the range from 280 to 370 nm with the maximum at about 330 nm were detected for samples with all considered Yb³⁺ concentrations. Moreover, the intensity of the bands in the spectra depends on the Yb³⁺ concentration. The intensity of excitation bands increases gradually starting from 0.5 at %, but reaches a maximum for 4.0 at % concentration of Yb³⁺ ions in BTBO:Yb³⁺ powder, and for the sample with the highest concentration of Yb³⁺ ions 7.5 at %, the intensity of the excitation band is already weaker than that for 4.0 at %.

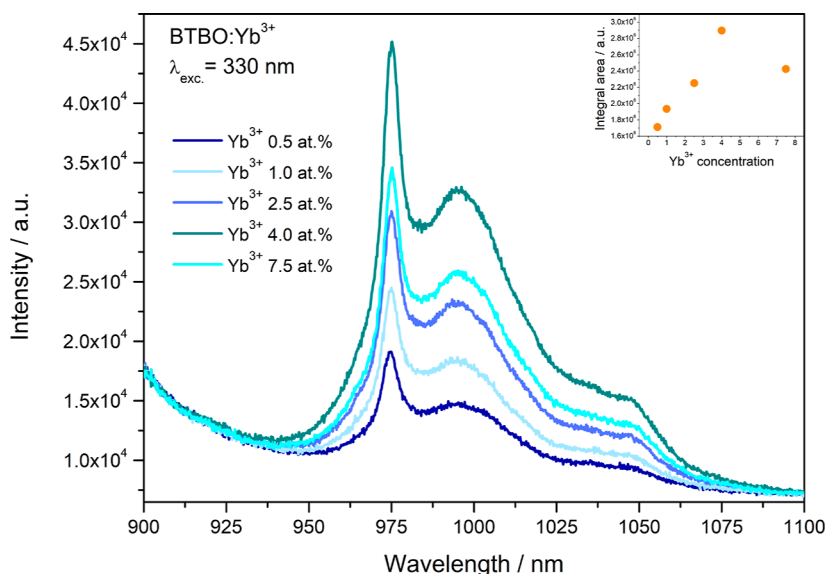


Figure 7. Emission spectra of BTBO:Yb³⁺ powders, assigned to Yb³⁺ ion emission, upon excitation at 330 nm recorded at 300 K and the integral area of the emission spectra of BTBO:Yb³⁺ samples determined in the 925–1075 nm range (inset).

The emission spectra of BTBO:Yb³⁺ powders excited in the UV spectral range by Bi³⁺ ions (the ¹S₀ → ³P₁ transition) were detected for Bi³⁺ ions emission (the ³P₀ → ¹S₀ transition) and Yb³⁺ ions emission (the ²F_{5/2} → ²F_{7/2} transition) in VIS and NIR spectral ranges, respectively, which are presented in Figures 6 to 7.

As shown in Figure 6, the broad emission bands with the maximum at about 550 nm, assigned to the ³P₀ → ¹S₀ transition of Bi³⁺ ions, were recorded for BTBO:Yb³⁺ powders with all concentrations of Yb³⁺ ions. The determined integral area of emission spectra of BTBO:Yb³⁺ samples, presented in the inset of Figure 6, is the highest for the sample with the lowest concentrations of Yb³⁺ ions (0.5 at %). For other samples, the integral area is significantly lower, but with increasing concentrations of Yb³⁺ ions from 1.0 to 7.5 at %, it gradually increases.

The emission spectra of BTBO:Yb³⁺ powders presented in Figure 7 show broad and intense bands in the range of 925–1075 nm with a maximum intensity at about 975 and 995 nm, which are related to the ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ ions. This suggests that Bi³⁺ ions present in the BTBO matrix can be used as a UV absorption sensitizer for Yb³⁺ ions in the considered systems. Interestingly, the highest intensity emission bands in NIR spectral range were detected in the spectra of BTBO:Yb³⁺ powders doped with Yb³⁺ ions in a concentration of 4.0 at %. For the highest concentration of Yb³⁺ ions (7.5 at %), we observed the higher intensity in comparison to that for other samples, except for the sample with a concentration of 4.0 at %. The observed effect is due to the luminescence concentration quenching (LCQ) resulting from the high concentration of Yb³⁺ ions in the BTBO:Yb³⁺ (7.5 at %) sample. The determined integral area of the emission spectra of BTBO:Yb³⁺ samples, presented as the inset in Figure 7, increases for the samples with Yb³⁺ ions concentration from 0.5 to 4.0 at % and then decreases for the sample with Yb³⁺ ions concentration 7.5 at %.

The luminescence lifetimes of BTBO:Yb³⁺ powders measured for the emission of Bi³⁺ and Yb³⁺ ions for the ³P₀ → ¹S₀ and ²F_{5/2} → ²F_{7/2} transitions, respectively, were used for analysis of the kinetics of the luminescence processes in

BTBO:Yb³⁺ systems. The luminescence decay time curves of BTBO:Yb³⁺ powders monitored for the abovementioned emissions at 550 and 975 nm upon the excitation at 330 nm are presented in Figure 8.

From the decay curves shown in Figure 8, the average lifetimes were calculated using the following formula

$$\langle \tau \rangle = \int_0^{\infty} \frac{I(t)}{I(0)} dt \quad (2)$$

where $\langle \tau \rangle$ is the average lifetime, $I(t)$ denotes the measured intensity of the photoluminescence decay curve as a function of time, and $I(0)$ is the initial intensity (at $t = 0$ s).³⁰ The luminescence decay times of the emissions of BTBO:Yb³⁺ powders at 550 and 975 nm determined by using formula 2 are presented in Table 4.

As follows from Table 4, the average lifetimes calculated from the experimental decay curves reveal the influence of the dopant concentration on the kinetics of the luminescence processes in the BTBO:Yb³⁺ systems. The short lifetimes of the emission of Bi³⁺ ions (³P₀ → ¹S₀ transitions) and relatively long lifetimes of the emission of Yb³⁺ ions (²F_{5/2} → ²F_{7/2} transitions) result from the ET mechanisms between Bi³⁺ and Yb³⁺ ions in the studied BTBO:Yb³⁺ systems. After excitation at 330 nm of BTBO:Yb³⁺ samples, some energy is transferred to the lower lying energy levels of Bi³⁺ ions, which relax in a very short time, showing the emission at 550 nm (Figure 6) and a significant part of energy is transferred to the Yb³⁺ ions, which relax for a long time with a relatively high intensity emission band at 975 nm (Figure 7). In particular, as it is also seen from Table 4, the lifetimes assigned to the ³P₀ → ¹S₀ transitions of Bi³⁺ ions decrease for BTBO:Yb³⁺ samples with increasing concentration of Yb³⁺ ions, which means that simultaneously Yb³⁺ ions accept part of the energy from the excited Bi³⁺ ions that can be observed as increasing lifetimes of the ²F_{5/2} → ²F_{7/2} transitions of Yb³⁺ ions with increasing concentration of Yb³⁺ ions in BTBO:Yb³⁺ samples. Moreover, the lifetimes of Yb³⁺ emission (²F_{5/2} → ²F_{7/2} transitions) increase from 248 to the maximum value 381 μs with respect to Yb³⁺ ions' concentration in the BTBO matrix, increasing from 0.5 to 4.0 at %, which corresponds to increasing intensity

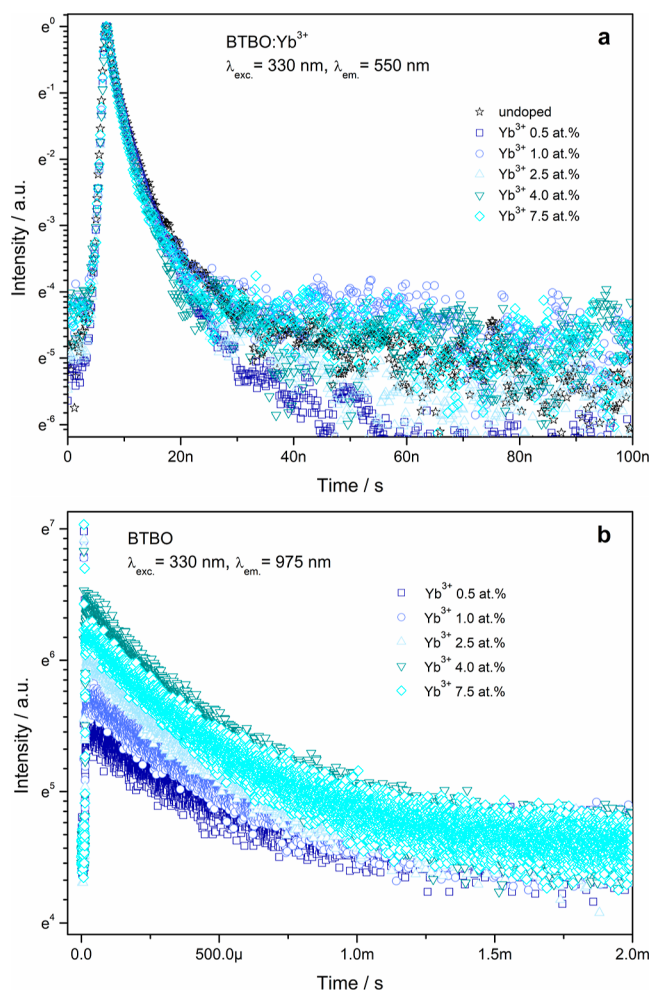


Figure 8. Luminescence decay time curves of BTBO:Yb³⁺ powders recorded at RT by monitoring the emission of (a) Bi³⁺ ions at 550 nm and (b) Yb³⁺ ions at 975 nm upon the excitation at 330 nm.

Table 4. Decay Times of the Emissions at 550 and 975 nm of BTBO:Yb³⁺ Powders

compounds	average decay lifetimes	
	$\langle\tau\rangle/\text{ns}$ $^3\text{P}_0 \rightarrow ^1\text{S}_0$ transitions	$\langle\tau\rangle/\mu\text{s}$ $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ transitions
BTBO	2.89	
BTBO:Yb ³⁺ (0.5 at %)	2.65	248
BTBO:Yb ³⁺ (1.0 at %)	2.66	276
BTBO:Yb ³⁺ (2.5 at %)	2.56	313
BTBO:Yb ³⁺ (4.0 at %)	2.50	381
BTBO:Yb ³⁺ (7.5 at %)	2.46	344

of this emission (Figure 7). For the BTBO:Yb³⁺ sample with the highest concentration of Yb³⁺ ions (7.5 at %) the emission lifetime is shorter (344 μs) and the corresponding intensity of emission band of Yb³⁺ ions is weaker (Figure 7) due to a weak Yb³⁺–Yb³⁺ interaction resulting in the LCQ effect. A possible mechanism of energy transfer from Bi³⁺ to Yb³⁺ active ions in BTBO:Yb³⁺ systems after UV excitation is illustrated schematically in Figure 9.

The energy level diagram for the BTBO:Yb³⁺ system was constructed on the basis of the excitation and emission spectra. After the absorption of UV energy (at 330 nm), Bi³⁺ ions are excited from the ¹S₀ ground to the ³P₁ excited state. A part of

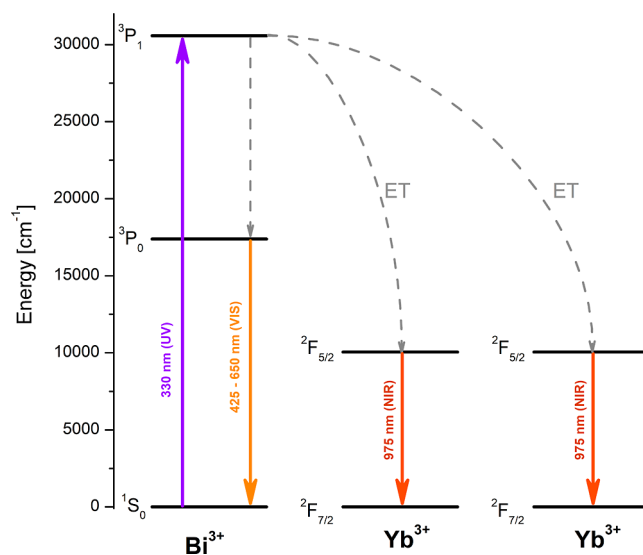


Figure 9. Schematic energy level diagram showing the possible ET from Bi³⁺ to Yb³⁺ ions upon the excitation at 330 nm.

the energy from the excited state of Bi³⁺ ions can relax to its ¹S₀ ground state by emitting photons in the VIS (wide bands in the 425–650 nm spectral range with maximum intensity at about 550 nm, presented in Figure 6) and the remaining energy from the ³P₁ excited state can be transferred to the nearest Bi³⁺ or Yb³⁺ ions. In particular, the energy of the excited Bi³⁺ ions can be transferred by the energy migration process to the unexcited Bi³⁺ ions. This process leads to the quenching of luminescence of Bi³⁺ ions and it is very possible for undoped and Yb³⁺-doped BTBO systems due to a short distance between the nearest Bi³⁺ ions in the BTBO matrix. Another possible mechanism is the ET process from the ³P₁ level of Bi³⁺ ions to the excited levels of Yb³⁺ ions. Since the ³P₁ level of Bi³⁺ ions is located at higher energy than the ²F_{5/2} level of Yb³⁺ ions, the ET process from excited Bi³⁺ to two Yb³⁺ ions can be realized to achieve the NIR emission of Yb³⁺ (at 975 nm). This corresponds to the observed high intensity emission of Yb³⁺ for the BTBO:Yb³⁺ samples presented in Figure 7.

The mentioned above luminescence lifetimes of BTBO:Yb³⁺ powders were used for the calculation of the energy transfer efficiency (ETE) determined by the η_{ET} coefficient and the total quantum efficiency (QE) determined by the η_{QE} coefficient of the ET process from Bi³⁺ to Yb³⁺ ions.^{15,31}

As mentioned above, the ETE and QE were calculated for the ET from Bi³⁺ to Yb³⁺ ions, where Bi³⁺ is a donor and Yb³⁺ is an acceptor of energy. The ETE can be obtained by dividing the integrated intensity of the experimentally measured luminescence decay curves of BTBO:Yb³⁺ samples containing donor and acceptor ions by the luminescence decay curves of the undoped BTBO containing donor ions. In particular, for calculations, only the lifetimes determined for the ³P₀ → ¹S₀ transitions of Bi³⁺ ions for undoped and Yb³⁺-doped BTBO samples were considered (Table 4).

The η_{ET} coefficients for the mentioned above ET were calculated from the following equation

$$\eta_{\text{ET}} = 1 - \frac{\langle\tau\rangle_{\text{Bi/Yb}}}{\langle\tau\rangle_{\text{Bi}}} \quad (3)$$

where $\langle\tau\rangle_{\text{Bi/Yb}}$ is the average lifetime of decay curves recorded for the powders containing donor (Bi³⁺) and acceptor (Yb³⁺)

ions, and $\langle\tau\rangle_{\text{Bi}}$ is the average lifetime of decay curves recorded for pure BTBO powder.

The corresponding η_{QE} coefficients were calculated using the following equation

$$\eta_{\text{QE}} = \eta_{\text{Bi}}(1 - \eta_{\text{ET}}) + 2\eta_{\text{Yb}}\eta_{\text{ET}} \quad (4)$$

where η_{Bi} and η_{Yb} stand for the luminescent QE of the donor (Bi^{3+} ions) and acceptor (Yb^{3+} ions), respectively, assuming that all the excited Bi^{3+} ions and the residual excited Yb^{3+} ions decay radiatively, i.e., $\eta_{\text{Bi}} = \eta_{\text{Yb}} = 1$.¹⁵ The complete set of coefficients determined for all investigated BTBO: Yb^{3+} samples is included in Table 5.

Table 5. Calculated Values of ET and Total QE Coefficients for ET from Bi^{3+} to Yb^{3+} of BTBO: Yb^{3+} Powders

compounds	$\eta_{\text{ET}}/\%$	$\eta_{\text{QE}}/\%$
BTBO: Yb^{3+} (0.5 at %)	8.5	108.5
BTBO: Yb^{3+} (1.0 at %)	8.0	108.0
BTBO: Yb^{3+} (2.5 at %)	11.5	111.5
BTBO: Yb^{3+} (4.0 at %)	13.5	113.5
BTBO: Yb^{3+} (7.5 at %)	15.0	115.0

As follows from Table 5 the values of ET and total QE coefficients for ET from Bi^{3+} to Yb^{3+} increase with increasing concentration of Yb^{3+} ions in BTBO: Yb^{3+} samples. The highest values of QE coefficients calculated to be $\eta_{\text{QE}} = 115.0\%$ were obtained for the BTBO: Yb^{3+} sample with the highest concentration of Yb^{3+} ions (7.5 at %). However, as already mentioned, the emission lifetime is shorter and the corresponding intensity of the emission band of Yb^{3+} ions is weaker for the BTBO: Yb^{3+} sample doped with 7.5 at % in comparison to that determined for the BTBO: Yb^{3+} sample doped with 4.0 at % concentration of Yb^{3+} ions due to the LCQ effect.

Some examples of the total QE calculated for Bi^{3+} to Yb^{3+} ions ET determined for other systems are given in Table 6.

Table 6. Total QE Calculated for Bi^{3+} to Yb^{3+} Ions ET in %

samples	η_{QE}
$\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (5%) ¹²	158.49
$\text{Gd}_2\text{O}_3:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (5%) ¹⁵	134.47
$\text{YNbO}_4:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (8%) ¹⁶	121.00
$\text{Lu}_2\text{GeO}_5:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (1%) ³²	111.00
$\text{Lu}_2\text{GeO}_5:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (3%) ³²	120.00
$\text{Lu}_2\text{GeO}_5:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (5%) ³²	132.00
$\text{Y}_2\text{O}_3:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (2%) ³³	113.80
$\text{Y}_2\text{O}_3:\text{Bi}^{3+}$ (1%)/ Yb^{3+} (5%) ³³	135.40
$\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}$ (5%) ²¹	122.65

As follows from Tables 5 and 6, the values of the total QE coefficient for ET from Bi^{3+} to Yb^{3+} of the investigated BTBO: Yb^{3+} (4 at %) system are comparable to the values obtained for other crystalline matrices doped with Bi^{3+} and Yb^{3+} ions at the corresponding concentration level, which suggests that BTBO: Yb^{3+} (4 at %) can be a good alternative as an efficient optical converter from UV to NIR.

4. CONCLUSIONS

Efficient Yb^{3+} emission of BTBO: Yb^{3+} microcrystalline powders in the NIR spectral range with a maximum at 975

nm was sensitized by Bi^{3+} ions at 330 nm. A series of BTBO: Yb^{3+} powders doped with different concentrations of Yb^{3+} ions (0.5, 1.0, 2.5, 4.0, and 7.5 at %) were prepared by the modified Pechini method. The hexagonal structure with the $P6_3$ space group of BTBO: Yb^{3+} powders was determined by XRD measurements. The morphology of BTBO: Yb^{3+} powders investigated using the SEM technique revealed the variety of grain sizes: from about 5 to 30 μm , while the size of smaller ones ranges between one and a few microns. The results of the μ -Raman investigation of BTBO: Yb^{3+} powders indicate a low phonon energy of the BTBO matrix, which allow for effective phonon-assisted energy transfer between Bi^{3+} and Yb^{3+} ions. The analysis of results of luminescence measurements allows us to conclude the ET mechanism from the excited Bi^{3+} to Yb^{3+} ions. Upon the excitation of BTBO: Yb^{3+} systems by Bi^{3+} ions (at 330 nm), the lowering intensity of Bi^{3+} ions emission in the VIS and increasing intensity of Yb^{3+} ions emission in NIR for increasing concentration of Yb^{3+} ions from 0.5 to 4.0 at % in BTBO: Yb^{3+} systems was observed. Moreover, the lifetimes of Yb^{3+} emission in NIR increase from 248 to the maximum value 381 μs with increasing from 0.5 to 4.0 at % concentration of Yb^{3+} ions in the BTBO matrix. For the BTBO: Yb^{3+} sample with the highest concentration of Yb^{3+} ions (7.5 at %), the emission lifetime is shorter (344 μs), and the corresponding intensity of the emission band of Yb^{3+} ions is weaker due to the LCQ effect. The ETE and the upper limit values of the total QE coefficients were obtained for the BTBO: Yb^{3+} sample doped with the optimal concentration of Yb^{3+} ions of 4.0 at % as $\eta_{\text{ET}} = 13.5\%$ and $\eta_{\text{QE}} = 113.5\%$, respectively. The efficient conversion of energy from the UV to NIR range is desired in many advanced applications in various fields. In the field of optoelectronics, this phenomenon can be employed to produce more efficient LEDs and improved photodetectors that cover a wider range of wavelengths. In solar energy harvesting, it is crucial to increase the efficiency of solar panels by converting a wider spectrum of sunlight into electrical energy since traditional solar cells mainly absorb visible light. As a result, the investigated BTBO: Yb^{3+} powders with effective energy conversion from the UV to NIR spectral range can be potentially used as optical converters in a new generation of silicon-based solar cells.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcc.4c04134>.

Wavenumbers and assignment of the Raman bands of BTBO: Yb^{3+} powders (PDF)

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Author Contributions

T.Z.: conceptualization, investigations, calculations, interpretation of results, and writing, P.G.: investigation of luminescence properties, M.N.: SEM measurements, B.S.: XRD measurements, M.C.: synthesis of powders and XRD calculations, and D.K.: conceptualization, interpretation of results, writing, and draft preparation.

Notes

The authors declare no competing financial interest.

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1. D. Kasprowicz, T. Zhezhera, A. Łapiński, **M. Chrunik**, A. Majchrowski, A.V. Kityk, Ya. Shchur, **“Lattice dynamics of Bi_3TeBO_9 microcrystals: μ -Raman/IR spectroscopic investigation and ab initio analysis”**, Journal of Alloys and Compounds, 782 (2019) 488–495.
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Oświadczam, że w poniższej publikacji: D. Kasprowicz, T. Zhezhera, A. Łapiński, M. Chrunik, A. Majchrowski, A.V. Kityk, Ya. Shchur, "*Lattice dynamics of Bi₃TeBO₉ microcrystals: μ -Raman/IR spectroscopic investigation and ab initio analysis*", Journal of Alloys and Compounds, 782 (2019) 488–495, wchodzącej w skład rozprawy doktorskiej mgr. inż. Tarasa Zhezhery z Wydziału Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej, moim udziałem było zarejestrowanie widm w zakresie bliskiej i średniej podczerwieni mikrokrystalicznych proszków Bi₃TeBO₉ oraz współudział w opracowaniu wyników pomiarów.

prof. dr hab. Andrzej Łapiński

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Oświadczenie

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1. D. Kasprowicz, T. Zhezhera, A. Łapiński, M. Chrunik, **A. Majchrowski**, A.V. Kityk, Ya. Shchur, **"Lattice dynamics of Bi_3TeBO_9 microcrystals: μ -Raman/IR spectroscopic investigation and ab initio analysis"**, Journal of Alloys and Compounds, 782 (2019) 488–495.
2. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, **A. Majchrowski**, K. M. Kosyl and D. Kasprowicz, **"Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors"**, Journal of Materials Science, 57 (2022) 185–203.
3. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, **A. Majchrowski** and D. Kasprowicz, **"Enhanced near-infrared emission of Er^{3+} as a synergistic effect of energy transfers in $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$ phosphors"**, Journal of Luminescence, 258 (2023) 119774.

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Prof., dr hab. Andriy Kityk

Częstochowa, 05.06.2025

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Statement on the contribution

With regard to the PhD thesis procedure of M.Sc.Eng. Taras Zhezhera from the Faculty of Materials Engineering and Technical Physics, Poznan University of Technology, I would like to state that my contribution to the publication D. Kasprowicz, T. Zhezhera, A. Łapiński, M. Chrunik, A. Majchrowski, **A.V. Kityk**, Ya. Shchur, **“Lattice dynamics of Bi₃TeBO₉ microcrystals: μ -Raman/IR spectroscopic investigation and *ab initio* analysis”**, Journal of Alloys and Compounds, 782 (2019) 488–495 was related to the *ab initio* calculation of phonon modes.

Andriy Kityk

D.Sc., Senior Research Fellow Yaroslav Shchur

Lviv, 3 June 2025

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Statement on the contribution

With regard to the PhD thesis procedure of M.Sc. Eng. Taras Zhezhera from the Faculty of Materials Engineering and Technical Physics, Poznan University of Technology. I would like to state that my contribution to the publication D. Kasprowicz, T. Zhezhera, A. Łapiński, M. Chrunik, A. Majchrowski, A.V. Kityk, **Ya. Shchur**, “**Lattice dynamics of Bi₃TeBO₉ microcrystals: μ -Raman/IR spectroscopic investigation and *ab initio* analysis**”, Journal of Alloys and Compounds, 782 (2019) 488–495 was related to the *ab initio* calculation of phonon modes, the analysis of the aforementioned calculations and experimental data, and the editing of the manuscript.



D.Sc. Yaroslav Shchur



Dr hab. inż. Paweł Głuchowski

Wrocław, 13.06.2025

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Oświadczenie

Oświadczam, że w poniższych trzech publikacjach [1-3], wchodzących w skład rozprawy doktorskiej mgr. inż. Tarasa Zhezhery z Wydziału Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej, współuczestniczyłem w wykonaniu następujących pomiarów: widma odbicia [1-2], widma wzbudzenia [1-2], widma emisji [1-3] oraz czasy zaniku luminescencji [1-3] mikrokrystalicznych proszków $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9\text{:Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$ oraz ceramiek $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$. Ponadto, w publikacji [4] wykonałem pomiary widm wzbudzenia, emisji oraz czasów zaniku luminescencji mikrokrystalicznych proszków $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}$.

1. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, A. Majchrowski, K. M. Kosyl and D. Kasprowicz, "Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors", Journal of Materials Science, 57 (2022) 185–203.
2. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, A. Majchrowski and D. Kasprowicz, "Enhanced near-infrared emission of Er^{3+} as a synergistic effect of energy transfers in $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$ phosphors", Journal of Luminescence, 258 (2023) 119774.
3. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, A. Miklaszewski and D. Kasprowicz, "Pressure modified upconversion luminescence of Yb^{3+} and Er^{3+} -doped Bi_3TeBO_9 ceramics", Journal of Luminescence, 268 (2024) 120401.
4. T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, B. Szczęśniak and D. Kasprowicz, "Enhancement of Yb^{3+} emission in Bi_3TeBO_9 through efficient energy transfer from Bi^{3+} ions", Journal of Physical Chemistry C, 128(34) (2024) 14357–14367.

Paweł Głuchowski

Dr hab. inż. Paweł Głuchowski

Dr inż. Katarzyna Kosyl

Warszawa, 30.05.2025

Instytut Fizyki

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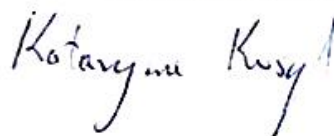
Aleja Lotników 32/46, 02-668 Warszawa

Oświadczenie

Oświadczam, że w poniższej publikacji, wchodzącej w skład rozprawy doktorskiej mgr. inż. Tarasa Zhezhera z Wydziału Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej, współuczestniczyłam w wykonaniu pomiarów XRD mikroproszków krystalicznych $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$.

T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, A. Majchrowski, K. M. Kosyl and D. Kasprowicz, "Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors", Journal of Materials Science, 57 (2022) 185–203.

Dr inż. Katarzyna Kosyl



Oświadczenie

Oświadczam, że w poniższych czterech publikacjach, wchodzących w skład rozprawy doktorskiej mgr. inż. Tarasa Zhezhery z Wydziału Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej, moim udziałem było wykonanie pomiarów technikami SEM [1-4] oraz EDX [1,3-4] mikroproszków krystalicznych $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$, $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$, $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}$, $\text{Bi}_3\text{TeBO}_9\text{:Er}^{3+}$ oraz ceramiek $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$.

1. T. Zhezhera, P. Gluchowski, **M. Nowicki**, M. Chrunik, A. Majchrowski, K. M. Kosyl and D. Kasprowicz, **"Efficient near-infrared quantum cutting by cooperative energy transfer in $\text{Bi}_3\text{TeBO}_9\text{:Nd}^{3+}$ phosphors"**, Journal of Materials Science, 57 (2022) 185–203.
2. T. Zhezhera, P. Gluchowski, **M. Nowicki**, M. Chrunik, A. Majchrowski and D. Kasprowicz, **"Enhanced near-infrared emission of Er^{3+} as a synergistic effect of energy transfers in $\text{Bi}_3\text{TeBO}_9\text{:Yb}^{3+}/\text{Er}^{3+}$ phosphors"**, Journal of Luminescence, 258 (2023) 119774.
3. T. Zhezhera, P. Gluchowski, **M. Nowicki**, M. Chrunik, A. Miklaszewski and D. Kasprowicz, **"Pressure modified upconversion luminescence of Yb^{3+} and Er^{3+} -doped Bi_3TeBO_9 ceramics"**, Journal of Luminescence, 268 (2024) 120401.
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Dr inż. Marek Nowicki



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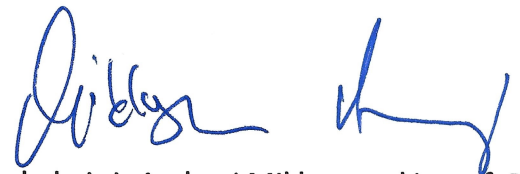
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Oświadczenie

Oświadczam, że w poniższej publikacji, wchodzącej w skład rozprawy doktorskiej mgr. inż. Tarasa Zhezhera z Wydziału Inżynierii Materiałowej i Fizyki Technicznej Politechniki Poznańskiej, moim udziałem było wykonanie pomiarów XDR ceramiek $\text{Bi}_3\text{TeBO}_9:\text{Yb}^{3+}/\text{Er}^{3+}$.

T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, **A. Miklaszewski** and D. Kasprovicz, "Pressure modified upconversion luminescence of Yb^{3+} and Er^{3+} -doped Bi_3TeBO_9 ceramics", Journal of Luminescence, 268 (2024) 120401.



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T. Zhezhera, P. Gluchowski, M. Nowicki, M. Chrunik, **B. Szczęśniak** and D. Kasprowicz, "Enhancement of Yb^{3+} emission in Bi_3TeBO_9 through efficient energy transfer from Bi^{3+} ions", Journal of Physical Chemistry C, 128(34) (2024) 14357–14367.



Dr inż. Barbara Szczęśniak