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LUMINESCENCE PROPERTIES OF Bi^{3+}-DOPED $Sr_3B_2O_6$[**]

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The purpose of this study was to investigate the photoluminescence properties of Bi^{3+}-activated $Sr_3B_2O_6$. Pure $Sr_3B_2O_6$ and Bi^{3+}-doped $Sr_3B_2O_6$ were synthesized by a solution combustion method. The phase and photoluminescence analyses of the borates that were synthesized were determined by using X-ray diffraction and a spectrofluorometer respectively at room temperature. It was observed that the synthesized Bi^{3+}-doped $Sr_3B_2O_6$ emitted blue light (441 nm) upon excitation with 366 nm. Finally, the Stokes shift of $Sr_3B_2O_6$:Bi^{3+} was calculated and found to be 4646 cm^{-1}.

Keywords: *luminescence, X-ray diffraction, inorganic borate, Bi^{3+} ion.*

ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА БОРАТА $Sr_3B_2O_6$, ЛЕГИРОВАННОГО ИОНАМИ Bi^{3+}

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Изучены фотолюминесцентные свойства Bi^{3+}-активированного $Sr_3B_2O_6$. Чистый $Sr_3B_2O_6$ и $Sr_3B_2O_6$, легированный Bi^{3+}, синтезированы методом сжигания раствора. Фазовый и фотолюминесцентный анализ синтезированных боратов проведен с использованием рентгеновской дифракции и спектрофлуорометра при комнатной температуре. Отмечено, что синтезированный $Sr_3B_2O_6$, легированный Bi^{3+}, излучает синий свет (441 нм) при возбуждении 366 нм. Рассчитанный стоксов сдвиг для $Sr_3B_2O_6$:Bi^{3+} составляет 4646 $см^{-1}$.

Ключевые слова: *люминесценция, дифракция рентгеновских лучей, неорганический борат, ион Bi^{3+}.*

Introduction. The bismuth ion (Bi^{3+}) is a heavy metal with a $6s^2$ electronic configuration. When this ion is added in small amounts to a crystal structure, it gives a luminous property. For this reason, examining the optical properties of Bi-activated inorganic materials has attracted the attention of several scientists [1, 2]. Materials that contain boron have interesting physical and chemical properties. Therefore, alkaline earth and alkaline metal borates have long been the focus of research owing to the structural diversity of the boron–oxygen bond [3]. Strontium orthoborate, formulated with $Sr_3B_2O_6$, is an example of an alkaline–earth metal borate compound, and it was first determined and reported by Richter and Muller [4]. Also, it has been synthesized using various preparation techniques, including the solid-state reaction [5], the sol gel method [6], and the solution combustion method (SCM) [7, 8]. It is known that strontium orthoborate formulated with $Sr_3B_2O_6$ is very suitable as a host in luminescence studies. Also, the luminescence properties of $Sr_3B_2O_6$ activated with Dy^{3+}, Tb^{3+}, Sm^{3+}, Ce^{3+}, and Eu^{2+} have been studied in detail [5–10].

This paper addresses the preparation of pure and Bi^{3+}-activated $Sr_3B_2O_6$ materials by the solution combustion method. The synthesized strontium orthoborates were characterized by using the XRD powder, and

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the photoluminescence (PL) property of Bi^{3+}-activated strontium orthoborate was investigated in detail at room temperature.

Experimental. Pure and Bi^{3+}-activated $Sr_3B_2O_6$ were synthesized by the SCM. The starting materials were $Sr(NO_3)_2$ (Sigma-Aldrich, ≥99%), H_3BO_3 (Merck, ≥99.8%), $Bi(NO_3)_3 \cdot 5H_2O$ (Sigma-Aldrich, ≥99.99%) and $CO(NH_2)_2$ (Merck, ≥99%). The stoichiometric amounts of $Sr(NO_3)_2$, H_3BO_3, $CO(NH_2)_2$, and activator ($Bi(NO_3)_3 \cdot 5H_2O$) were dissolved in a minimum amount of distilled water, and the dissolved materials was placed in a porcelain container. The porcelain container was placed in a muffle furnace and heat treated at 500ºC for 30 min. Then, the porcelain container was removed from the furnace, and the contents were mixed and milled. Finally, the precursor powders were introduced into an Al_2O_3 crucible and slowly heated in air in a Nabertherm Furnace for 4 h at 1000ºC.

The phase of the Bi^{3+}-activated strontium orthoborates was performed on an X-ray Bruker AXS D8 Advance, and the photoluminescence analysis was performed using a Thermo Scientific Lumina fluorescence spectrometer.

Results and discussion. *X-ray powder diffraction analysis.* $Sr_3B_2O_6$ was reported to have the trigonal unit cells, with $a = b = 9.046$ Å and $c = 12.5660$ Å [11]. Figure 1 shows the XRD pattern of pure $Sr_3B_2O_6$ and $Sr_3B_2O_6$:Bi^{3+} phosphor. The relative intensities and positions of all diffraction peaks were in agreement with the PDF Card No: 00-031-1343. The structure of $Sr_3B_2O_6$:Bi^{3+} was consistent with that of $Sr_3B_2O_6$, and the doping of the Bi^{3+} ions did not noticeably affect the crystal structure of the prepared strontium orthoborates.

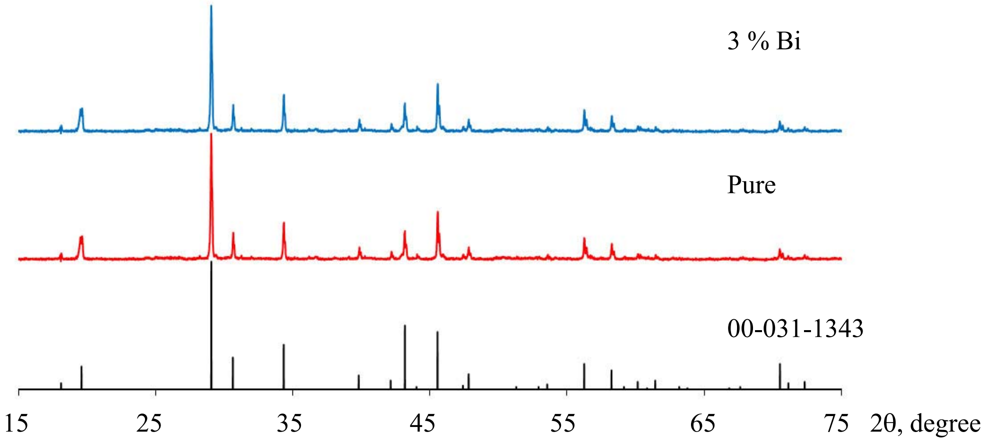

Fig. 1. XRD pattern obtained for $Sr_{3-x}B_2O_6$: Bi^{3+} ($x = 0$ and 0.03 mol).

Photoluminescence characterization. The photoluminescence (PL) of the Bi^{3+} ion in inorganic solids, such as oxides, silicates, and borates, has been studied extensively for decades [12–24]. Table 1 shows that the excitation and emission peaks of the Bi^{3+} ion in different hosts are between 250 and 550 nm. There are three main reasons why materials that have been doped with the Bi^{3+} ion emit at different wavelengths of the spectrum, i.e., the crystal structure of the host lattice, the site occupied by the Bi^{3+} ions, and the electronegativity of the cation [21]. Figure 2a shows that the excitation peak of $Sr_{3-x}B_2O_6$: Bi^{3+} ($x = 0$, 0.02, and 0.03 mol) was observed at 366 nm, which is assigned to the $^1S_0 \rightarrow {}^3P_1$ transition. It is known that the emission peak at room temperature is observed from the $^3P_1 \rightarrow {}^1S_0$ transition [12, 23–25]. Based on the related literature, it can be said that the emission peak is observed at 441 nm from the $^3P_1$ excited state level to the $^1S_0$ ground state upon excitation with 366 nm (Fig. 2b). Also, no peaks were observed in the excitation and emission spectra of pure $Sr_3B_2O_6$. Thus, it can be said that pure $Sr_3B_2O_6$ does not show luminescence properties in the UV and visible regions. Using 366 and 441 nm in this study, the Stokes shift of $Sr_3B_2O_6$: Bi^{+3} was also calculated as 4646 cm^{-1}. In addition, it can be said that this value is small compared with the other Bi-doped inorganic solids given in Table 1. Also, Blasse and his team observed that the value of the Stokes shift depends on the coordination number of the cation in the host [22]. Here, the coordination number of the Sr atom is 6, which is small compared with the coordination numbers of the others.

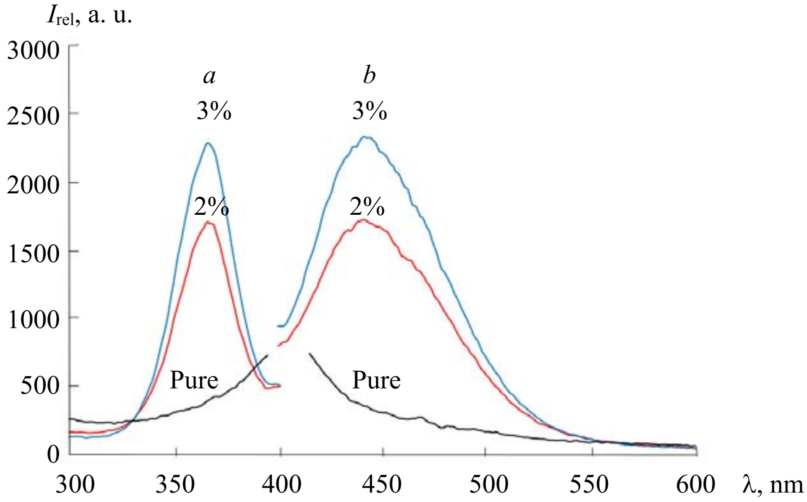

Fig. 2. The excitation (*a*) and emission (*b*) spectra of $Sr_{3-x}B_2O_6$: Bi^{3+} ($x = 0$, 0.02, and 0.03 mol); $\lambda_{exc} = 366$ nm and $\lambda_{em} = 441$ nm.

Recently, the luminescence properties of $Ca_3B_2O_6$ activated with Bi^{3+} was studied by Gawande and co-authors [12], and its spectroscopic properties are provided in Table 1. Table 1 shows that the emission peak of Bi^{3+}-doped $Ca_3B_2O_6$ was observed at 365 nm upon excitation with 290 nm. It is known that the luminescent behavior of Bi^{3+} ions in solids depends strongly on increasing the radius of the cation ion in the hosts [21]. In this study, it was observed that increasing the radius of the A^{2+} (A: Ca < Sr) ion in $A_3B_2O_6$ (A: Ca, Sr), resulted in the emission peak of Bi^{3+} in $Sr_3B_2O_6$ (441 nm) shifting to a longer wavelength compared with $Ca_3B_2O_6$ (365 nm). Thus, the result of the study is compatible with the available literature. The best example of this is Bi^{3+}-doped MO (M: Ca, Sr). In addition, under UV excitation, their emission peaks are 390 and 445 nm, respectively [26, 27].

TABLE 1. The Spectroscopic Properties of Some Bi^{3+}-Doped Inorganic Solids, at Room Temperature

Host	λ_{exc}, nm	λ_{em}, nm	Stokes shift, cm^{-1}	Reference
$Ca_3B_2O_6$	290	365	7086	[12]
$Sr_3B_2O_6$	366	441	4646	This study
$SrAl_4O_7$	330	512	10772	[13]
$SrAl_2O_4$	340	378	2956	[14]
SrY_2O_4	330	410	5913	[15]
$SrZnO_2$	375	513	7173	[16]
$Sr_2MgSi_2O_7$	330	450	8081	[17]
$Sr_3Lu_2Ge_3O_{12}$	390	466	4182	[18]
$Sr_6YAl(BO_3)_6$	325	422	7129	[19]

Conclusions. $Sr_{3-x}B_2O_6$:Bi^{3+} ($x = 0$, 0.02, and 0.03 mol) phosphors were prepared by an solution combustion method. The photoluminescence of $Sr_3B_2O_6$:Bi^{3+} was investigated using a fluorescence spectrometer. The excitation and emission peaks of $Sr_3B_2O_6$:Bi^{3+} (0.03 mol) were observed at 366 and 441 nm, respectively. Additionally, the luminescence behavior of the synthesized $Sr_3B_2O_6$:Bi^{3+} was compared with some Bi-doped inorganic solids depending on the crystal structure. It was concluded that the luminescence of Bi^{3+}-ion-doped inorganic solids was related to the crystal structure. Consequently, a blue-emitting bismuth(III) ion-doped strontium orthoborate was prepared using a combustion method. Finally, it may be considered as a suitable luminescent material for the improvement of blue LED applications.

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