## PHOTOLUMINESCENCE PROPERTIES OF $Dy^{3+}$-DOPED $Ba_2Be_2B_2O_7$**

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*$Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ was prepared and characterized using a combustion method and X-ray diffraction analysis. The photoluminescence (PL) properties of the synthesized borates were analyzed using a fluorescence spectrometer. $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ emits 483, 575, and 667 nm light in response to the UV excitation of 351 nm. Subsequently, different mole ratios of $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ were prepared, and their PL properties were studied in detail. Finally, the optimal concentration of $Dy^{3+}$ ions in $Ba_2Be_2B_2O_7$ was found to be 0.05 mole.*

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

## ФОТОЛЮМИНЕСЦЕНТНЫЕ СВОЙСТВА $Ba_2Be_2B_2O_7$, ЛЕГИРОВАННОГО ИОНАМИ $Dy^{3+}$

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*$Ba_2Be_2B_2O_7$, легированный ионами $Dy^{3+}$, получен методом сжигания и охарактеризован с использованием рентгенодифракционного анализа. Фотолюминесцентные свойства синтезированных боратов проанализированы с помощью флуоресцентного спектрометра. $Ba_2Be_2B_2O_7$:$Dy^{3+}$ излучает свет длин волн 483, 575 и 667 нм при возбуждении УФ-излучением с длиной волны 351 нм. Изучены фотолюминесцентные свойства образцов $Ba_2Be_2B_2O_7$:$Dy^{3+}$ с различными мольными соотношениями. Установлено, что оптимальная концентрация ионов $Dy^{3+}$ в $Ba_2Be_2B_2O_7$ составляет 0.05 моль.*

***Ключевые слова:*** *люминесценция, рентгеновская дифракция, неорганический борат, ион $Dy^{3+}$.*

**Introduction.** The $Dy^{3+}$ ions are referred to as lanthanide, and they have complicated $4f^n$ energy levels. The emission spectrum shows diversity in the visible region owing to the transitions between the $4f^n$ energy levels [1]. Borates have been investigated for many years because of the diversity of the B–O groups [2]. They are known for their transparency in the UV region and their high polarizability. For these reasons, metal borates have been investigated extensively for many years as nonlinear optical materials [3, 4] and as hosts for luminescent materials [5, 6]. Also, the luminescence properties of borate crystals and glasses activated using rare-earth ions have been examined extensively owing to their varied 4*f* energy levels [7–16]. Barium beryllium borate formulated with $Ba_2Be_2B_2O_7$ is a new metal borate compound. Initially, it was synthesized by Qi and Chen [17], and its nonlinear optical properties were examined using the SHG effect. Recently, the luminescence characterization of $Pb^{2+}$-doped $Ba_2Be_2B_2O_7$ has been reported in detail [18], but the characterization of the photoluminescence of $Ba_2Be_2B_2O_7$ activated with $Dy^{3+}$ ions has not been analyzed.

The aim of this study is to research and characterize the photoluminescence of $Ba_2Be_2B_2O_7$:$Dy^{3+}$. Thus, different mole ratios of $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ were prepared using a combustion method and characterized by XRD analysis. Finally, the photoluminescence (PL) properties of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ were analyzed in detail using a fluorescence spectrometer.

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**Experimental.** $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ was prepared using a solution combustion method at 950ºC for 12 h in air. $Ba(NO_3)_2$ (Merck ≥99%), $Be(NO_3)_2$ (Sigma-Aldrich ≥99%), $H_3BO_3$(Merck ≥99.8%), $Dy(NO_3)_3$ (Alfa Aesar ≥99.99%), and $CO(NH_2)_2$ (Fluka ≥99.5%) were used as the starting materials. The combustion procedure of $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ is the same as that shown in the literature [18].

The XRD analyses of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ phosphors were performed on an X-ray Bruker AXS D8 Advance equipped with Cu$K_\alpha$ (30 kV, 15 mA, λ= 1.54051 Å) radiation at room temperature. The photoluminescence analyses of the $Ba_2Be_2B_2O_7$:$Dy^{3+}$ phosphors were performed using a Thermo Scientific Lumina fluorescence spectrometer equipped with a 150 W Xenon lamp. The measurements of excitation and emission were performed at between 190 and 800 nm at room temperature.

**Results and discussion.** *X-ray powder diffraction analysis.* $Ba_2Be_2B_2O_7$ was reported to have hexagonal unit cells, with $a = b = 8.289(2)$ Å and $c = 8.048(2)$ Å [17]. Figure 1 shows the XRD pattern of pure $Ba_2Be_2B_2O_7$ and $Ba_2Be_2B_2O_7$: $Dy^{3+}$ phosphor. The relative intensities and positions of all diffraction peaks are in agreement with the XRD data of $Ba_2Be_2B_2O_7$ in [17, 18]. The structure of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ is consistent with that of $Ba_2Be_2B_2O_7$, and the doping of the $Dy^{3+}$ ion does not noticeably affect the crystal structure of the prepared borates.

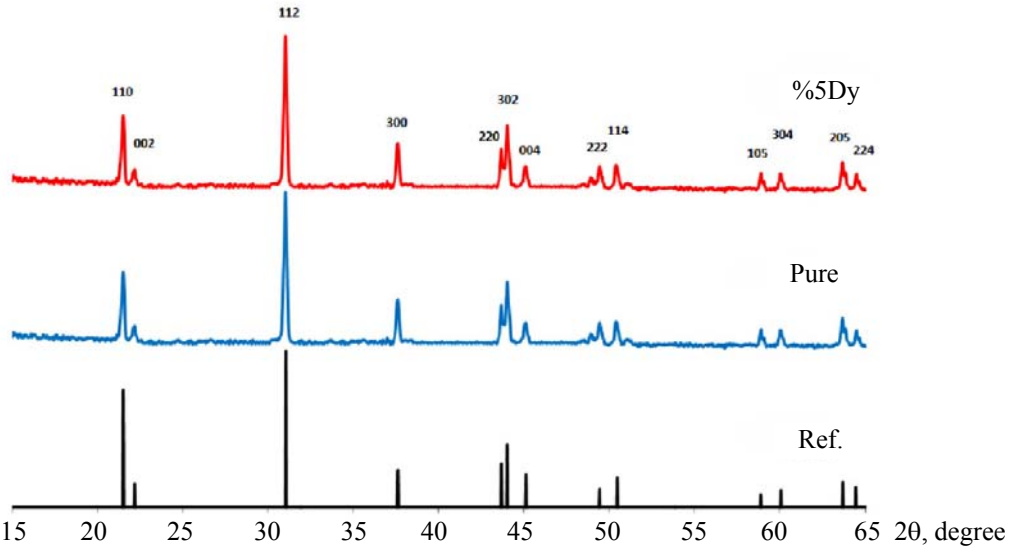


Fig. 1. XRD pattern obtained for $Ba_{1.95}Dy_{0.05}Be_2B_2O_7$ and $Ba_2Be_2B_2O_7$.

*Photoluminescence characterization.* Figure 2a shows the photoluminescence excitation (PLE) spectra (within the range 200–500 nm) of $Ba_{1.95}Dy_{0.05}Be_2B_2O_7$ phosphors, which were measured with 575 nm emission. The excitation spectrum consists of a charge transfer band (CTB) of $Dy^{3+}$–$O^{2-}$, the *f–d* spin-forbidden transition of $Dy^{3+}$, and the *f–f* transitions of $Dy^{3+}$. It can be seen that a strong band at 234 nm is assigned to a CTB of $Dy^{3+}$–$O^{2-}$ [19–21]. Also, the sharp band at 296 nm was assigned to the *f–d* spin-forbidden transition of $Dy^{3+}$ [22–26]. Finally, the excitation peaks between 325 and 500 nm are the *f–f* transitions of $Dy^{3+}$, which are attributed to the electronic transitions. Thus, the peaks at 325, 351, 366, 388, 426, 453, and 472 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 [25, 26].

Figure 2b shows the emission spectra of the $Ba_{1.95}Dy_{0.05}Be_2B_2O_7$ phosphors excited by 351 nm. Three peaks were observed in the visible region, i.e., blue at 483 nm, yellow at 575 nm, and red at 667 nm, and they were attributed to the transitions from the $^4F_{9/2}$ state to the $^6H_{15/2}$, $^6H_{13/2}$, and $^6H_{11/2}$ states, respectively [25–29]. The peak at 667 nm was weaker than the other two peaks. As seen in the emission spectra, the intensity of transition ($^4F_{9/2}\rightarrow{}^6H_{13/2}$) was stronger than the other two transitions, and it is referred to as the forced electric dipole transition. This transition is extremely affected by the outside surrounding environment [30–32].

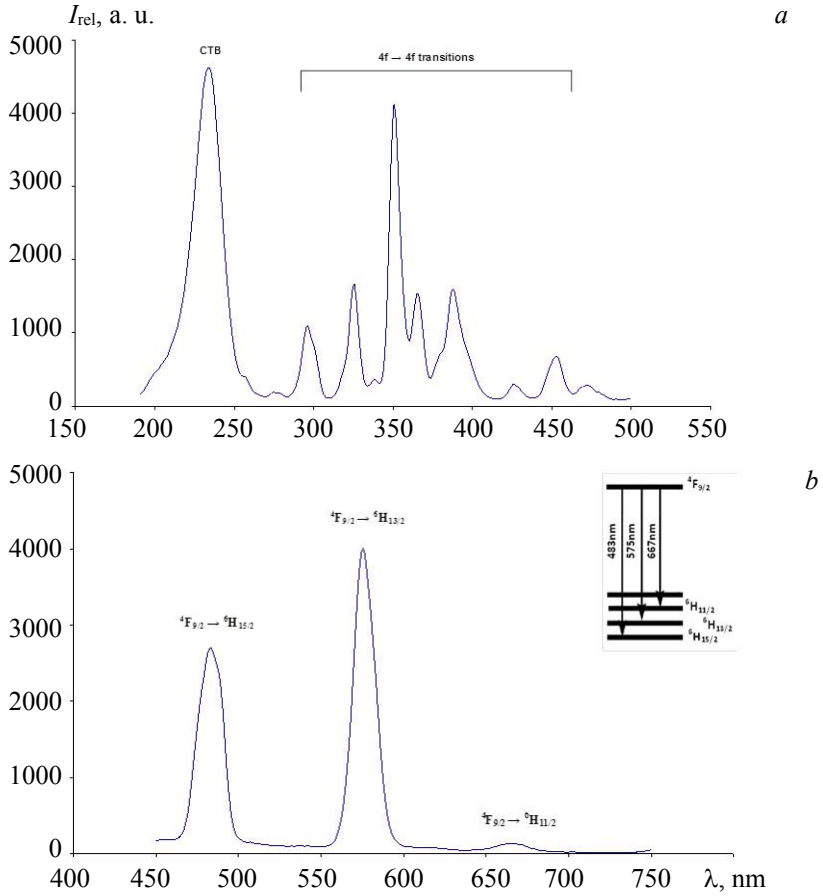


Fig. 2. The excitation (a) and emission (b) spectra of $Ba_{2-x}Dy_xBe_2B_2O_7$ ($x$ = 0.05) at room temperature, $\lambda_{em}$ = 575 nm (a), $\lambda_{exc}$ = 351 nm (b).

Figure 3 shows the dependence of the emission intensity on the $Dy^{3+}$ concentration for the $Ba_{2-x}Dy_xBe_2B_2O_7$ ($0.04 \leq x \leq 0.07$). The positions of the peaks of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ have not displayed definitive changes with different $Dy^{3+}$ doping concentrations. When the $Dy^{3+}$ concentration was increased in $Ba_2Be_2B_2O_7$, the peak intensity of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ increased and reached its maximum value at 0.05 mol. After this critical concentration is reached, the peak intensity of $Ba_2Be_2B_2O_7$:$Dy^{3+}$ decreases because of concentration quenching [19, 26–28].

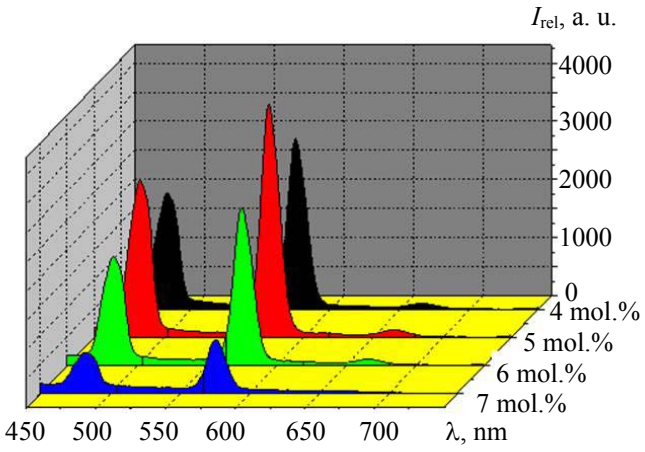


Fig. 3. Emission spectra of $Dy^{3+}$ (4, 5, 6, and 7 mol.%): $Ba_2Be_2B_2O_7$ phosphors ($\lambda_{exc}$ = 351 nm).

**Conclusions.** $Ba_2Be_2B_2O_7:Dy^{3+}$ materials were prepared and characterized by a combustion method and XRD analysis, respectively. The photoluminescence of $Ba_2Be_2B_2O_7:Dy^{3+}$ was investigated by a fluorescence spectrometer. The photoluminescence excitation spectrum of $Dy^{3+}$ is composed of a charge transfer band at 234 nm, the *f–d* spin-forbidden transition at 296 nm, and *f–f* transitions between 325 and 500 nm. The emission spectrum is composed of three bands that correspond to the transitions from the $^4F_{9/2}$ to the $^6H_{15/2}$ (483 nm), the $^6H_{13/2}$ (575 nm), and the $^6H_{11/2}$ (667 nm). Finally, different mole ratios of $Dy^{3+}$-doped $Ba_2Be_2B_2O_7$ were prepared, and their photoluminescence properties were studied in detail. The optimal concentration of $Dy^{3+}$ ions in $Ba_2Be_2B_2O_7$ was found to be 0.05 mol. Consequently, a novel borate-based material was prepared for the first time and may be considered as suitable luminescent material for the improvement of new white light-emitting diode applications.

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