

Luminescent properties of Eu^{3+} doped layered perovskite-like polycrystalline powders of the $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ ($x = 0-2$) titanate compounds

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The photoluminescent properties of concentration set of barium and lanthanum titanium compounds doped with europium ions, $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, where $x = 0-2$, were investigated. It was found that the luminescence of mentioned materials is caused by ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) radiation transitions in luminescence centers formed by Eu^{3+} ions. Two types of luminescence centers which differ by symmetry of neighborhood of Eu^{3+} ions were found in luminescent emission. It was shown that luminescent characteristics of Eu^{3+} ions are in close relation with their content in $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ compounds that can be caused by both changing their crystal structure and phase composition when the ratio of La^{3+} and Eu^{3+} ions is changed.

Исследованы фотолюминесцентные характеристики концентрационной серии легированных ионами европия титанатов бария и лантана, $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, где $x = 0-2$. Установлено, что люминесценция указанных материалов вызвана излучательными переходами ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ и 4) в центрах люминесценции, сформированных ионами Eu^{3+} . По данным спектров излучения найдено два типа центров люминесценции, которые отличаются симметрией ближайшего окружения ионов Eu^{3+} . Показано, что характеристики ионов Eu^{3+} тесно связаны с их содержанием в соединениях $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, причиной этого может быть как изменение структуры кристалла, так и изменение фазового состава материала с изменением соотношения содержания ионов La^{3+} и Eu^{3+} .

1. Introduction

Oxide compounds which contain rare earth (RE) ions are attractive materials for multi-color luminophores which can be used in plasma and cathodoluminescent displays and detectors of ionizing radiation as well [1, 2]. Last time some efforts were undertaken to design new phosphors on the base of doped

with praseodymium ions Ca/Ba/SrTiO_3 perovskites, e.g. Such type phosphors could be used in combined LEDs. But, luminescence intensity (PL) of these phosphors is very low and researchers aimed to enhance it have to introduce some additional impurities, Al or Ga ions, e.g., into mentioned matrix [3-7].

$\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ belongs to Dion-Jacobson family of layered perovskite-like titanates

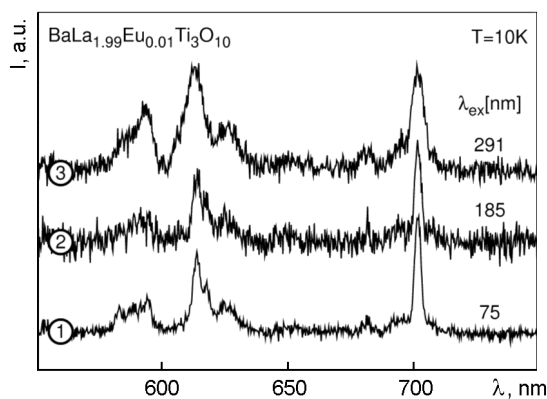


Fig. 1. Luminescence spectra of the $\text{BaLa}_{1.99}\text{Eu}_{0.01}\text{Ti}_3\text{O}_{10}$ crystal at VUV and UV excitation — $\lambda_{ex} = 75$ (1), 185 (2) and 291 (3) nm; $T = 10$ K.

of common formulae $\text{Ba}[\text{Ln}_{n-1}\text{Ti}_n\text{O}_{3n+7}]$ where Ln is RE element from La to Sm. The some part of the La atoms in $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ can be easily replaced by another RE atoms [8, 9]. Surely, active in visible photoluminescence RE ions can be among them. We synthesized and investigated here the PL properties of the $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, compounds, where $x = 0-2$.

2. Experimental

Synthesis of $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, microcrystalline powders was made using thermo treatment ($T = 1520$ K, $t = 2$ h.) of simultaneously precipitated barium, titanium, and rare earth hydroxycarbonates. Doped with 0.01 mas. % of Eu^{3+} BaTiO_3 was synthesized by the similar way.

PL was excited by radiation from the N_2 ($\lambda_{ex} = 337.1$ nm) lasers, powerful xenon lamp DKsL-1000 and PL was registered by using MDR-2 and DFS-12 diffraction spectrometers which cover wide spectral region from 225 to 1200 nm. Some of luminescence spectra were investigated using exciting synchrotron radiation from the 50–330 nm region. Experiments with synchrotron radiation were carried on at SUPERLUMI station at HASYLAB (Hamburg, Germany).

3. Results and discussion

The $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ compounds doped with europium manifest orange-red PL covering the range 570–750 nm of the emission spectra and this luminescence is typical for emission of three charged Eu^{3+} ions. The PL spectra of the samples consist of four well-distinguished groups of lines. The least intensive of all group lies in the 640–670 nm region, the other ones lie in the ranges 570–605, 605–640,

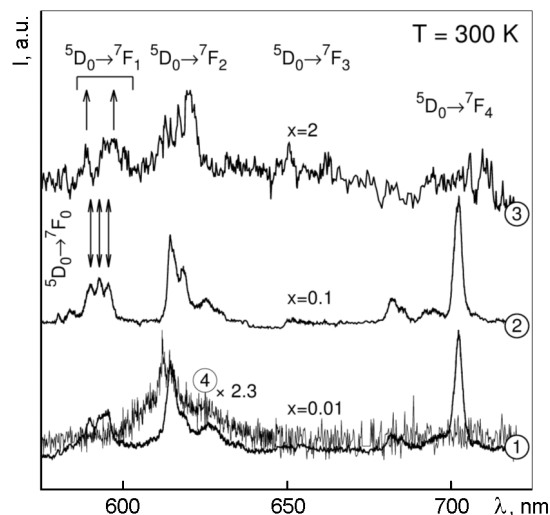


Fig. 2. The PL spectra of the $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ at various concentration of Eu^{3+} ions ($x = 0.01$ (1), 0.1 (2), and 2.0 (3) and PL spectra of the BaTiO_3 compound (4); $T = 300$ K; $\lambda_{ex} = 337.1$ nm.

and 670–750 nm. The shape of the spectra does not depend considerably on the excitation wave length (λ_{ex}) either it lies in the region of lattice absorption, $\lambda_{ex} = 75$, 185, and 291 nm, (Fig. 1) or it corresponds to inner transitions in Eu^{3+} ions, $\lambda_{ex} = 337.1$ nm, (Fig. 2 and Fig. 3). The intensity of the doped with Eu^{3+} ions BaTiO_3 luminescence is lower by factor 2.3 in comparison with the PL intensity of the $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ which contains the same amount of Eu^{3+} (see Fig. 2, curves 1 and 4).

Observed emission is associated with radiation transitions from excited 5D_0 level on 7F_J ($J = 0, 1, 2, 3, 4$) manifold levels of the ground state of the Eu^{3+} ion [2–4]. There were not any radical changes in luminescence characteristics with temperature decreasing from 300 K up to 4.2 K (Fig. 3). Low intensity line caused by ${}^5D_0 \rightarrow {}^7F_0$ transition is observed near 580 nm; the lines associated with ${}^5D_0 \rightarrow {}^7F_1$ transitions compose the group located in diapason 585–605 nm; the lines of the ${}^5D_0 \rightarrow {}^7F_2$ transitions form the spectral group in diapason 605–640 nm; the lines of ${}^5D_0 \rightarrow {}^7F_3$ transitions can be found in the region 640–670 nm, and ${}^5D_0 \rightarrow {}^7F_4$ transitions determine spectral details in the region 670–750 nm. Low temperature PL spectra of non-concentrated compounds, $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, $x = 0.01-0.5$, manifest up to 5 lines of emission in the diapason of the ${}^5D_0 \rightarrow {}^7F_1$ transitions (marked with arrows in Figures). We can find up to 9 lines in

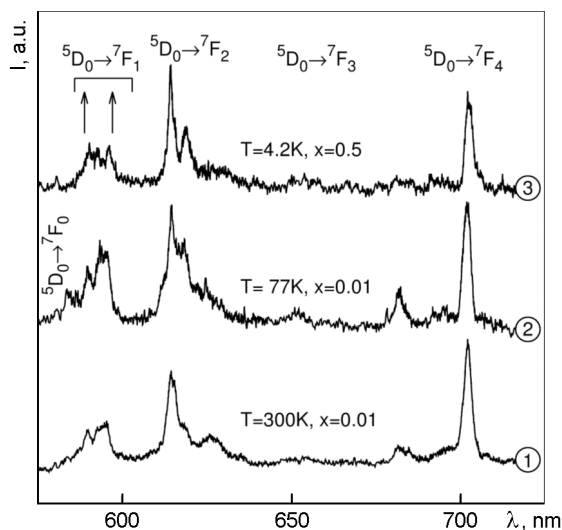


Fig. 3. The PL spectra of the $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ at various temperatures: $T = 300$ (1), 77 (2) and 4.2 K (3); $x = 0.01$ (1, 2), and 0.5 (3); $\lambda_{ex} = 337.1$ nm.

the region of ${}^5D_0 \rightarrow {}^7F_2$ transitions. Eight lines can be seen in the region of ${}^5D_0 \rightarrow {}^7F_4$ transition. It is well known that it has to be the most 1, 3, 5, 7 and 9 lines in the regions of ${}^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0, 1, 2, 3$ and 4), respectively. Thus, the number of experimentally observed lines exceeds indicated maximal theoretical value in the limits of each spectral diapason. So, we have to assume that more than one type of the luminescence centers (LC) based on the Eu^{3+} ions exist. If regard that only three intensive lines and two lower intensity lines are observed in the region of the ${}^5D_0 \rightarrow {}^7F_1$ transitions and there are 4–5 intensive lines and another ones are measured as only low intensity peaks on the background of the noted intensive lines in the region of the ${}^5D_0 \rightarrow {}^7F_2$ transitions we have to conclude that only two types of Eu^{3+} LC are formed in investigated compounds. Moreover, one of them has the lowest symmetry (three lines in the spectra of ${}^5D_0 \rightarrow {}^7F_1$ transitions) and other one has higher symmetry that keeps some partial degeneracy of electronic states.

Some opportunities to characterize the peculiarities of these two types of LC arise from analysis of redistribution of the intensity of emission caused by various transitions and the total intensity of the PL too. Total integral intensity of the Eu^{3+} ions PL (550–750 nm) and integral intensity of the PL in the spectral regions corresponding to

${}^5D_0 \rightarrow {}^7F_1$ (I_1 — region from 585 to 605 nm) and ${}^5D_0 \rightarrow {}^7F_2$ (I_2 — region from 605 to 640 nm) transitions were evaluated.

Significant change of the total integral spectral intensity of PL is the most noticeable manifestation of the Eu^{3+} ions concentration changing. The total integral PL intensity increases by 3 times if Eu^{3+} content increases from $x = 0.01$ to $x = 0.5$. If future concentration increasing occurs by 4 times from $x = 0.5$ to $x = 2.0$, the following PL intensity decrease by factor of 16 takes place. Samples where $x = 0.5$ are characterized with the most intensity of PL and the line with position (λ_m) near 703 nm has the most peak intensity for non-concentrated samples, $x = 0.01$ – 0.5 (Fig. 1). The line at λ_m near 615 nm is the second at intensity order. The changes of the peak intensity of various lines are not proportional to the change of the integral PL intensity, therefore the ratio of the intensity of the main lines changes too. Thus, the ratio $I(703)/I(615)$ decreases from value 1.32 to value 0.93 in the interval of concentration enhancement of emission intensity (from $x = 0.01$ to $x = 0.5$). This ratio falls down to value 0.3 when x varies from 0.5 up to 2.0. As result, line at 618 nm becomes the most intensive in the spectra of $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ compound (Fig. 2).

It is common knowledge that ${}^5D_0 \rightarrow {}^7F_{0,1}$ transition is directed by selection rules for intermediate magnet-dipole coupling $\Delta J = 0, \pm 1$. The ${}^5D_0 \rightarrow {}^7F_{2,4,6}$ are allowed electro-dipole transitions [1, 2]. The ${}^5D_0 \rightarrow {}^7F_1$ transition is practically insensitive for changing of Eu^{3+} ions surround while the ${}^5D_0 \rightarrow {}^7F_2$ transition called as "supersensitive" as its intensity is very sensitive to any changes in neighborhood surround of Eu^{3+} ions. Therefore this circumstance is used for characterization of Eu^{3+} interaction with neighbors. We analyzed the ratio I_2/I_1 and have found that its value decreases slowly when x increases from 0.01 to 0.5. Then, the value of I_2/I_1 increases rapidly after $x = 0.5$ and it reaches the value of 2.7 for $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ compound. As result, the group of lines of the ${}^5D_0 \rightarrow {}^7F_2$ transition becomes the most intensive in the spectra of this crystal (Fig. 2, curve 3). So, the behavior of I_2/I_1 ratio is a "mirror" reflection of behavior of total integral intensity of the PL.

Summarizing, we can conclude that manifestation of two type of LC, behavior of total integral intensity of the PL and dependence of the I_2/I_1 value on the Eu^{3+}

ions concentration are related each other and they caused by formation of two types of LC and competition of their contribution into luminescence processes takes place. Only ${}^5D_0 \rightarrow {}^7F_1$ transition is allowed when Eu^{3+} ion is placed in position with high symmetry and inversion center. When the symmetry of neighborhood is lower and covalence of Eu^{3+} ion bonding with O^{2-} ligandes becomes stronger an intensity of the ${}^5D_0 \rightarrow {}^7F_2$ transition has to increase. Mentioned above is agreed with described above experimental observations. So, we conclude that emission of the high symmetry LC (first type — LC I) is dominant in the spectra of non-concentrated compounds. The relative quantity of the low symmetry LC (second type — LC II) increases when the content of Eu^{3+} ions is higher than $x = 0.5$ that causes redistribution of the intensity of the ${}^5D_0 \rightarrow {}^7F_J$ transitions and among the lines of each group too. The concentration quenching also takes place but we are not able to separate its role for LC I and LC II centers.

Emission lines are widening with the Eu^{3+} content increasing and their widths rich maxima for the most concentrated compound $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$. This fact is the better revealed if consider the behavior of the total halfwidth of the lines caused by ${}^5D_0 \rightarrow {}^7F_2$ transition (Fig. 2). The value of this halfwidth is changed from 98 cm^{-1} ($\text{BaLa}_{1.99}\text{Eu}_{0.01}\text{Ti}_3\text{O}_{10}$ compound, where $x = 0.01$, Fig. 2, curve 1) up to 302 cm^{-1} (for $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ compound, where $x = 2.0$, Fig. 2, curve 3). Aimed to clarify this behavior we investigated another set of samples, namely $\text{BaLa}_{2-x}\text{Gd}_x\text{Ti}_3\text{O}_{10}$ ($x \leq 0.01$) compounds and $\text{BaLa}_{1.99}\text{Gd}_{0.01}\text{Ti}_3\text{O}_{10}$ among them, with very low Eu^{3+} concentration (≤ 0.001). These samples show larger value of I_2/I_1 ratio (up to 4.7) in comparison with one for $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ ($I_2/I_1 = 2.7$). Besides, the spectra of mentioned Gd-compounds are widened similar to PL spectra of the most concentrated, $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$, compound (Fig. 2). It means that neighborhood surround of the majority of Eu^{3+} ions in $\text{BaLa}_{1.99}\text{Gd}_{0.01}\text{Ti}_3\text{O}_{10}$ are similar to one in $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ crystal.

The reason for this similarity can be the next. The spectral components diffuseness shows that rising of Eu^{3+} ions content ($x = 0.5$ – 2.0) as well as incorporation of Gd^{3+} ions into lattice lead to accumulation of Eu^{3+} , or Gd^{3+} , ions in positions which differ from La ions positions in $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ compound that follow destroying layered struc-

ture of its crystal lattice and other crystal phases can be formed as result. It is possible also that crystal structure of high concentrated $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ samples or $\text{BaLa}_{2-x}\text{Gd}_x\text{Ti}_3\text{O}_{10}$ compounds is closer to the structures of crystalline solid solutions.

Obtained results correspond to data about structure of investigated compounds [8, 9]. The $\text{BaLa}_2\text{Ti}_3\text{O}_{10}$ crystal structure belongs to C_{mcm} space group (centre of inverse is element of this group) and formed by two-dimensional perovskite-like blocks (deformed TiO_6 octahedrons connected by vertices only) which interlaced by one layered blocks of Ba cations. This crystal arrangement determines existence of two types of La ions each on them is located in deformed cubic-octahedral coordination. This fact allows two ways of Eu^{3+} or Gd^{3+} substitution for La ions. Besides, there is a possibility to substitute for Ba ions. Some structural disordering of Ba^{3+} and La^{3+} between perovskite-like and Ba-blocks was found recently [9].

We have also established using X-ray scattering that $\text{BaLa}_{2-x}\text{Ln}_x\text{Ti}_3\text{O}_{10}$ ($\text{Ln} = \text{La-Sm}$) compositions form continuous sets of solid solutions if $\text{Ln} = \text{Pr-Sm}$ and they form limited sets of solid solutions if $\text{Ln} = \text{Eu-Lu}$. For instance, the $\text{BaEu}_2\text{Ti}_3\text{O}_{10}$ ($x = 2$) sample from $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ set, has to comprise of perovskite-type crystal phase (based on BaTiO_3) and pyrochlore structure (based on $\text{Eu}_2\text{Ti}_2\text{O}_7$) while single phase samples of $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, with layered structure are formed only for $x \leq 1.5$ [9].

4. Conclusions

For the first time, the main luminescent characteristics of the $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ compounds (x varies from 0 to 2) were investigated. It was found that the luminescence of mentioned materials is caused by radiation transitions in luminescence centers formed by Eu^{3+} ions. The sets of lines observed in the regions 578–582, 585–605, 605–640 and 670–750 nm were related with ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) manifold transitions, respectively. Two types of luminescence centers which different symmetry of Eu^{3+} ions neighborhood were found. Concentration quenching of Eu^{3+} ions luminescence takes place and luminescence intensity is the most if $x = 0.5$. Characteristics of Eu^{3+} ions luminescence are in close relation with composition of $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ compound, that can be caused by both changing their crystal structure and formation of

new crystal phases when the content of Eu^{3+} ions rises.

Orange-red luminescence of $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, perovskite-like compounds is effectively excited by the light of VUV diapason and the intensity of PL is about 2 times higher than the luminescence of the started BaTiO_3 perovskite doped with Eu^{3+} . Obtained data allow us to characterize the investigated materials as luminophores capable to be used in plasma displays.

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Люмінесцентні властивості полікристалічних порошків шаруватих перовскітоподібних титанатних сполук $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$ ($x = 0-2$), легованих іонами Eu^{3+}

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Досліджено фотолюмінесцентні властивості концентраційної серії легованих іонами Європію титанатів барію і лантану, $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, де $x = 0-2$. Показано, що люмінесценція цих матеріалів викликано радіаційними переходами ${}^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ та 4) у центрах люмінесценції сформованих іонами Eu^{3+} . За даними спектрів випромінювання знайдено два типи центрів люмінесценції, які відрізняються симетрією найближчого оточення іонів Eu^{3+} . З'ясовано, що характеристики люмінесценції іонів Eu^{3+} тісно пов'язані із їх вмістом у сполуках $\text{BaLa}_{2-x}\text{Eu}_x\text{Ti}_3\text{O}_{10}$, причиною цього може бути як зміна структури кристала, так і зміна фазового складу матеріалу при зміні співвідношення вмісту іонів La^{3+} та Eu^{3+} .