Synthesis and luminescent properties of Ln$^{3+}$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) -doped Bi$_2$ZnB$_2$O$_7$ phosphors

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Abstract

The new phosphors Bi$_2$ZnB$_2$O$_7$: Ln$^{3+}$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) were synthesized by solid-state reaction technique. The obtained phosphors were investigated by means of X-ray powder diffraction (XRD), photoluminescence excitation and emission spectra with the aim of enhancing the fundamental knowledge about the luminescent properties of Eu$^{3+}$ and Dy$^{3+}$ ions in the Bi$_2$ZnB$_2$O$_7$ host lattice. XRD analysis shows that all these compounds are of a single phase of Bi$_2$ZnB$_2$O$_7$. The excitation and emission spectra of Bi$_2$ZnB$_2$O$_7$: Ln$^{3+}$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) at room temperature show the typical 4f-4f transitions of Eu$^{3+}$ and Dy$^{3+}$, respectively. The hypersensitive transitions of $^5D_0 \rightarrow ^7F_2$ (Eu$^{3+}$) and $^4F_{9/2} \rightarrow ^6H_{13/2}$ (Dy$^{3+}$) are relatively higher than those of the insensitive transitions in Bi$_2$ZnB$_2$O$_7$. It is conceivable that the Bi$_2$ZnB$_2$O$_7$ structure provides asymmetry sites for activators (Eu$^{3+}$, Dy$^{3+}$). The optimum concentrations of Eu$^{3+}$ and Dy$^{3+}$ ions in Bi$_2$ZnB$_2$O$_7$ phosphors are both $x = 0.05$.

Keywords: phosphor; Bi$_2$ZnB$_2$O$_7$; luminescent properties; concentration quenching

1 Introduction

Rare-earth ions have been extensively used as active ions in phosphors for several decades. They are characterized by a partially filled 4f shell that is well-shielded by the 5s$^2$ and 5p$^6$ orbitals. The f-f transitions of trivalent rare-earth ions (except Ce$^{3+}$ ion) is forbidden by the parity selection rule, so the emission of trivalent rare-earth ions (except Ce$^{3+}$ ion) doped phosphors yield sharp lines in the optical spectra and a good color rendering index [1]. Recently, the development of field emission displays (FEDs), plasma display panels (PDPs) and white light emitting diode (LED) has accelerated the research into rare-earth ions doped luminescent materials [2–4].

Melilites, with the general formula A$_2$X$_2$O$_7$, are a series of significant compounds expected as excellent hosts for luminescent materials. In the past decades, many melilite-type aluminates, silicates and gallates have been reported, in which the luminescent properties of rare-earth ions were extensively investigated [5–7]. However, few researches have been concerned with melilite-type borates. In 1997, Liebertz et al. [8] was the first to report a ternary bismuth borate, i.e., Bi$_2$ZnB$_2$O$_7$. Thereafter, the structure and the nonlinear optical properties of Bi$_2$ZnB$_2$O$_7$ were studied by Jacques et al. [9]. The Bi$_2$ZnB$_2$O$_7$ compound is a derivative of melilite with a noncentrosymmetric orthorhombic structure type that consists of ZnB$_4$O$_6^-$ layers alternating with layers of Bi$^{3+}$ cations. The borate layers in Bi$_2$ZnB$_2$O$_7$ contain both tetrahedral B$_2$O$_4$ and triangular B$_2$O$_3$ diborate groups. The Bi$^{3+}$ cations occupy two distinct sites, both asymmetrically six-coordinated with three short Bi-O bonds in the range of 2.14–2.31 nm.

Recently, the luminescent properties of Sm$^{3+}$-doped Bi$_2$ZnB$_2$O$_7$ were investigated [10]. In this paper, Eu$^{3+}$ and Dy$^{3+}$ ion-activated Bi$_2$ZnB$_2$O$_7$ were prepared by a solid-state reaction and the structural character and photoluminescent properties of these phosphors were studied.

2 Experimental

The phosphors (Bi$_{1-x}$Ln$_x$)$_2$ZnB$_2$O$_7$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) ($x = 0.01$, 0.03, 0.05, 0.07, 0.09) were synthesized by conventional solid-state reaction. The starting materials were Bi$_2$O$_3$ (A. R.), ZnO (A. R.), H$_3$BO$_3$ (A. R.), Eu$_2$O$_3$ (99.99%) and...
Dy$_2$O$_3$ (99.99%). The stoichiometric amount of the raw materials were thoroughly mixed by grinding in an agate mortar and then heated to 873 K for 60 h in several stages with intermediate re-mixing. The XRD patterns were recorded in the range of 10° ≤ 2θ ≤ 64° by using a Rigaku D/max 2200 Diffractometer with Cu K radiation at 40 kV, 30 mA. The photoluminescent excitation and emission spectra of (Bi$_{1-x}$Ln$_x$)$_2$ZnB$_2$O$_7$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) were measured by a JOBIN YVON FL3-21 spectrofluorometer equipped with a 450 W xenon lamp at room temperature.

3 Results and discussion

3.1 Structure properties

It was reported that Bi$_2$ZnB$_2$O$_7$ has an orthorhombic structure with the space group Pba$_2$ [9]. The purity of (Bi$_{1-x}$Ln$_x$)$_2$ZnB$_2$O$_7$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) (x = 0.01, 0.03, 0.05, 0.07, 0.09) were checked by X-ray diffraction (XRD). As samples, the patterns of (Bi$_{1-x}$Ln$_x$)$_2$ZnB$_2$O$_7$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) (x = 0.05) are shown in Fig. 1. It can be concluded that the as-synthesized samples are generally of a single phase that is consistent with the XRD pattern of Bi$_2$ZnB$_2$O$_7$ reported by Jacques et al. [9]. Some weak peaks (■) are due to the minor impurity in the H$_3$BO$_3$ phase. The substitute of Ln$^{3+}$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) ions does not induce any significant phase change. It is reasonable because Eu$^{3+}$ and Dy$^{3+}$ ions show the same valence (3+) and close efficient ionic radius with Bi$^{3+}$ ions, 94.7, 91.2 and 103 pm in the site of CN = 6, respectively [11].

3.2 Luminescent properties of Eu$^{3+}$-doped Bi$_2$ZnB$_2$O$_7$

Fig. 2 presents the photoluminescent excitation and emission spectra of Eu$^{3+}$ ion-doped Bi$_2$ZnB$_2$O$_7$. All the absorption and emission peaks are marked by the numbers 1–13. The excitation spectrum of Bi$_2$ZnB$_2$O$_7$:Eu$^{3+}$ monitoring at 614 nm is shown in Fig. 2(1). The excitation spectrum consists of two parts. A broad band in the range of 250–350 nm (peak 1) is the charge-transfer state (CTS) which is ascribed as ligand-to-Eu$^{3+}$ charge-transfer transitions (LMCT) [12]. The sharp peaks in the range from 360 to 584 nm (peaks 2–8) are associated with typical intra-4f transitions of the Eu$^{3+}$ ion. The two main sharp peaks centered at about 394 nm (peak 4) and 465 nm (peak 6) correspond to the $^7F_0 \rightarrow ^5L_6$ and $^7F_0 \rightarrow ^5D_2$, respectively. In comparison with the conventional Eu$^{3+}$-doped phosphors [13–16], it is noteworthy that the intensity of CTS transition is significantly weaker than that of intra-4f transitions. This phenomenon is uncommon, because the typical Eu$^{3+}$-activated phosphors always show strong CTS transition band absorptions at around 200–300 nm. This phenomenon is also observed in some other phosphors such as AgGd(WO$_4$)$_2$,(MoO$_4$)$_x$:Eu$^{3+}$ (x = 0–2) and LaAlGd$_2$O$_7$:Eu$^{3+}$ [17–18]. There is still no reasonable explanation for this experimental phenomenon. The strong absorption of ultraviolet (394 nm) and visible blue light (465 nm) makes the phosphor more suitable for LED based on Near UV or blue chips.

![Fig. 1 XRD patterns of (Bi$_{1-x}$Ln$_x$)$_2$ZnB$_2$O$_7$ (Ln$^{3+}$ = Eu$^{3+}$, Dy$^{3+}$) (x = 0.05)](image)

![Fig. 2 Excitation and emission spectra of Bi$_2$ZnB$_2$O$_7$:Eu$^{3+}$](image)

(1) Excitation spectra (λ$_{em}$ = 614 nm); (2) Emission spectra (λ$_{ex}$ = 394 nm); (3) Emission spectra (λ$_{em}$ = 465 nm)

The emission spectra of Bi$_2$ZnB$_2$O$_7$:Eu$^{3+}$ phosphor are shown in Fig. 2(2) and Fig. 2(3). Both emission spectra are composed of several narrow spectral lines and show no significant changes in the shape and peak position under excitation wavelengths at 394 and 465 nm in the 500–730 nm range. These narrow lines (peaks 9–13) could be assigned to the transitions from the $^7D_0$ to $^5F_{J}$ (J = 0–4) of Eu$^{3+}$ ions. The electric dipole transition $^5D_0 \rightarrow ^5F_1$ with J = 2 is hypersensitive, and the intensity is strongly influenced by the local environment [19]. However, the magnetic dipole transition $^5D_0 \rightarrow ^5F_2$ is insensitive to the local symmetry. When the Eu$^{3+}$ ions occupy non-centrosymmetric sites, the emission intensity ratio of the $^5D_0 \rightarrow ^5F_1$ to $^5D_0 \rightarrow ^5F_2$ is smaller. The emission spectra of the studied sample exhibits a weak emission of $^5D_0 \rightarrow ^5F_1$ transition at 593 nm (peak 10) and a