

RED LUMINESCENCE PROPERTIES OF Pr^{3+} -DOPED $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$)**İlhan Pekgözlü**

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Pr^{3+} -doped $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) were synthesized and determined by a combustion method and by X-ray powder diffraction analysis. The photoluminescence (PL) behavior of the borates that were prepared was investigated by using a fluorescence spectrometer. The emission peaks of the Pr^{3+} -doped $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) were observed at 609 and 606 nm, respectively. Finally, the PL spectra of $\text{LiSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ and $\text{NaSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ with different Pr^{3+} doping concentrations were analyzed in detail.

Keywords: Photoluminescence, Pr^{3+} ion, combustion synthesis, inorganic borate.

ЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА БОРАТОВ $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$), ЛЕГИРОВАННЫХ ИОНАМИ Pr^{3+} **İ. Pekgözlü**

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Бораты $\text{MSr}_4(\text{BO}_3)_3$, легированные Pr^{3+} ($\text{M} = \text{Li, Na}$), синтезированы методом сжигания и выполнены их рентгенофазовый анализ. Фотолюминесценция исследуемых боратов исследована с помощью флуоресцентного спектрометра. Максимумы излучения $\text{MSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ ($\text{M} = \text{Li, Na}$) наблюдаются при 609 и 606 нм. Зарегистрированы спектры фотолюминесценции $\text{LiSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ и $\text{NaSr}_4(\text{BO}_3)_3:\text{Pr}^{3+}$ с различными концентрациями ионов Pr^{3+} .

Ключевые слова: фотолюминесценция, ион Pr^{3+} , метод сжигания, неорганический борат.

Introduction. The praseodymium ion (Pr^{3+}) is a rare earth element with a $4f^2$ electronic configuration. It is known that Pr^{3+} -doped inorganic materials emit orange or red light in the visible spectral region owing to the transitions between the $4f$ levels. Thus, they have been attractive as a candidate for red luminescent material for monitoring systems, LED lamps, and medical applications. The red emission of Pr^{3+} is attributed to the 1D_2 to 3H_4 transition of the Pr^{3+} ion [1–3]. Borates have been investigated for many years because of their variety of crystal lattices, high physical properties, vacuum ultraviolet–ultraviolet transparency, and the fact that the spectral behavior of inorganic borates is affected by the BO_3 and BO_4 groups [4]. Therefore, to date, many Pr^{3+} -doped borate phosphors have been studied [2, 5, 6].

The phases of $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) are examples of alkaline-earth borates, and they have been reported in detail by Wu et al. Their crystal structures are characterized by having an association of BO_3 triangles, the SrO_8 polyhedral, and the MO_6 (where $\text{M} = \text{Li or Na}$) cubic octahedral [7]. Both alkaline-earth borates are useful luminescence hosts for activator ions. Recently, the detailed luminescent behaviors of $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) doped with Eu^{2+} , Eu^{3+} , Ce^{3+} , Tb^{3+} , Sm^{3+} , Dy^{3+} , and Pb^{2+} have been analyzed [8–16], but the luminescence characterization of Pr^{3+} -doped $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) have not been published yet.

The purpose of this study is to research the luminescence characterization of Pr^{3+} -doped $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$). Thus, different mole ratios of Pr^{3+} -doped $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li, Na}$) were prepared and characterized by a combustion method and X-ray diffraction (XRD) analysis, and the photoluminescence (PL) characterizations of the newly prepared materials were analyzed in detail.

Experimental. Pr³⁺-doped MSr₄(BO₃)₃ (M: Li, Na) were prepared using a combustion method at 800°C and 750°C, respectively. In the synthesis stage, Sr(NO₃)₂ (Sigma-Aldrich ≥99%), LiNO₃ (Sigma-Aldrich ≥99%), NaNO₃ (Sigma-Aldrich ≥99%), H₃BO₃ (Merck ≥99.8%), Pr(NO₃)₃·6H₂O (Sigma-Aldrich ≥99.9%), and CO(NH₂)₂ (Fluka ≥99.5%) were used as the raw materials. The combustion procedure of Pr³⁺-doped MSr₄(BO₃)₃ (M = Li, Na) is the same as that described in the literature [13–16].

The XRD analysis was performed using an X-ray Rigaku SmartLab equipped with CuK_α radiation ($\lambda = 1.54051 \text{ \AA}$, 40 kV, 30 mA). The scanning angle (2θ) was generally performed between 10 and 90°. Measurements were made with 0.05° steps and a 0.002°/s scan rate. A Thermo Scientific Lumina fluorescence spectrometer was used for the PL spectral measurement, and the fluorescence measurements were analyzed in the UV-visible region. Both the XRD and the fluorescence measurements were performed at room temperature.

Results and discussion. *X-Ray powder diffraction analysis.* Figure 1a shows the XRD pattern of the Pr³⁺-doped LiSr₄(BO₃)₃ phosphors, which is in agreement with PDF Card (No. 01-073-3772). Figure 1b shows the XRD pattern of Pr³⁺-doped NaSr₄(BO₃)₃ phosphors, which matches PDF Card No. 01-073-3773. Both the NaSr₄(BO₃)₃ and the LiSr₄(BO₃)₃ structures crystallized in the cubic space group *Ia3d*. The fundamental building units of NaSr₄(BO₃)₃ and LiSr₄(BO₃)₃ are isolated planar [BO₃]³⁻ groups that are perpendicular

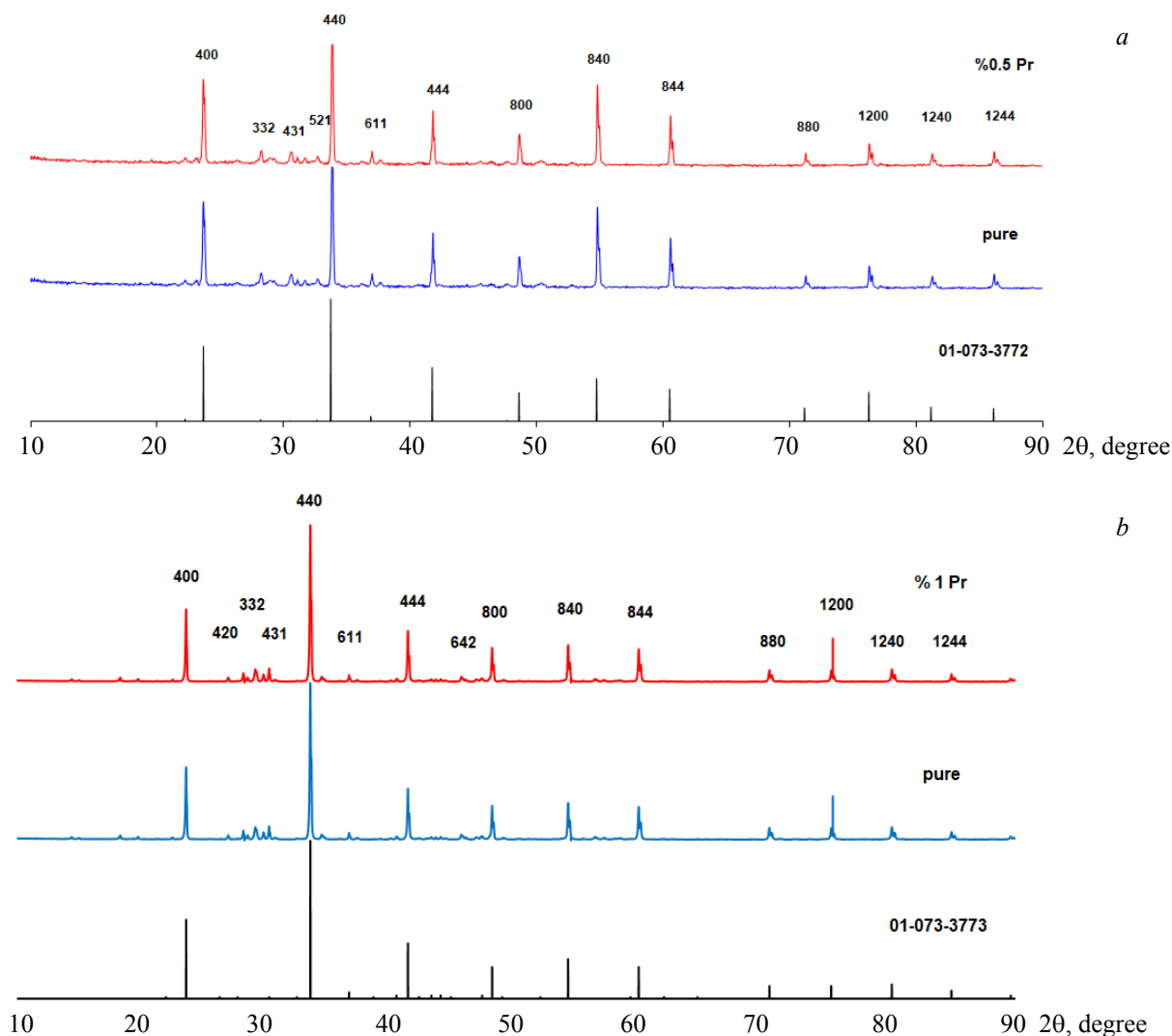


Fig. 1. XRD pattern obtained for (a) LiSr_{4-x}Pr_x(BO₃)₃ ($x = 0$ and 0.005) and (b) NaSr_{4-x}Pr_x(BO₃)₃ ($x = 0$ and 0.01) prepared by a solution combustion synthesis.

to each other, and both Li and Na atoms are coordinated with six oxygen atoms, forming MO_6 cubic octahedra ($\text{M} = \text{Li}$ or Na), that were located at the centers of the cubic grids consisting of eight Sr atoms [7]. When the Pr^{3+} ions are incorporated into $\text{MSr}_4(\text{BO}_3)_3$ ($\text{M} = \text{Li}, \text{Na}$), the Pr^{3+} ions are expected to occupy the Sr^{2+} sites owing to the difference in the ionic radii of the cations.

Photoluminescence properties. Figure 2a shows the PL spectra (within the range 200–750 nm) of $\text{LiSr}_{4-x}\text{Pr}_x(\text{BO}_3)_3$ ($x = 0.005$). The excitation spectrum was monitored with the 609-nm emissions of Pr^{3+} ($^1D_2 \rightarrow ^3H_4$). The excitation spectrum of Pr^{3+} comprised several peaks at 243, 446, 467, and 484 nm, respectively. The band around 243 nm has been attributed from the intervalence charge transfer band (IVCTB) of Pr^{3+} [17, 18]. The other excitation peaks at 446, 467, and 484 nm have been assigned to the transition from 3H_4 to 3P_2 , 3P_1 , and 3P_0 of Pr^{3+} , respectively [3, 18–25]. The emission spectrum was measured using 446-nm excitation. The observed band was stronger and was located at 609 nm owing to the 1D_2 to 3H_4 transition of Pr^{3+} [3, 18–22, 24–26]. Also, the PL spectra (within the range 200–750 nm) of $\text{NaSr}_{4-x}\text{Pr}_x(\text{BO}_3)_3$ ($x = 0.01$) are indicated in Fig. 2b. The excitation spectrum was monitored with the 606-nm emissions of Pr^{3+} ($^1D_2 \rightarrow ^3H_4$). The excitation spectrum of Pr^{3+} comprised several peaks at 252, 444, 470, and 487 nm, respectively. The band around 252 nm resulted from the IVCTB of Pr^{3+} [17, 18]. The other excitation peaks at 444, 470, and 487 nm were assigned to the transition from 3H_4 to 3P_2 , 3P_1 , and 3P_0 of Pr^{3+} , respectively [3, 18–25]. The emission spectrum was measured using 444-nm excitation. The observed band was stronger and was located at 606 nm owing to the 1D_2 to 3H_4 transition of Pr^{3+} [3, 18–22, 24–26].

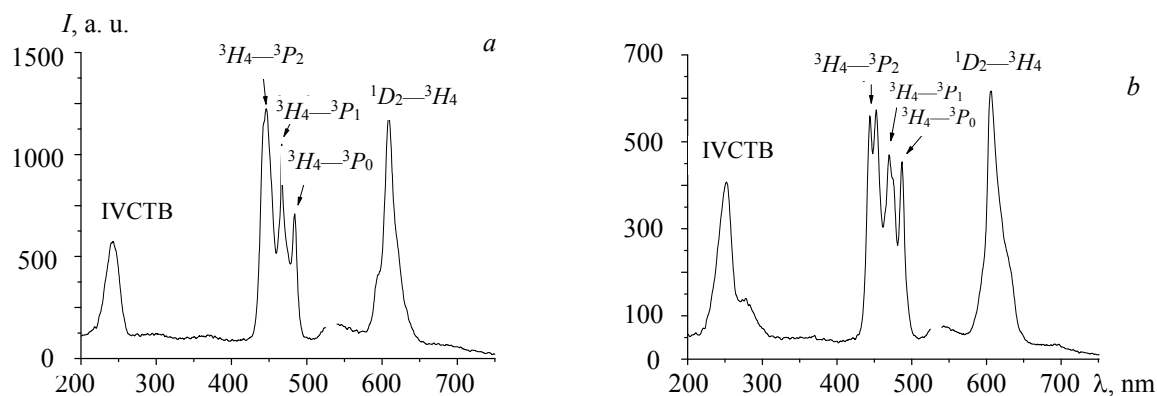


Fig. 2. The excitation and emission spectra of (a) $\text{LiSr}_{4-x}\text{Pr}_x(\text{BO}_3)_3$ ($x = 0.005$) and (b) $\text{NaSr}_{4-x}\text{Pr}_x(\text{BO}_3)_3$ ($x = 0.01$) at room temperature ($\lambda_{\text{exc}} = 446$ nm, $\lambda_{\text{ems}} = 609$ nm).

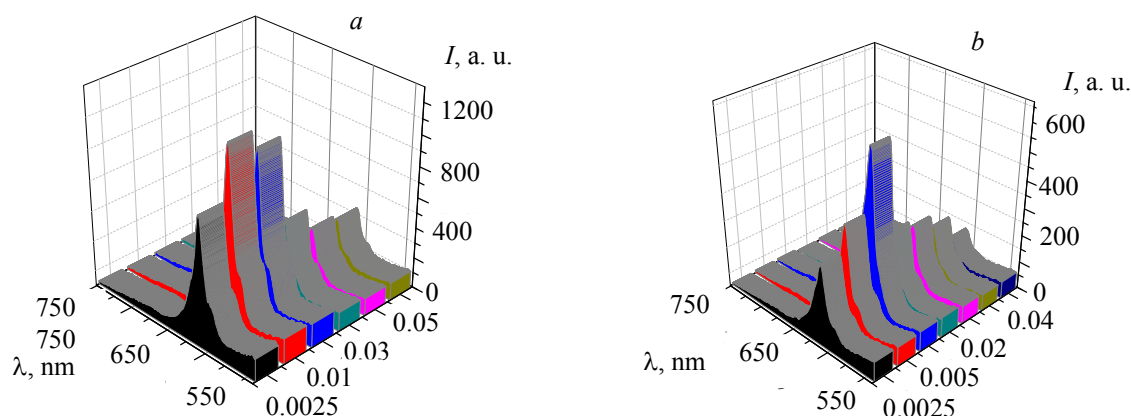


Fig. 3. Emission spectra of (a) $\text{LiSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ (0.0025, 0.005, 0.01, 0.02, 0.03, and 0.04 mol) phosphors ($\lambda_{\text{exc}} = 446$ nm) and (b) $\text{NaSr}_4(\text{BO}_3)_3: \text{Pr}^{3+}$ (0.0025, 0.005, 0.01, 0.02, 0.03, 0.04, and 0.05 mol) phosphors ($\lambda_{\text{exc}} = 444$ nm).

In addition, the PL spectra of both phosphors with different Pr³⁺ doping concentrations were investigated at room temperature. The effect of the Pr³⁺ concentration on the emission intensity for both LiSr_{4-x}Pr_x(BO₃)₃ (0.0025 ≤ *x* ≤ 0.04) and NaSr_{4-x}Pr_x(BO₃)₃ (0.0025 ≤ *x* ≤ 0.05) are presented in Fig. 3. Based on the results of the analysis, no obvious changes were observed in the shapes and positions of the emission peaks of all of the phosphors. According to the data displayed in Fig. 3, the concentration quenching of the Pr³⁺ doped MSr₄(BO₃)₃ (M = Li, Na) were observed at 0.005 and 0.01 mol, respectively.

Conclusions. Two new luminescent materials were prepared for the first time using a combustion method. First, phosphor LiSr₄(BO₃)₃:Pr³⁺ exhibited a stronger emission peak at 609 nm under excitation with 446 nm, and the second phosphor, i.e., NaSr₄(BO₃)₃:Pr³⁺ showed a stronger emission peak at 606 nm under excitation with 444 nm. In addition, the PL properties of both materials with different Pr³⁺ doping concentrations were investigated in detail. The optimal concentrations of the Pr³⁺ ion in LiSr₄(BO₃)₃ and NaSr₄(BO₃)₃ were observed to be 0.005 and 0.01 mol, respectively.

As a result, the Pr³⁺-doped borates that were prepared exhibited a strong red emission, and they could be considered to be suitable red-emitting phosphors for the improvement of lighting, screening, and monitoring systems.

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