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Luminescence properties of BaB_8O_{13}:Eu under UV and VUV excitation

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Abstract: The phosphor BaB_8O_{13}:Eu^{3+} were synthesized by solid-state reaction, and their luminescent properties were studied under 254 and 147 nm excitation. The excitation spectrum showed two broad bands in the range of 100–300 nm: one was the host lattice absorption with the maxima at 160 nm and the other was Ba-O absorption overlapped with the CT band of Eu^{3+}, which indicated that the energy of the host lattice absorption could be efficiently transferred to the Eu^{3+}. The overlapped bands were tended to separate when monitored by different wavelength, which indicated that at least two Ba^{2+} sites were available in BaB_8O_{13}. The emissions of Eu^{3+} (612 nm) and Eu^{2+} (405 nm) were both observed in the emission spectra of BaB_8O_{13}:Eu^{3+} under the excitation of either 254 or 147 nm. With the doping concentration of Eu^{3+} increasing, the 612 nm emission was enhanced while 405 nm emission was decreased under 254 nm excitation, which was due to the persistent energy transfer from Eu^{2+} to Eu^{3+}. While under 147 nm excitation, the 612 nm emission was quenched and the 405 nm emission was enhanced. It was concluded that the preferential excitation of Eu^{2+} under 147 nm excitation was one of the reasons for this facts.

Keywords: phosphor; BaB_8O_{13}: Eu; photoluminescence; rare earths

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Much attention has been paid to phosphors for vacuum ultraviolet (VUV) due to the demands of plasma display panels (PDP). This energy domain implies the use of wide band-gap insulators doped with optically active ions into which a visible luminescence can be activated[1]. For all VUV-excited phosphors, the current requirement is a high quantum efficiency which implies an efficient energy transfer from the host lattice to the activator. $(Y,Gd)BO_3$:Eu is widely used in PDP because of its high photoluminescence efficiency, chemical stability, and large color gamut. However, this phosphor yields orange red light due to the presence of the rather intense emission line at 592 nm, which is ascribed to the magnetic dipole transition $^5D_0\rightarrow^7F_1$ of Eu^{3+}. The pure red emission around 612 nm is ascribed to the electric dipole transition of $^5D_0\rightarrow^7F_2$ of Eu^{3+}, and that can be obtained in the lack of inversion symmetry at the Eu^{3+} site in the lattice[2]. So, great efforts have been made to discover new host materials as well as activators with high performance for phosphor applications[3,4]. Trivalent europium ions based phosphors play an important role, because Eu^{3+} doped inorganic phosphors show potential applications in optical displays due to strong red emission from Eu^{3+}[5,6].

The BaB_8O_{13} structure is built up by two separate interlocking three-dimensional networks as triborate and pentaborate groups and forms BO_3 and BO_4 tetrahedral units[7]. It consists of two BO_4 tetrahedral groups and six BO_3 triangular groups[8]. The rare-earth ions can be enclosed by such a big anion and isolated from each other. Since the interaction between the luminescence ions is weak, a rare-earth ion doped BaB_8O_{13} with highly efficient output luminescence is expected. BaB_80_{13}:Eu has been reported to be an efficient photoluminescence material under UV excitation[4], and the ultraviolet (UV) excited emission of BaB_8O_{13}:R (R=Sm^{2+}, Yb^{2+}, Eu^{2+},Tb^{3+}, Tm^{3+})[9–11] were reported. In previous studies, it was reported that the BO_4 tetrahedral units showed strong absorption of the excitation energy under VUV region[12–14]. Furthermore, the study on luminescence properties of BaB_8O_{13}:Eu is helpful to understand the luminescence mechanisms of rare earth doped phosphors in the VUV range. Finally, the photoluminescence properties of BaB_8O_{13}: Eu^{3+} have scarcely been investigated in VUV region. Therefore, in this paper, the luminescence properties of BaB_8O_{13}:Eu^{3+} in UV-VUV range were studied for the purpose of exploiting a new red VUV phosphor.

1 Experimental

BaB_8O_{13}:Eu^{3+} phosphors were prepared by solid-state re-

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action. $BaCO_3$ (A.R.), Eu_2O_3(99.99%), $SrCO_3$(A.R.), $CaCO_3$ (A.R.) and H_3BO_3(99.9%) were used as staring materials. An excess of the boric acid was used to compensate for the evaporation of H_3BO_3 in high-temperature solid-state reaction. After intimately mixing the staring materials, it was heated at 300 °C for 2 h, then ground and reheated at 800 °C for another 3 h. The obtained samples were white powder. The series samples of $Ba_{1-x}Eu_xB_8O_{13}$ were prepared by the same process.

All the samples were characterized with Rigaku D/max-2000 powder X-ray diffraction (XRD) using Cu Kα (λ= 0.15418 nm) radiation. The excitation and emission spectra were measured at room temperature by using an Edinburgh instruments FLS920T combined fluorescence lifetime and steady state spectrophotometer with Xe900 and VM504 vacuum monochromator as excitation source. The VUV excitation spectra were corrected by dividing the excitation intensity of sodium salicylate at same measurement conditions.

2 Results and discussion

Fig.1 showes the powder XRD patterns of $Ba_{1-x}Eu_xB_8O_{13}$ ($0\leq x\leq 0.2$). When the doping concentration of Eu^{3+} was ≤15%, all the samples could be identified as single phase in terms with JCPDF(20-0097), and there was no second phase observed. When doping concentration of Eu^{3+} was above 15%, the impurity phase appeared. The intensity of XRD peaks was strong, indicating the high crystallinity.

Fig.2 shows the excitation spectra of $Ba_{1-x}Eu_xB_8O_{13}$ ($0<x<0.2$) monitored at 612 nm with Xe900 as excitation source. A broad band at 246 nm in the excitation spectra is assigned to the charge transition band (CT) of O^{2-}–Eu^{3+} and the excitation peaks around 392 nm are due to the intra-configuration $4f^6$ excitation peaks of Eu^{3+}. The CT band of Eu^{3+} in the BaB_8O_{13}:Eu^{3+} is increased with the increasing concentration of Eu^{3+}. When the concentration of Eu is 15%, the excitation intensity is the strongest.

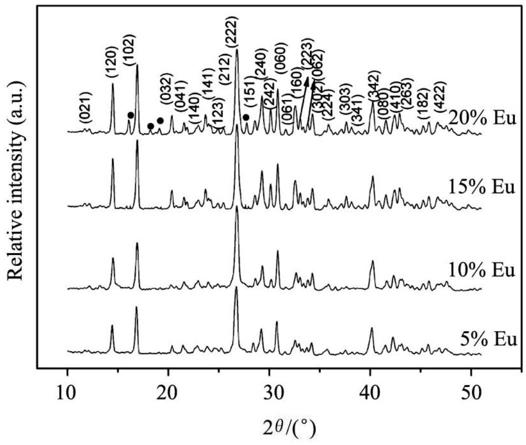

Fig.1 XRD patterns of the $Ba_{1-x}Eu_xB_8O_{13}$ ($0\leq x\leq 0.2$)

The emission spectra of BaB_8O_{13}:Eu^{3+} are recorded at different concentration of Eu^{3+}. Fig.3 shows the emission spectra of $Ba_{1-x}Eu_xB_8O_{13}$ ($0<x<0.2$) under 254 nm excitation. The main peak due to the electric dipole transition of $^5D_0$–$^7F_2$ of Eu^{3+} was observed at 612 nm, which was much higher than the emission of magnetic $^5D_0$–$^7F_1$ transition at 591 nm. This indicated that Eu^{3+} occupied the crystallographic sites without inversion symmetry. In alkaline earth borates such as SrB_4O_7[15], SrB_6O_{10}, SrB_5O_9Cl and BaB_8O_{13}[16], when trivalent rare earth ions are substituted for the divalent cations, such as Sr^{2+} and Ba^{2+}, they may tend to be reduced to divalent by the negative hole of Sr^{2+} and Ba^{2+}. Furthermore, the structures in alkaline earth borates contained the tetrahedral BO_4 unit which can stabilize the divalent rare earth ions formed in the solid state reaction in air at high temperature. Because of the existence of Eu^{3+} and Eu^{2+} in the BaB_8O_{13}, the broad-band emission region at about 400–460 nm of Eu^{2+} also appeared in the emission spectra, which would be due to the parity-allowed electronic transitions of $4f^65d$-$4f^7$ of Eu^{2+}. Because the position of 5d levels depends strongly on the crystalline environment of Eu^{2+}, the changes in the energy levels between the excited and ground states can vary by tens of thousand of cm^{-1} for the same rare

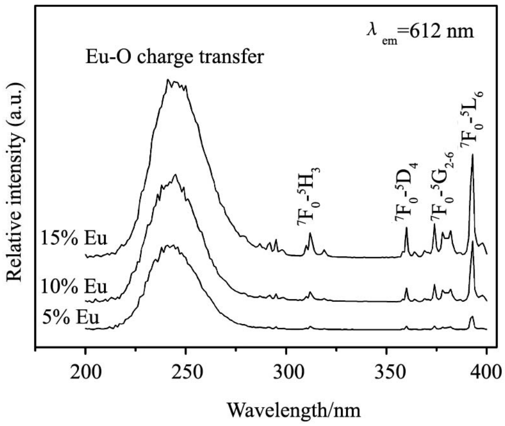

Fig.2 Excitation spectra of $Ba_{1-x}Eu_xB_8O_{13}$($0<x<0.2$) with Xe900 as excitation source

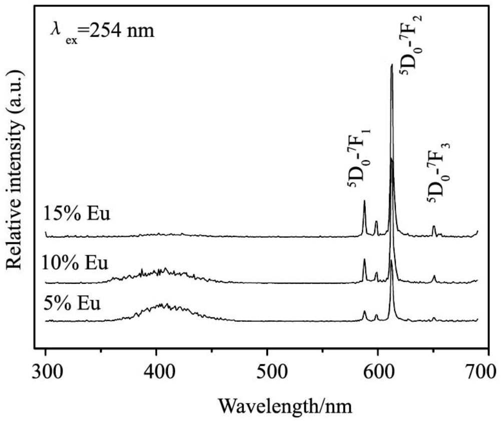

Fig.3 Emission spectra of $Ba_{1-x}Eu_xB_8O_{13}$($0<x<0.2$) (λ_{ex}=254 nm)