

A new red phosphor BaZr(BO₃)₂ doped with Eu³⁺ for PDP applications

*Lian-hua Tian, Byung-Yong Yu^a, Chong-Hong Pyun^a and Sun-il Mho**

Department of Molecular Science and Technology, Ajou University, Suwon 442-749, Korea

^aKorea Institute of Science and Technology, P.O.Box 131, Seoul 130-640, Korea

*E-mail: mho@ajou.ac.kr, Phone: +82-31-219-2599, Fax: +82-31-219-1615

Abstract

The photoluminescence (PL) properties are studied for a new phosphor BaZr(BO₃)₂ doped with Eu³⁺ activator ion. The excitation spectrum shows strong absorption in the vacuum ultraviolet (VUV) region with an absorption band edge at 200 nm. The PL spectrum shows the strongest emission at 615 nm corresponding to the electric dipole ⁵D₀ → ⁷F₂ transition of Eu³⁺, which results in a good color purity.

1. Introduction

Plasma display panels (PDPs) are most promising large size flat-panel information-display devices in which the pixels consist of small gas-discharge cells. The discharge gas most widely adopted in present PDPs is a mixture of Xe and other rare gases. Plasma resonance VUV radiation lines of Xe atoms at 147 nm and a molecular Xe at 173 nm are used for the phosphor excitation to emit visible luminescence [1-3].

Borates are of interest as host lattices for luminescent ions, because of their large band gap. The band edge transition absorbs efficiently the VUV photons generated by the Xe plasma. The Y_{0.65}Gd_{0.35}BO₃:Eu³⁺ had found application as a red phosphor in PDPs. A draw back of this phosphor is the presence of an intense ⁵D₀ → ⁷F₁ emission line at 593 nm in the orange region of the visible spectrum, so that the red emission color purity is not good enough [4]. Yttrium aluminum borate, YAl₃(BO₃)₄, is known to supply the non-centrosymmetric site for Eu³⁺ activator as the host lattice. Hence, (Y,Gd)Al₃(BO₃)₄:Eu³⁺ phosphor was recommended as a good red phosphor for PDP applications with excellent color purity [5].

In this work, BaZr(BO₃)₂ doped with Eu³⁺ is investigated as a new red phosphor due to the non-

centrosymmetric structure of the lattice site for europium ion and its high stability for PDP requirements. The major emission peak for Eu³⁺ activator in non-centrosymmetric site is the hypersensitive electric dipole ⁵D₀ → ⁷F₂ transition.

2. Experimental

The compounds of BaZr(BO₃)₂:Eu³⁺ was prepared by a typical solid state reaction. The stoichiometric mixtures of BaCO₃, ZrO₂, H₃BO₃, and activator Eu₂O₃ were heated at 1300°C for 2 hrs.

The VUV and UV excitation spectra in the wavelength range of 120-300 nm were measured at room temperature by a home-built VUV spectrometer [5], which is composed of a 30 W deuterium lamp (Acton Research Corp., ARC DS775-100), a vacuum monochromator (1200 line/nm; f.l. = 200 mm, D⁻¹ = 4 nm/mm; ARC VM502), a vacuum sample compartment, and a photomultiplier tube (PMT, ARC DA-780). A high vacuum of 1×10⁻⁵ Torr was maintained for the excitation monochromator and the sample compartment by a molecular pump (Alcatel, ACT200T). The VUV and UV excitation spectrum was corrected by sodium salicylate, whose quantum efficiency is almost constant in the region. The PL spectra were measured by a spectrofluorometer (Kontron SFM25), which is composed of a 150 W Xe high-pressure arc lamp, two monochromators (1200 line/nm; f.l. = 100 mm, D⁻¹ = 8 nm/mm), and a photomultiplier tube (PMT Hamamatsu R928) [6].

3. Results and discussion

The excitation spectrum of BaZr(BO₃)₂:Eu³⁺ shows the absorption of host lattice in the VUV region, with the band-edge wavelength at 200 nm as shown in Fig. 1(a). The band-edge absorption wavelength for Y_{0.65}Gd_{0.35}BO₃ is 175 nm as shown in Fig. 1(b) [5]. The strong Xe plasma emission lines at 147 nm and

173 nm are absorbed efficiently by the borates, $\text{BaZr}(\text{BO}_3)_2$, $\text{Y}_{0.65}\text{Gd}_{0.35}\text{BO}_3$ and $\text{YAl}_3(\text{BO}_3)_4$. In $\text{BaZr}(\text{BO}_3)_2:\text{Eu}^{3+}$, the charge transfer band of Eu^{3+} does not appear strongly in the excitation spectrum. The weak band at ca. 228 nm is thought to be the charge transfer band. The position and the intensity of charge transfer band depend strongly on the lattices; the strong charge transfer bands appear at 220 nm for $\text{Y}_{0.65}\text{Gd}_{0.35}\text{BO}_3$ and at 240 nm for $\text{YAl}_3(\text{BO}_3)_4$, respectively. The charge transfer from O_{2p} to Eu^{3+} in

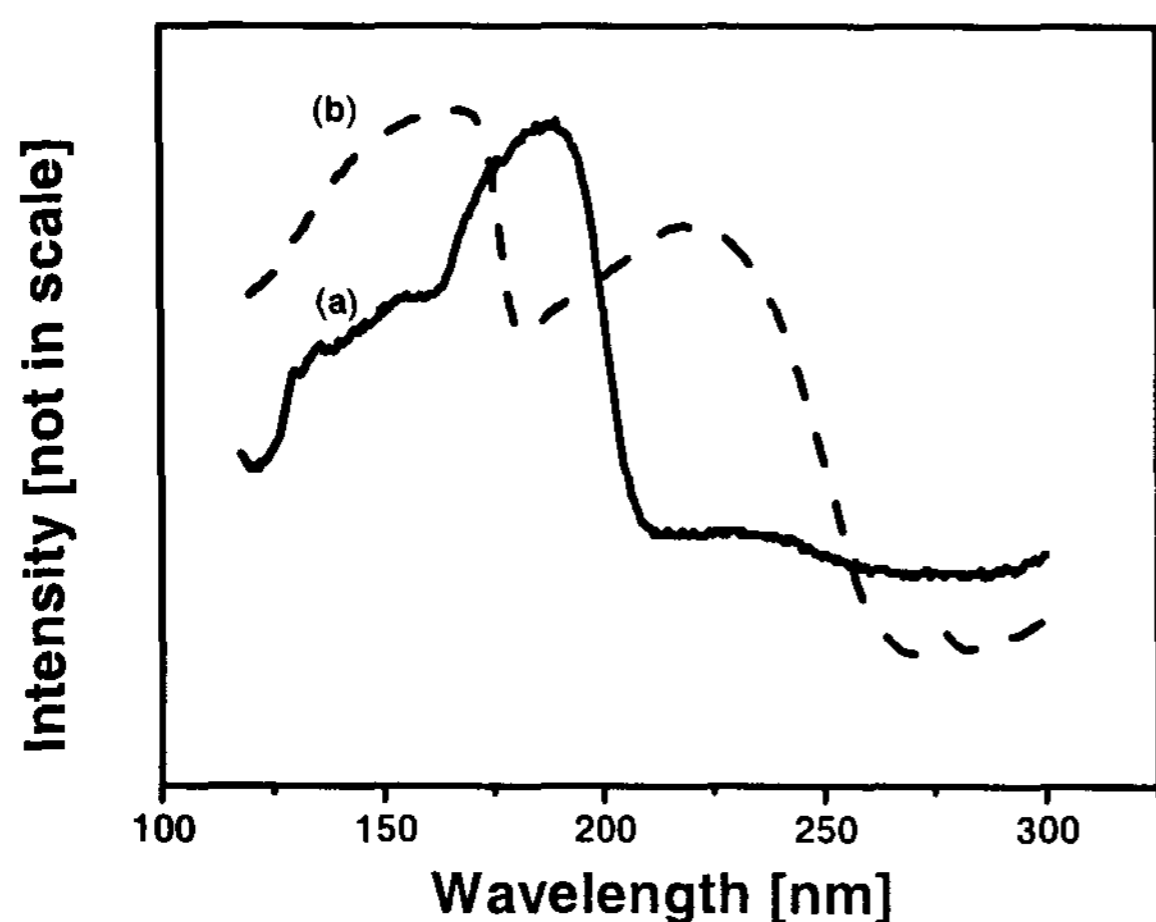


Fig. 1. The vacuum UV excitation spectra of (a) $\text{BaZr}(\text{BO}_3)_2:\text{Eu}^{3+}$ (10 mol%) and (b) $\text{Y}_{0.65}\text{Gd}_{0.35}\text{BO}_3:\text{Eu}^{3+}$ (10 mol%).

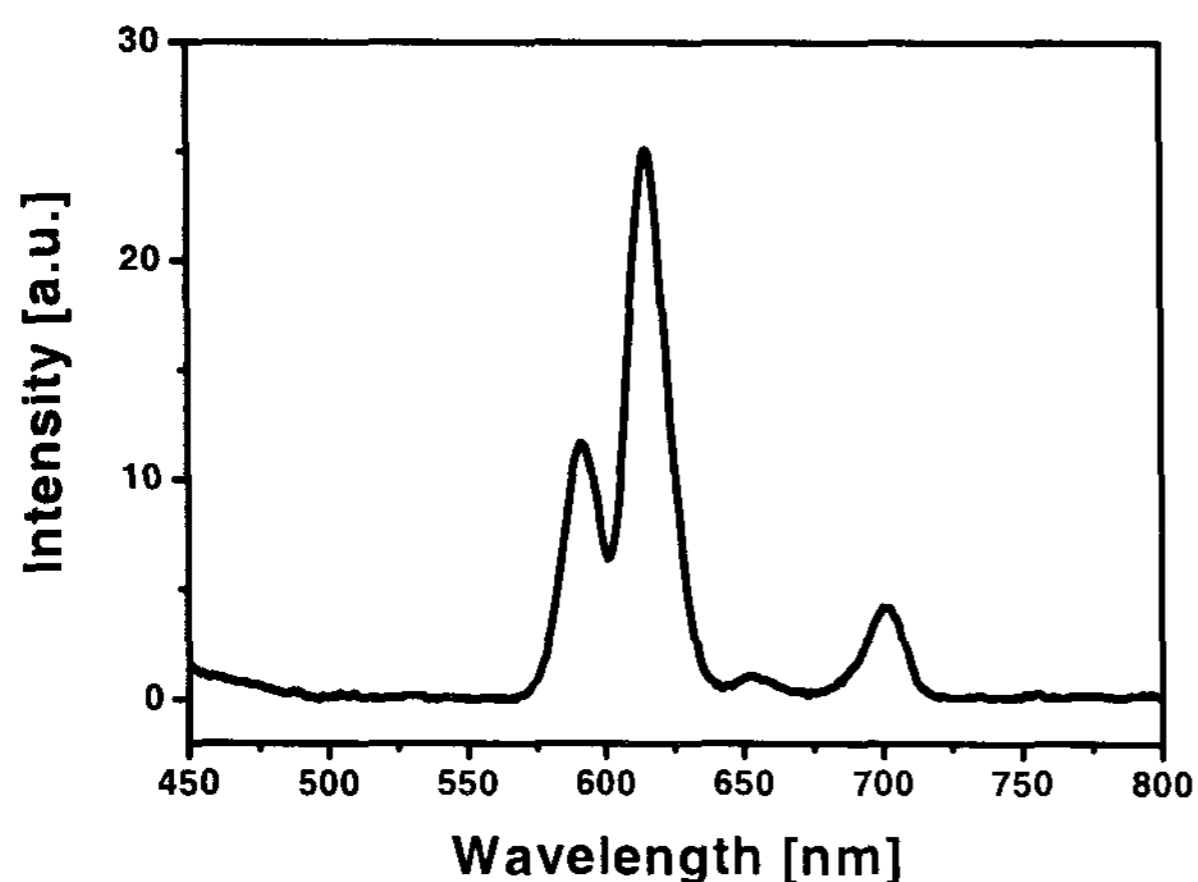


Fig. 2. Photoluminescence spectrum of $\text{BaZr}(\text{BO}_3)_2:\text{Eu}^{3+}$ (10 mol%) obtained with the excitation wavelength of 394 nm.

$\text{BaZr}(\text{BO}_3)_2$ lattices is very weak compared with that in YBO_3 and $\text{YAl}_3(\text{BO}_3)_4$ lattices. It is speculated that the 2p electrons of oxygen are tightly bound to zirconium ions and that the charge transfer to europium ion resulted very weak.

$\text{BaZr}(\text{BO}_3)_2$ crystallizes in the trigonal symmetry with space group R3c [7]. The structure derived from the dolomite-type with a doubling of the c parameter. Along the c-axis, alternated layers of Ba atoms and layers of Zr atoms are separated by planes of BO_3 groups. Ba centered distorted trigonal prisms is linked with six ZrO_6 octahedra and to six BO_3 groups. The activator Eu^{3+} occupies Ba^{2+} site, which does not have an inversion symmetry, so that the emission of electric dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ is stronger than magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ [8] as shown in Fig. 2. The strong emission line at 615 nm is due to the hypersensitive electric dipole transition of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$.

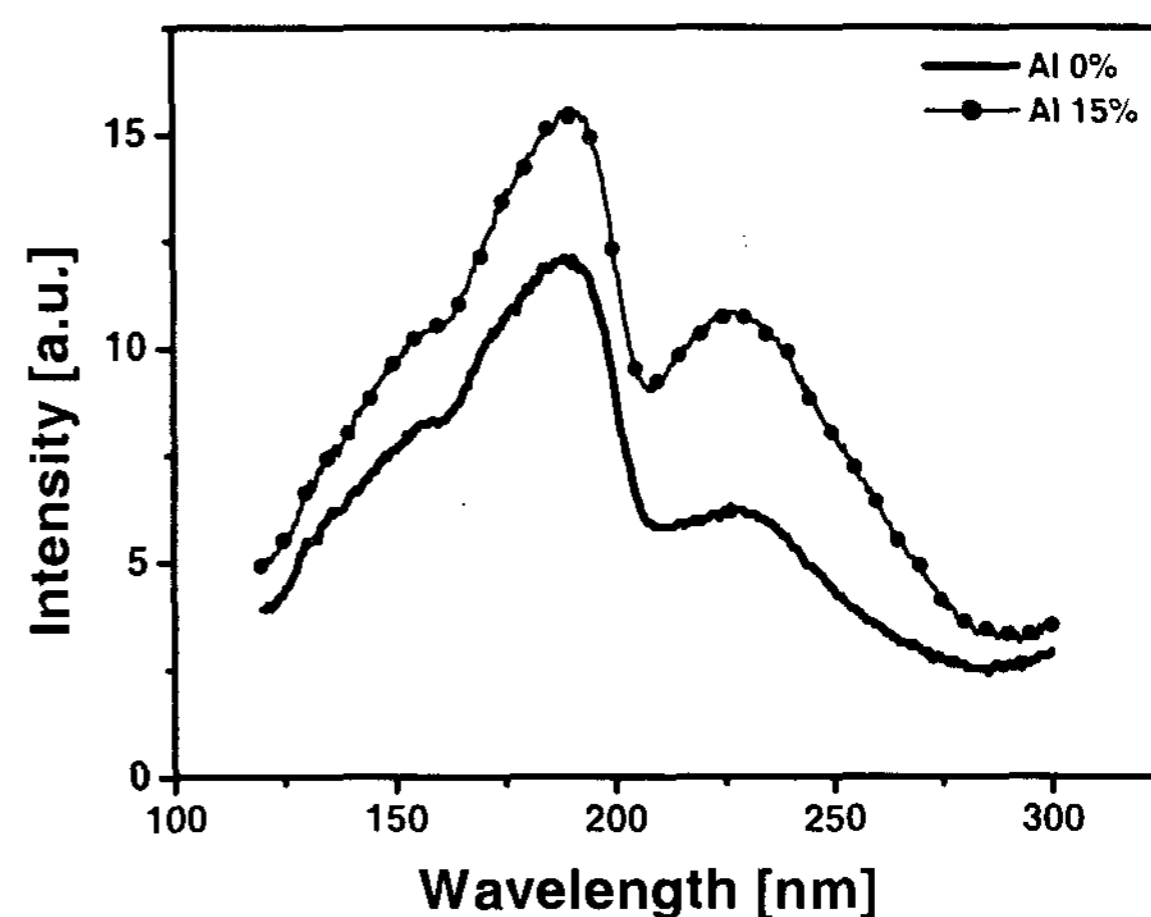


Fig. 3. The vacuum UV excitation spectra of $\text{BaZr}(\text{BO}_3)_2:\text{Eu}^{3+}$ (3 mol%) and co-doped with Al (15 mol%).

The weaker emission of 592 nm is due to the magnetic dipole transition ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$, which is insensitive to the site symmetry. Hence the intensity of pure red emission is stronger than that of Eu^{3+} in $\text{Y}_{0.65}\text{Gd}_{0.35}\text{BO}_3$ that has an inversion symmetry. The CIE chromaticity coordinates for this luminescence spectrum is (0.643, 0.356). The vacuum UV excitation and luminescence were enhanced by incorporation of

Al³⁺ into BaZr(BO₃)₂ lattices, as shown in Fig. 3. The aluminum incorporation enhanced both the band edge absorption of the host lattice and the charge transfer absorption.

4. Conclusion

A new red phosphor BaZr(BO₃)₂:Eu³⁺ is investigated for PDP applications. The emission at 615 nm is stronger than at 592 nm, due to the non-centrosymmetric structure of the host lattice. The excited spectrum shows strong band-edge absorption of host lattice in the VUV region. The strong Xe plasma emission lines at 147 nm and 173 nm are absorbed efficiently by this host, which results in strong luminescence. The PL spectrum shows the strongest emission at 615 nm corresponding to the electric dipole ⁵D₀ → ⁷F₂ transition of Eu³⁺, which results in a good color purity.

5. References

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