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КРАТКИЕ СООБЩЕНИЯ

SYNTHESIS AND PHOTOLUMINESCENCE CHARACTERIZATION OF $NaSr_4(BO_3)_3$ ACTIVATED WITH Dy^{3+} ION [**]

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Dy^{3+} doped $NaSr_4(BO_3)_3$ phosphors were prepared using the combustion method.The prepared phosphors were characterized by X-Ray powder diffraction analysis. The excitation and emission spectra of the synthesized phosphors were analyzed with a fluorescence spectrometry. It is established that the $NaSr_4(BO_3)_3$:Dy^{3+} phosphor emits blue (482 nm), yellow (575 nm), and red (666 nm) light under ultraviolet excitation of 352 nm. Finally, the photoluminescence properties of the synthesized phosphors with different Dy^{3+} doping concentrations were analyzed. The optimum concentration of the Dy^{3+} ion in $NaSr_4(BO_3)_3$ was found to be 0.0025 mole.

Keywords: *photoluminescence, X-Ray powder diffraction, inorganic borate, Dy^{3+} ion.*

СИНТЕЗ И ИССЛЕДОВАНИЕ ФОТОЛЮМИНЕСЦЕНЦИИ ЛЮМИНОФОРА $NaSr_4(BO_3)_3$, ЛЕГИРОВАННОГО ИОНАМИ Dy^{3+}

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Полученные методом сжигания люминофоры $NaSr_4(BO_3)_3$, легированные ионами Dy^{3+}, изучены методом порошковой рентгенографии. Спектры возбуждения и излучения люминофоров проанализированы с помощью флуоресцентной спектрометрии. Установлено, что $NaSr_4(BO_3)_3$, легированный ионами Dy^{3+}, при возбуждении УФ излучением с $\lambda = 352$ нм испускает синий (482 нм), желтый (575 нм) и красный (666 нм) свет. Проанализированы фотолюминесцентные свойства синтезированных люминофоров с различными концентрациями Dy^{3+}. Оптимальная концентрация ионов Dy^{3+} в $NaSr_4(BO_3)_3$ 0.0025 моль.

Ключевые слова: *фотолюминесценция, порошковая рентгенография, неорганический борат, ион Dy^{3+}.*

Introduction. The Dysprosium ion (Dy^{3+}) has a $4f^9$ electronic configuration and various possible transitions between the $4f$ levels. Dy^{3+} doped inorganic materials are of interest as a candidate for a yellow/blue luminescent material in display systems. The Dy^{3+}emission is attributed to ${}^4F_{9/2}\rightarrow{}^6H_{15/2}$ (blue) and ${}^4F_{9/2}\rightarrow{}^6H_{13/2}$ (yellow) transitions of the Dy^{3+} ion [1, 2]. Inorganic borates have excellent transparency in the UV region due to the large difference between the electronegativity of boron and oxygen atoms. So, they are widely used in laser frequency-converting technology and nonlinear optical crystals [3–5]. The compound

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of $NaSr_4(BO_3)_3$ is an example of alkaline-earth metal borates. It is characterized by having an association of the BO_3 triangle ($Sr(1)O_6$ octahedra and $Sr(2)O_8$ polyhedra) and NaO_6 octahedra. The crystal structure of $NaSr_4(BO_3)_3$ is studied in detail by Chen et al. [6]. $NaSr_4(BO_3)_3$ has been a useful luminescent host for activator ions. Recently, the luminescence properties of Pb^{2+}, Sm^{3+}, Ce^{3+}, and Tb^{3+} doped $NaSr_4(BO_3)_3$ have been reported [7–10]. Moreover, the luminescence of $NaSr_4(BO_3)_3$:Dy^{3+} phosphors has been studied by Omanwar et al. [11]. To the best of my knowledge, the luminescence properties in the UV-visible region of Dy^{3+} doped $NaSr_4(BO_3)_3$ have not been investigated in detail.

The purpose of this paper is to study the photoluminescence properties of $NaSr_4(BO_3)_3$:Dy^{3+}phosphors. So, different mole ratios of Dy^{3+} doped $NaSr_4(BO_3)_3$ were prepared using the combustion method and characterized by X-Ray powder diffraction (XRD) analysis. Finally, the luminescence characterization of the prepared phosphors was examined in the UV-visible region in detail.

Experimental. $NaSr_4(BO_3)_3$:Dy^{3+}phosphors were synthesized using the combustion method at 750°C for 8 h in air. In the synthesis stage, $NaNO_3$ (Sigma-Aldrich ≥99%), $Sr(NO_3)_2$ (Sigma-Aldrich ≥99%), H_3BO_3 (Merck ≥99.8%), and $Dy(NO_3)_3$ (Alfa Aesar ≥99.99%) were used as the raw materials. Also, $CO(NH_2)_2$ (Fluka, ≥99.5%) was used as the organic fuel. The combustion process has already been described in [7, 8].

The XRD structural analysis of the synthesized materials was performed on an X-ray Rigaku Ultima IV system equipped with CuK_α (30 kV, 15 mA, λ = 1.54051 Å) radiation at room temperature. Scanning was generally performed between 10° and 90°. Measurements were made with a 0.05º step and at a 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.

XRD analysis. Figure 1 shows the XRD pattern of $NaSr_{4-x}Dy_x(BO_3)_3$ (x = 0, 0.001, 0.0025, 0.005, 0.01) phosphors. The positions and relative intensities of all diffraction peaks are in agreement with the JCPDS (56-0118). $NaSr_4(BO_3)_3$ was reported to have cubic unit cells with a = 15.14629(6) Å [6]. The two possible sites available for incorporating Dy^{3+} in the $NaSr_4(BO_3)_3$ lattice are either the Na^+ or the Sr^{2+}ones. When Dy^{3+} ions (0.912 Å for CN = 6) were doped in $NaSr_4(BO_3)_3$ the activator ions replaced the Sr^{2+} (1.18 Å for CN = 6) in the host material due to their ionic radius. As a consequence, the substitution of trivalent Dy^{3+} ions in $NaSr_4(BO_3)_3$ needs the charge compensation, the mechanism of which is described by the following equation:

$$3Sr^{2+} \leftrightarrow 2Dy^{3+} + \text{vacancy}$$

Also, doped Dy^{3+} ions do not significantly influence the crystal structures of the synthesized phosphors.

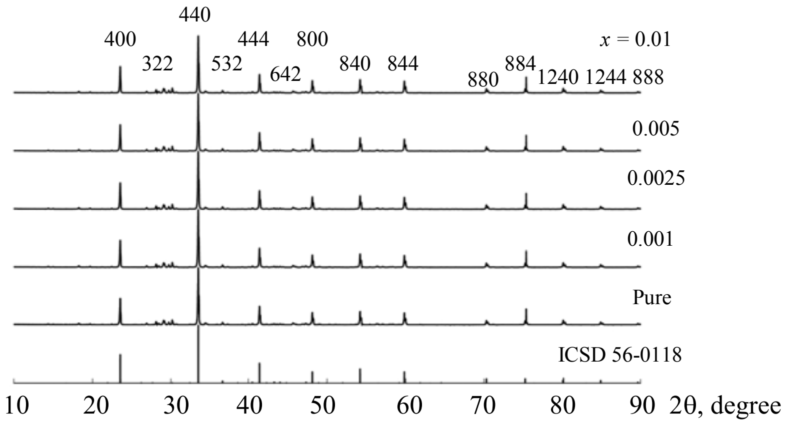

Fig. 1. XRD pattern obtained for $NaSr_{4-x}Dy_x(BO_3)_3$ (x = 0, 0.001, 0.0025, 0.005, 0.01).

Photoluminescence properties of $NaSr_4(BO_3)_3$:Dy^{3+}. Figure 2 shows the excitation spectrum of the $NaSr_4(BO_3)_3$:Dy^{3+} phosphor. The excitation spectrum was recorded in the wavelength range 190–500 nm measured by monitoring the 575 nm emission. As seen in Fig. 2, while a strong band at 201 nm is attributed to a charge transfer band (CTB) of Dy^{3+}–O^{2-} [12, 13], the sharp band located at 298 nm is attributed to the *f–d* spin-forbidden transitions of Dy^{3+} [14–18]. The other excitation peaks at 326, 352, 366, 389, 427, 454, and 475 nm have been assigned to the transitions from $^6H_{15/2}$ to $^4L_{19/2}$, $^6P_{7/2}$, $^6P_{5/2}$, $^4I_{13/2}$, $^4G_{11/2}$, $^4I_{15/2}$, and $^4F_{9/2}$ of Dy^{3+}, respectively [17, 18].

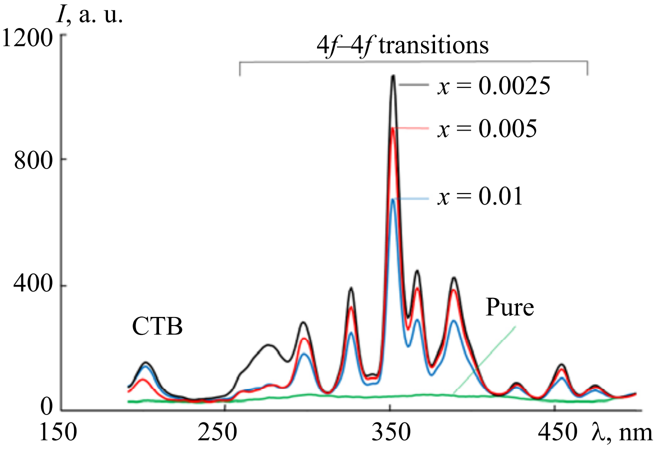

Fig. 2. Excitation spectra of $NaSr_{4-x}Dy_x(BO_3)_3$ ($x = 0$, 0.0025, 0.005, 0.01), $\lambda_{ems} = 575$ nm.

Figure 3 shows the emission spectrum of the $NaSr_4(BO_3)_3$:Dy^{3+} phosphor. The emission spectrum was recorded in the wavelength range 450–750 nm measured by monitoring the 352 nm excitation. The spectrum consists of two main bands with maxima at 482 and 575 nm and a weaker band at 666 nm. These are assigned to the transitions from the $^4F_{9/2}$ to the $^6H_{15/2}$, $^6H_{13/2}$, and $^6H_{11/2}$ states, respectively [17–20]. As seen in Fig. 3, the intensity of the yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) emission is much stronger than that of the blue one ($^4F_{9/2}\rightarrow{}^6H_{15/2}$). It is well known that the yellow ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) emission of Dy^{3+} belongs to the hypersensitive (forced electric dipole) transition with the selection rule $\Delta J = 2$, which is strongly influenced by the outside surrounding environment. The blue ($^4F_{9/2}\rightarrow{}^6H_{15/2}$) emission corresponding to the magnetic dipole transition hardly varies with the crystal field strength around the Dy^{3+} ion. When the Dy^{3+} ion is located at a low-symmetry local site (without inversion symmetry), the yellow emission is often dominant in the emission spectrum [21–24].

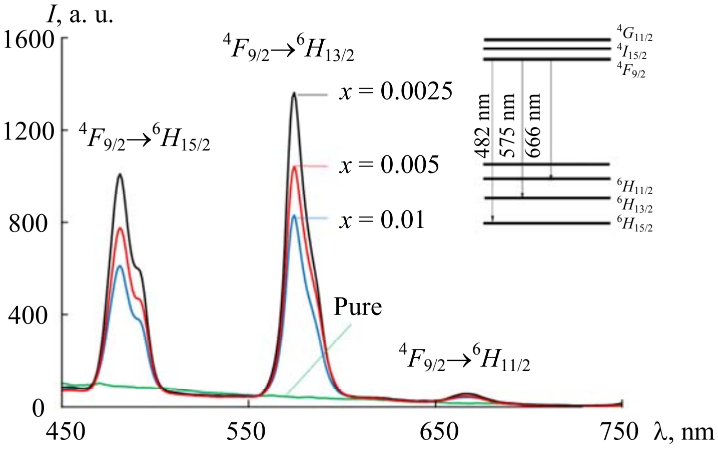

Fig. 3. Emission spectra of $NaSr_{4-x}Dy_x(BO_3)_3$ ($x = 0$, 0.0025, 0.005, 0.01), $\lambda_{exc} = 352$ nm.

Finally, the effect of the Dy^{3+} ion concentration on the emission spectrum of the $NaSr_4(BO_3)_3$:Dy^{3+} phosphor was investigated. The emission spectra of $NaSr_{4-x}Dy_x(BO_3)_3$ ($x = 0$, 0.0025, 0.005, 0.01) phosphors with different Dy^{3+} molar fractions are shown in Fig. 3. With increasing the Dy^{3+} concentration in $NaSr_4(BO_3)_3$, the emission intensity of the prepared phosphors increases and reaches a maximum at 0.0025 mole. When the mole concentration of the Dy^{3+} ion exceeds this concentration level, the emission intensity decreases due to concentration quenching [2, 18].

Conclusion. Dy^{3+} doped $NaSr_4(BO_3)_3$ phosphors were prepared using the combustionmethod. The prepared phosphors were characterized by X-Ray powder diffraction analysis. The excitation and emission spectra of all phosphors were analyzed in detail. A lot of bands were observed in the excitation spectrum.

While a strong band at 201 nm was attributed to a CTB of Dy^{3+}–O^{2-}, the sharp band located at 298 nm was attributed to the *f–d* spin-forbidden transition of Dy^{3+}. Also, the excitation peaks between 325 and 475 nm were assigned to the 4*f*–4*f* transitions. Three bands were observed in the emission spectrum. These were assigned to the transitions from the $^4F_{9/2}$ to the $^6H_{15/2}$ (482 nm), $^6H_{13/2}$ (575 nm), and $^6H_{11/2}$ (666 nm) states, respectively. Finally, the photoluminescence properties of the synthesized phosphors with different Dy^{3+} doping concentrations were analyzed. The optimum concentration of the Dy^{3+} ion in $NaSr_4(BO_3)_3$ was found to be 0.0025 mole. As a consequence, the luminescence properties in the UV-visible region of Dy^{3+} doped $NaSr_4(BO_3)_3$ were investigated in detail.

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