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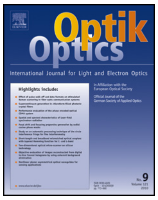

Original research article

Synthesis and luminescence of a new yellowish phosphor $PbGd_{1-x}B_7O_{13}:xDy^{3+}$

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ABSTRACT

A series of phosphors $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ (x = 0–0.14) were synthesized by the high temperature solid-state reaction method. The as-prepared products were characterized by powder X-ray diffractometer (XRD) and photoluminescence spectrometer (PL). The results indicate that $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ exhibits two emission peaks: the blue emission at around 488 nm due to $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and the yellow emission at around 572 nm due to $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition. The optimum doping concentration was found to be 6 mol% for Dy^{3+} ion. The commission international Del'Eclairage (CIE) chromaticity coordinates of the phosphors were about (0.394, 0.463), corresponding to yellowish color.

1. Introduction

Considerable attention has been attracted on exploring new phosphors owing to the demands of white light emitting diodes (W-LEDs) and plasma display panels (PDPs) [1–3]. Multicolor phosphors for W-LEDs and PDPs are required to have high colorimetric purity, proper decay time and high efficiency under UV or near-UV light excitation. A phosphor is usually composed of a host matrix and some activator ions. Among various host materials, inorganic borates posses low sintering temperature, low cost, broad band gap, high luminous efficiency, and high chemical stability [4–6].

On the other hand, Dy^{3+} ions can serve as efficient activators due to the intense fluorescent transitions in the blue region corresponding to the $^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and yellow region corresponding to the $^4F_{9/2} \rightarrow {}^6H_{13/2}$ [7]. In recent years, various Dy^{3+} activated borates have been reported as promising candidates for phosphors with high performance [8–10]. The Dy^{3+} ions within these phosphates possess unique optical behavior and have paved the way for the development of optical phosphors. Our previous study has succefully provied a new polyborate compound $PbGdB_7O_{13}$ [11]. Up to now, the phosphor of Dy^{3+} doped $PbGdB_7O_{13}$ has never been investigated. In this work, we will report the synthesis and luminescent properties of Dy^{3+} activated $PbGdB_7O_{13}$.

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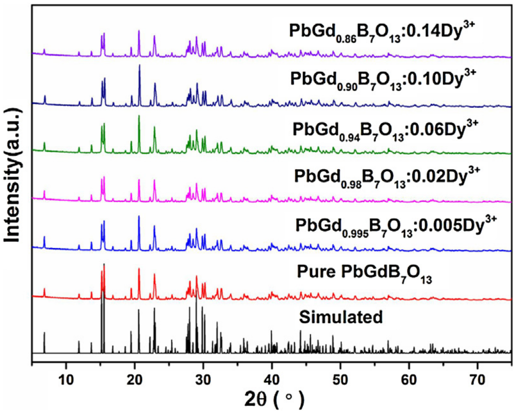

Fig. 1. XRD patterns of samples $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ ($0 \le x \le 0.14$) compared to the simulated data from single-crystal data.

2. Experimental section

2.1. Preparation

All of the reaction materials, Pb_3O_4 (≥99.5%, Shanghai Reagent Factory), H_3BO_3 (≥99.0%, Shanghai Reagent Factory), Gd_2O_3 (≥99.9%, Shanghai Reagent Factory) and Dy_2O_3 (≥99.9%, Shanghai Reagent Factory), were used without further purification. All powder samples of $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ (x = 0, 0.005, 0.02, 0.06, 0.10, 0.14) were obtained in quantitative yield by the solid state reaction of a mixture of Pb_3O_4, H_3BO_3, Gd_2O_3 and Dy_2O_3 in the stoichiometry molar ratio. The mixture was ground with an agate mortar and then pressed into a pellet to ensure optimal homogeneity and reactivity. The pellet was transferred to a 50 ml platinum crucible, which was placed into a muffle furnace heated to 760 °C in the open air for 40 h. In this stage, intermediate grindings were performed every ten hours to improve crystallinity.

2.2. Characterization

X-Ray powder diffraction (XRD) analysis was performed on a Rigaku DMax-2500/PC powder diffractometer, which uses graphite monochromated CuKα radiation in the angular range $2\theta = 5–75°$ with a step size of 0.02°. Photoluminescence (PL) spectra and the life time test were carried out using an FLS920 Edinburgh Analytical Instrument apparatus. A standard Xe900 continuous-wave xenon lamp (450 W) was used as the excitation source for steady-state measurements (stimulation slit width: 1.65 nm, emission slit width: 1.65 nm). The PL excitation and emission spectra was recorded with the step width of 1 nm and integration time of 0.2 s.

3. Results and discussion

3.1. Crystal structure

Single crystal structure of $PbGdB_7O_{13}$ has been studied in our previous work [11]. Its structure can be described as 2D layer structure that is composed of $[B_7O_{13}]_\infty$ layers, $[Gd]_\infty$ layers, and Pb_2O_8 dimers. The Pb_2O_8 dimers are encapsulated in a $[B_7O_{13}]_\infty$ layer to compensate the charge balance and to maintain structure stability. The XRD patterns of samples $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ (x = 0–0.14) and simulated from single crystal date of $PbGdB_7O_{13}$ were presented in Fig. 1. It can be clearly observed that all peaks can be indexed to the pure $PbGdB_7O_{13}$ phase and no impurity phase was observed in all samples. Therefore, we confirmed that the solid solutions $PbGd_{1-x}B_7O_{13}:xDy^{3+}$ have been formatted. If the reaction temperature increases to 850 °C, the samples will partially melt, resulting in some unknown impurity phases.

3.2. Excitation and emission spectra

As shown in Fig. 2 (left), the excited bands centered at 274 nm (Gd^{3+}:$^8S_{7/2} \to {}^6I_{J(J=11/2,9/2,7/2)}$), 311 nm ($Gd^{3+}$:$^8S_{7/2} \to {}^6P_J$), 324 nm ($Dy^{3+}$:$^6H_{15/2} \to {}^6P_{3/2}$), 348 nm ($Dy^{3+}$:$^6H_{15/2} \to {}^6P_{7/2}$), 363 nm ($Dy^{3+}$:$^6H_{15/2} \to {}^6P_{5/2}$), and 385 nm ($Dy^{3+}$:$^6H_{15/2} \to {}^4M_{21/2}$) are observed on monitoring the 572 nm emission of Dy^{3+} ions [12]. The strongest one was located in the 348 nm. The existence of two weak bands (Gd^{3+}:$^8S_{7/2} \to {}^6I_{J\,(J=11/2,9/2,7/2)}$) and 311 nm ($Gd^{3+}$:$^8S_{7/2} \to {}^6P_J$) reveals the occurrence of charge transfer from Gd^{3+} ions to Dy^{3+} ions. On the other hand, the excitation properties reveal that phosphor $PbGd_{0.94}B_7O_{13}:0.06Dy^{3+}$ can be effectively excited by near-UV light (350–420 nm).

As shown in Fig. 2 (right), the emission spectrum of Dy^{3+} ions mainly has two emission regions: blue and yellow. The blue emission in the 470–490 nm wavelength range can be attributed to the $^4F_{9/2} \to {}^6H_{15/2}$ ground-state transition of Dy^{3+}