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A NOVEL REDDISH ORANGE LUMINESCENT MATERIAL $Sr_3B_2O_6$:Sm^{3+} **

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The Sm^{3+} doped $Sr_3B_2O_6$ phosphors were synthesized using a solution combustion synthesis method followed by heating of the precursor combustion ash at 1000°C in air. The synthesized phosphors were characterized by powder XRD. The photoluminescence properties of Sm^{3+} doped $Sr_3B_2O_6$ were investigated at room temperature. The photoluminescence spectra at room temperature show the f–f transitions typical for Sm^{3+}. The emission spectrum of $Sr_3B_2O_6$:Sm^{3+} exhibited four sharp emission peaks corresponding to ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$ (563–572 nm), ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ (598–614 nm), ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ (647–666 nm), and ${}^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705–714 nm) transitions of Sm^{3+}. The relation between the charge transfer band of Sm^{3+} ion and the host composition was discussed.

Keywords: *photoluminescence, Sm^{3+} ion, combustion synthesis, $Sr_3B_2O_6$.*

НОВЫЙ ЛЮМИНЕСЦЕНТНЫЙ МАТЕРИАЛ $Sr_3B_2O_6$:Sm^{3+}

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Образцы люминофора $Sr_3B_2O_6$, легированного ионами Sm^{3+}, получены методом синтеза в процессе сжигания раствора с последующим нагревом зольного остатка в воздухе при 1000°С. Характеристики синтезированных порошкообразных образцов люминофора определены методом дифракционного рентгеновского анализа. Фотолюминесцентные свойства $Sr_3B_2O_6$:Sm^{3+} исследованы при комнатной температуре, в спектрах фотолюминесценции наблюдаются типичные для ионов Sm^{3+} f–f-переходы. Спектр испускания $Sr_3B_2O_6$:Sm^{3+} содержит четыре резких эмиссионных пика, соответствующих переходам ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$ (563–572 нм), ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ (598–614 нм), ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ (647–666 нм) и ${}^4G_{5/2}\rightarrow{}^6H_{11/2}$ (705–714 нм) иона Sm^{3+}. Обсуждается связь между полосой переноса заряда Sm^{3+} и составом люминофора.

Ключевые слова: *фотолюминесценция, ион Sm^{3+}, синтез в процессе горения, $Sr_3B_2O_6$.*

Introduction. Inorganic luminescent materials containing rare earth ions have been widely investigated for many years. The results of the investigations on luminescence characteristics of these phosphors have found wide commercial applications in the fields of LED, laser, and telecommunication [1]. Samarium ion (Sm^{3+}) has a $4f^5$ electronic configuration, and it has various possible transitions between $4f$ levels. Sm^{3+} doped inorganic materials are attractive as reddish-orange luminescent materials for display systems and applications [2]. The emission spectrum of Sm^{3+} ion consists of four relatively intense bands in the visible spectral region that correspond to the ${}^4G_{5/2}\rightarrow{}^6H_{5/2}$ (yellow), ${}^4G_{5/2}\rightarrow{}^6H_{7/2}$ (orange), ${}^4G_{5/2}\rightarrow{}^6H_{9/2}$ (red), and ${}^4G_{5/2}\rightarrow{}^6H_{11/2}$ (red) transitions. Therefore, the Sm^{3+} ions have been incorporated into host lattices in order to obtain reddish orange luminescent materials [3–7]. Inorganic borates have excellent transparency in the UV region due to the large difference between electronegativity of boron and oxygen atoms. In recent years,

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much attention has been paid to the synthesis and characterization of borates due to their interesting physical and chemical properties. So, they have been widely used in laser frequency-converting technology and nonlinear optical crystals [8–10]. Tristrontium bisborate, $Sr_3B_2O_6$, is an example of an alkaline-earth metal borate compound. It is characterized by having an association of BO_3 triangle and SrO_6 octahedra [11]. Its crystal structure was first reported by Richter and Müller [12]. Recently, the photoluminescence properties of Ce^{3+}, Eu^{2+}, Dy^{3+}, and Tb^{3+} doped $Sr_3B_2O_6$ have been studied in detail [13–16], but the photoluminescence properties of Sm^{3+} doped $Sr_3B_2O_6$ material have not been reported up to now.

The purpose of this present study is to research the luminescence characteristics of $Sr_3B_2O_6{:}Sm^{3+}$. So, Sm^{3+} doped $Sr_3B_2O_6$ phosphor was prepared by a combustion method and characterized by X-Ray powder diffraction analysis. Finally, the luminescence characteristics of the prepared phosphors were examined using a spectrofluorometer.

Experimental. $Sr_3B_2O_6{:}Sm^{3+}$ phosphor was synthesized using a solution combustion synthesis method followed by heating the precursor combustion ash at 1000 ºC in air. $Sr(NO_3)_2$ (Sigma-Aldrich ≥99%), H_3BO_3 (Merck ≥99.8%), $Sm(NO_3)_3$ (Alfa Aesar ≥99.99%), and $CO(NH_2)_2$ (Fluka ≥99.5%) were used as starting materials. The stoichiometric amounts of starting materials were mixed in a minimum amount of distilled water and placed in a porcelain container. The precursor solutions were introduced into a muffle furnace and maintained at 500ºC for 15 min. Then the precursor powders were removed from the furnace and milled to obtain a precursor powder of $Sr_{3-x}Sm_xB_2O_6$ ($x = 0$, 0.04, and 0.06). Finally, the well-mixed precursor powders were thoroughly mixed and then heated at 1000ºC for 12 h in air.

The XRD analysis of the synthesized materials was performed on an X-ray Rigaku Ultima IV instrument equipped with a CuK_α (30 kV, 15 mA, $\lambda = 1.54051$ Å) radiation source at room temperature. Scanning was generally performed between 10 and 90º 2θ. The measurement was made with 0.05º steps and 0.002º/s scan rate. The photoluminescence spectra were measured at room temperature with a Thermo Scientific Lumina fluorescence spectrometer equipped with a 150 W xenon lamp.

Results and discussion. *X-Ray powder diffraction analysis*. $Sr_3B_2O_6$ was reported to have the trigonal crystal structure with space group $R3c$(167); the lattice parameters values are $a = b = 9.046$ Å, and $c = 12.566$ Å [11]. Figure 1 shows the XRD pattern of $Sr_{2.96}Sm_{0.04}B_2O_6$ prepared by the solution combustion method. The positions and relative intensities of all diffraction peaks are in agreement with JCPDS Card No: 31-1343. The secondary phase was not observed due to impurities. Doping of Sm^{3+} ions does not significantly influence the crystal structure of the synthesized phosphors. The two possible sites available for incorporating Sm^{3+} in $Sr_3B_2O_6$ lattice are either the B^{3+} (0.11 Å for $CN = 4$) site or the Sr^{2+} (1.18 Å for $CN = 6$) site. When Sm^{3+} ions (0.958 Å for $CN = 6$) were doped in $Sr_3B_2O_6$, it was believed that the activator ions would replace Sr^{2+} in the host due to their ionic radius. So, it would be expected that Sm^{3+} would replace Sr^{2+} in the $Sr_3B_2O_6$ lattice. As a consequence, the substitution of trivalent Sm^{3+} ions in $Sr_3B_2O_6$ needs charge compensation mechanisms, which can be described as $3Sr^{2+} \leftrightarrow 2Sm^{3+}$ + vacancy.

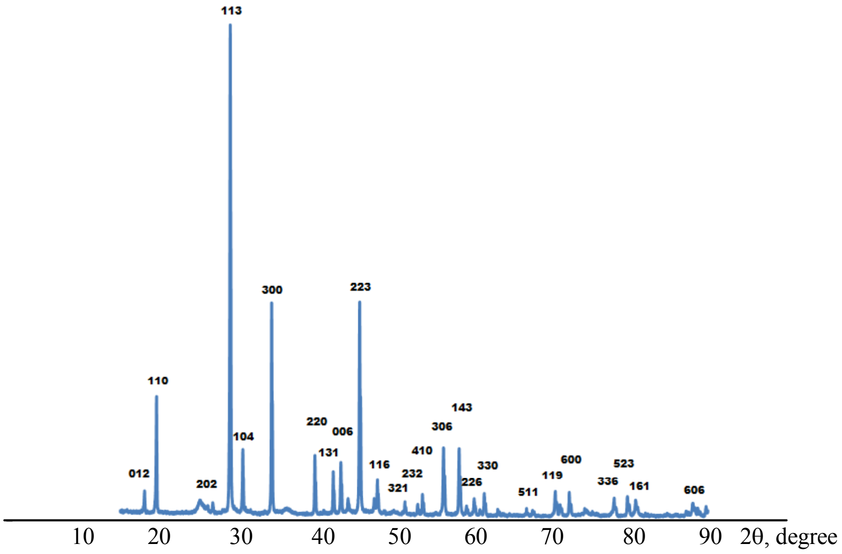

Fig. 1. XRD pattern of $Sr_{2.96}Sm_{0.04}B_2O_6$ prepared by the solution combustion method.

Photoluminescence properties of $Sr_3B_2O_6$:Sm^{3+}. Figure 2a shows the excitation spectrum of the $Sr_{3-x}Sm_xB_2O_6$ ($x = 0$, 0.04, and 0.06) phosphor. The excitation spectrum was recorded in the wavelength range of 200–500 nm measured by monitoring at 647 nm emission. As seen in Fig. 2a, the excitation spectrum of Sm^{3+} is composed of a broad band from 200 to 250 nm and $4f \rightarrow 4f$ transitions between 300–500 nm. The broad band at 225 nm is due to the charge transfer band (CTB) of Sm^{3+}–O^{2-}. The relation between the charge transfer band of Sm^{3+} ion and the host compositions is known. Many studies [17, 18] indicate that the energy of CTB of Sm^{3+}–O^{2-} depends on the site occupied by Sm^{3+} (activator ion) and the covalency of the Sm^{3+}–O^{2-} bond. Recently, the photoluminescence properties of $Ca_3B_2O_6$:Sm^{3+} have been reported by V. Kumar [19]. The CTB of Sm^{3+}–O^{2-} in $Ca_3B_2O_6$ was observed at 200 nm. When considering the bond structure of Sm^{3+} –O^{2-}–M^{2+} (M=Ca, Sr), the degree of covalency of the Sm^{3+}–O^{2-} bond is weaker in $Ca_3B_2O_6$ than in $Sr_3B_2O_6$. This is because Ca^{2+} atoms attract electrons of O^{2-} most strongly due to the fact that it has a larger electronegativity and a smaller radius than Sr^{2+} atoms. Therefore, electrons could more easily transfer from O^{2-} orbitals to the Sm^{3+} ion in $Sr_3B_2O_6$ than the other one [20]. Thus, the CTB of Sm^{3+} in both $Ca_3B_2O_6$ and $Sr_3B_2O_6$, are observed at 200 and 225 nm, respectively. Based on the observations, it can be explained that the CTB of Sm^{3+} in both $Ca_3B_2O_6$ and $Sr_3B_2O_6$ shifts to longer wavelength depending on the degree of covalency of the Sm^{3+}– O^{2-} bond in $M_3B_2O_6$ (M:Ca > Sr) and the ionic radius of the M^{2+} (M:Ca < Sr). The other excitation peaks at 343, 360, 374, 400, 414, 466, and 474 nm have been assigned to the transition from $^6H_{5/2}$ to $^4H_{9/2}$, $^4D_{3/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, and $^4I_{11/2}$ of Sm^{3+}, respectively [21, 22]. Also, any peak in the excitation spectrum of pure $Sr_3B_2O_6$ was not observed.

Figure 2b shows the emission spectrum of the $Sr_{3-x}Sm_xB_2O_6$ ($x = 0$, 0.04, and 0.06) phosphor. The emission spectrum was recorded in the wavelength range of 500–750 nm measured by monitoring at 400 nm excitation. It is composed of four bands corresponding to the transitions from the $^4G_{5/2}$ to the $^6H_{5/2}$ (563–572 nm), $^6H_{7/2}$ (598–614 nm), $^6H_{9/2}$ (647–666 nm), and $^6H_{11/2}$ (705–714 nm) [21–24]. The strongest one is located at 647 nm due to the $^4G_{5/2}$ to $^6H_{9/2}$ transition of Sm^{3+}. Although $Sr_3B_2O_6$:Sm^{3+} shows four emission bands including 563–572, 598–614, 647–666, and 705–714 nm under excitation with 400 nm, no peak in the emission spectrum of pure $Sr_3B_2O_6$ under excitation with 400 nm was observed. Based on the above observations, it can be stated that pure $Sr_3B_2O_6$ has no photoluminescence properties under excitation with 400 nm.

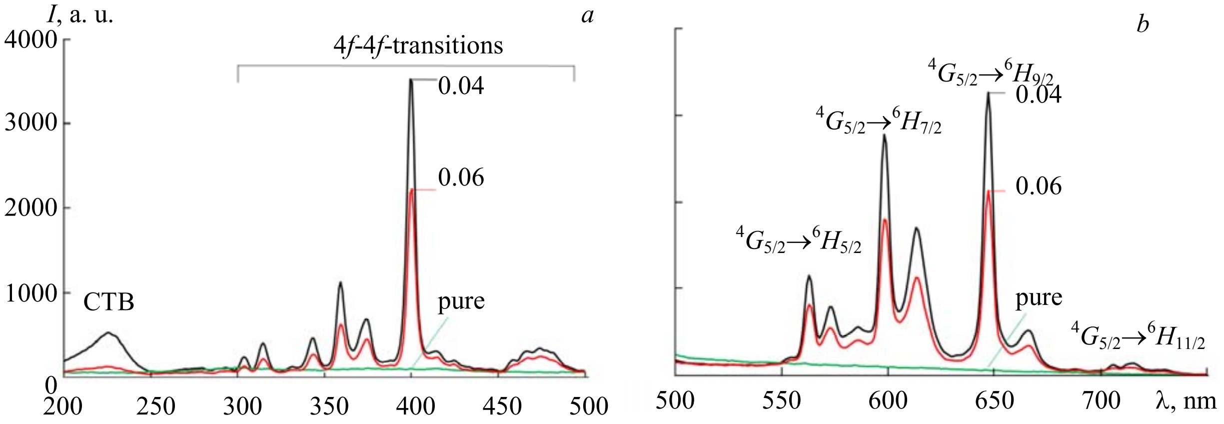

Fig. 2. The excitation at $\lambda_{em} = 647$ nm (a) and emission at $\lambda_{exc} = 400$ nm (b) spectra of $Sr_{3-x}Sm_xB_2O_6$ ($x = 0$, 0.04, and 0.06).

Conclusion. The Sm^{3+} doped $Sr_3B_2O_6$ phosphors were prepared by the solution combustion method. The synthesized phosphors were characterized by using powder XRD. The photoluminescence properties of all phosphors were investigated at room temperature. The emission spectrum of $Sr_3B_2O_6$:Sm^{3+} exhibited four sharp emission peaks corresponding to the $^4G_{5/2} \rightarrow {}^6H_{5/2}$ (563–572 nm), $^4G_{5/2} \rightarrow {}^6H_{7/2}$ (598–614 nm), $^4G_{5/2} \rightarrow {}^6H_{9/2}$ (647–666 nm), and $^4G_{5/2} \rightarrow {}^6H_{11/2}$ (705–714 nm) transitions of Sm^{3+}. Finally, the relation between the charge transfer band of Sm^{3+} ion and the host composition was discussed in detail. As a result, it can be explained that the CTB of Sm^{3+} in both $Ca_3B_2O_6$ and $Sr_3B_2O_6$ shifts to longer wavelength depending on the degree of covalency of the Sm^{3+}–O^{2-} bond in $M_3B_2O_6$ (M:Ca > Sr) and the ionic radius of M^{2+} (M:Ca < Sr). Consequently, the synthesized phosphor could be considered an ideal optical material for the reddish orange emitting phosphor.

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