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VUV phosphors in the $SrO–B_2O_3–P_2O_5$ ternary system

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Abstract

Photoluminescence properties under vacuum ultraviolet (VUV, 147 nm) excitation were investigated for a new borophosphate compound. The new phosphor, $Sr_6BP_5O_{20}$, has a relatively strong absorption band in a short wavelength region because of the strong covalent characters of B–O and P–O bonds. The phosphor activated by Eu^{2+} showed a strong blue luminescence. The luminance is about 2.2 times as bright as a commercial blue phosphor, $BaMgAl_{10}O_{17}:Eu^{2+}$. The phosphor is an attractive candidate of new phosphors for plasma display panels and mercury-free fluorescent lamps.

Keywords: PDP; Mercury-free lamps; Phosphor; Borophosphate; $Sr_6BP_5O_{20}$

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1. Introduction

In white fluorescent lamps, ultraviolet (UV, 254 nm) irradiation from mercury vapor is converted into visible light by several kinds of phosphors. Poisonous mercury causes serious damage to both humans and the environment [1]. The EU has adopted waste electrical and electronic equipment (WEEE) and restrictions of the use of certain hazardous substances (RoHS) in electrical and electronic equipment on February 13, 2003. WEEE and RoHS restrict the use of certain hazardous substances in electrical and electronic equipment. The use of six hazardous substances, including mercury and lead, will be prohibited from July 1, 2006. Xenon-gas based discharge is a promising candidate as an excitation source of mercury-free fluorescent lamps [2]. Because a main emission peak of this discharge is located at a fairly shorter wavelength (147 nm) than that of the conventional mercury discharge (254 nm), highly efficient VUV phosphors are required for mercury-free fluorescent lamps and plasma display panels (PDP). Although a current blue phosphor, $BaMgAl_{10}O_{17}:Eu^{2+}$ ($BAM:Eu^{2+}$), shows efficient blue emission under VUV excitation, it undergoes great thermal degradation during heat processing for PDP production [3].

This study evaluated a system of $AO–B_2O_3–P_2O_5$ ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$) doped with Eu^{2+} as a luminescence center. Because boron and phosphorous can form rigid BO_4 and PO_4 units in oxides systems, respectively, oxides in the ternary system should have a sufficiently large energy band gap. Such a band gap is expected to respond to excitation by high-energy VUV light.

2. Experimental

Polycrystalline samples of $AO–B_2O_3–P_2O_5:Eu^{2+}$ ($A = Ca^{2+}, Sr^{2+}, Ba^{2+}$) were synthesized using a conventional solid-state reaction. The starting material was a stoichiometric mixture of $CaCO_3$ (purity 99.9%), $SrCO_3$ (purity 99.9%), $BaCO_3$ (purity 99.9%), H_3BO_3 (purity 99.5%), $(NH_4)_2HPO_4$ (purity 99.0%) and Eu_2O_3 (purity 99.99%). The mixture was heated in air at 873 K for 12 h.

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The sample powders were pressed into 15 mm diameter disk-shaped pellets of 1 mm thickness under 30 MPa for 10 min. The pellets were heated at 1173–1273 K for 1–24 h in a reduction atmosphere (Ar:H_2 = 95:5).

Powder X-ray diffraction data were obtained using a diffractometer (MX-Labo; Mac Science Ltd.). The data were collected at a step-scanning mode in the 2θ range of 5–60° with a 0.02° step width. Excitation and emission spectra in the UV range were measured for the powder sample using a spectrofluorometer (FP-6500/6600; Jasco Inc.). Photoluminescence spectra in the VUV region were recorded under VUV excitation (146 nm) using a D_2 lamp. Relative luminance of the phosphors under VUV excitation (lamp: UER20H-146VA; Ushio Inc.) was recorded using a luminance colorimeter (BM-7; Topcon Corp.).

3. Results and discussion

3.1. Crystal structure

In the AO–B_2O_3–P_2O_5 (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) ternary system, three compounds – $ABPO_5$ and $A_3BP_3O_{12}$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) – and the new $Sr_6BP_5O_{20}$ were found to crystallize (Table 1). In all samples with various starting compositions, the compounds of $ABPO_5$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) [4–9] were obtained as a single phase. However, $ABPO_5$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) showed relatively weak luminescence under UV excitation; it showed no emission under VUV excitation. Among $A_3BP_3O_{12}$ (A = Ca^{2+}, Sr^{2+}, Ba^{2+}) [10–11] only $Ba_3BP_3O_{12}$ was obtained as a single phase. Other cases for Ca^{2+} or Sr^{2+} were unknown phases or mixtures of known phases [12]. No photoluminescence $Ca_3BP_3O_{12}$ was observed for the nominal composition of $Ca_3BP_3O_{12}$ under UV and VUV excitation. Although $Ba_3BP_3O_{12}$ showed strong luminescence under UV excitation, this material showed no emission under VUV excitation. An almost single phase was prepared for $Sr_6BP_5O_{20}$ as a noble compound. From the indexing of reflections observed, this compound was shown to be isomorphous of $Pb_6BP_5O_{20}$ [13] or $Pb_6BAs_5O_{20}$ [14–15]. The alkaline-earth ions might be located in the sites for Pb^{2+} because the ion radius of Pb^{2+} is similar to that of divalent alkaline earths. $Sr_6BP_5O_{20}$ doped with Eu^{2+} showed a strong blue luminescence under both UV and VUV excitations. Therefore, the new Sr-borophosphate compound, $Sr_6BP_5O_{20}$ (hereafter, abbreviated by SBP) was chosen as a new matrix for VUV phosphor and further investigated.

Table 1
Investigation of borophosphate compounds

A:B:P	XRD	UV	VUV
1:1:1			
$CaBPO_5$	Single phase	△	×
$SrBPO_5$	Single phase	△	×
$BaBPO_5$	Single phase	△	×
3:1:3			
$Ca_3BP_3O_{12}$	Unknown	×	×
$Sr_3BP_3O_{12}$	Unknown	○	○
$Ba_3BP_3O_{12}$	Single phase	○	×
6:1:5			
$Ca_6BP_5O_{20}$	Unknown	×	×
$Sr_6BP_5O_{20}$	Single phase	○	○
$Ba_6BP_5O_{20}$	Unknown	○	×

(○) Good, (△) weak and (×) poor.

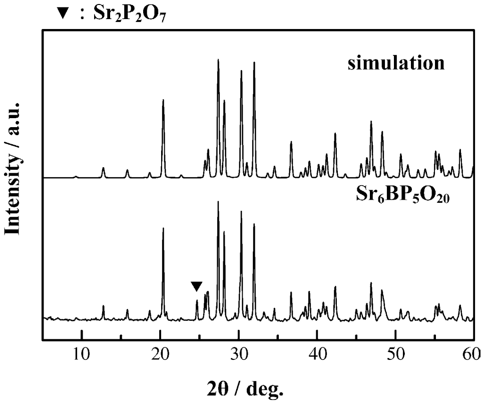

Fig. 1. Powder X-ray diffraction patterns of $Sr_6BP_5O_{20}$ and simulation.

In the high temperature solid-state reaction studied here, the SBP samples contained a small amount of an impurity phase. Therefore, optimization for the synthetic conditions was examined. The finally optimized conditions were heating temperature of 1273 K, heating rate of 1000 K/h and reaction time of 1 h. Powder X-ray diffraction patterns are shown in Fig. 1. $Sr_6BP_5O_{20}$ belongs to the tetragonal system, space group $P\bar{4}$, with $a = 0.6921(1)$ nm, $c = 0.9497(1)$ nm, $V = 45.471(7)\ \mathrm{nm}^3$ and $Z = 1$. A small amount of the impurity phase shown in Fig. 1 was revealed as $Sr_2P_2O_7$. The impurity phase often appeared on the pellet surface. This appearance might be attributable to evaporation of B component as B_2O_3 from the pellet surface. The SBP crystal structure is shown in Fig. 2. The anion frameworks in this compound are extremely complex. Two isolated groups exist as represented by an orthophosphate $[PO_4]^{3-}$ group with symmetry $\bar{4}$ and unusual anions of $[B(PO_4)_4]^{9-}$, which resembles a propeller and comprises a central $[BO_4]$ tetrahedron with symmetry $\bar{4}$ surrounded by arrays of four $[PO_4]$ tetrahedra.

3.2. Luminescence properties

As increasing Eu^{2+} concentration in the SBP, the amount of the impurity compound of $Sr_3Eu(PO_4)_3$ increased. The optimized activator concentration was revealed as a few atomic percent of Eu^{2+} relative to the alkaline-earth composition. The $Sr_6BP_5O_{20}$ sample doped with 1 mol% of Eu showed the highest luminescence intensity.

Emission and excitation spectra under UV excitation at room temperature are shown, respectively, in Figs. 3 and 4. The Eu^{2+} emission centers, which might occupy the sites for Sr^{2+}, showed a light-blue luminescence with a broad peak around 476 nm caused by the $4f^65d$–$4f^7$ transition of

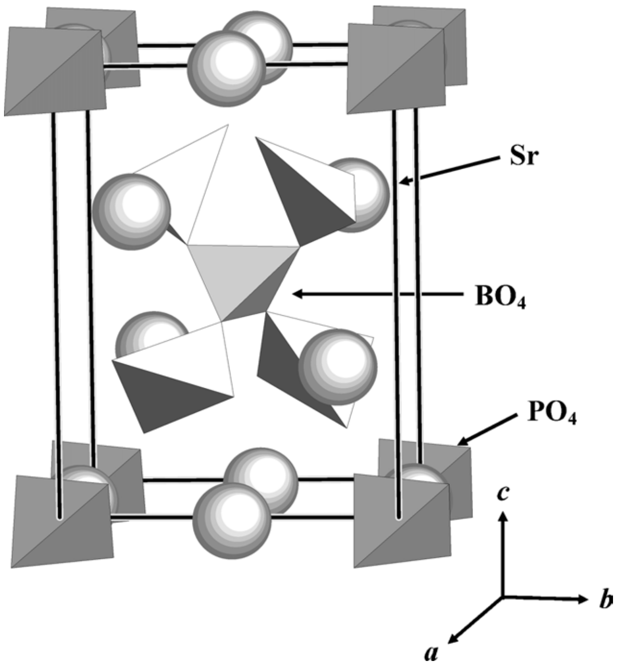

Fig. 2. Crystal structure of $Sr_6BP_5O_{20}$.

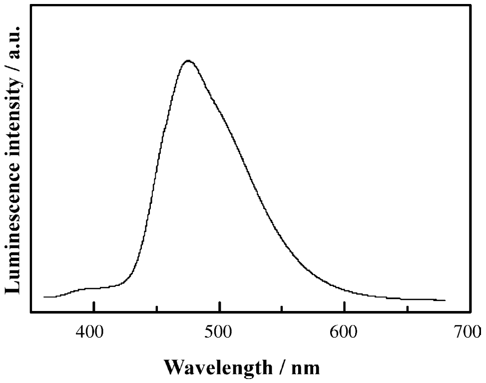

Fig. 3. Emission spectrum of $Sr_6BP_5O_{20}$ for 348 nm excitation (UV).

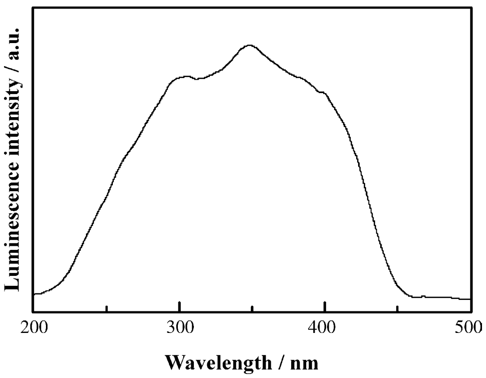

Fig. 4. Excitation spectrum of $Sr_6BP_5O_{20}$ for 476 nm emission (UV).

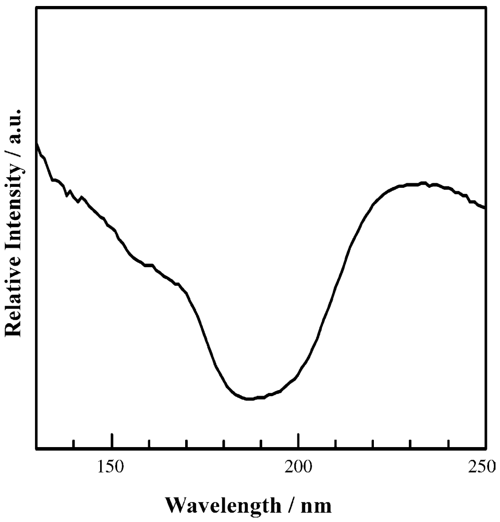

Fig. 5. Excitation spectrum of $Sr_6BP_5O_{20}$ for 476 nm emission (VUV).

Eu^{2+}. The optimal excitation wavelength was 348 nm, which is extended to the visible region.

In phosphors excited by VUV, physical properties of the host matrix are very primarily important because the matrix should absorb such high excitation energy first. That is, the matrix for the phosphor must show a strong VUV absorption, which is necessary to give high luminescence under VUV excitation. Fig. 5 shows that the borophosphate compound composed of borate and phosphate synthesized in this study meets such a requirement for absorption in the VUV region. The broad excitation absorption band in the VUV region may come from the rigid oxo groups of BO_4 and PO_4 units of SBP. The luminance of SBP was about 2.2 times brighter than that of a commercial blue phosphor, $BaMgAl_{10}O_{17}$:Eu^{2+} (BAM:Eu^{2+}). The emission spectrum of SBP under VUV excitation is almost identical to the spectrum under UV excitation (Fig. 3). Fig. 6 shows relative luminance under VUV excitation. It is estimated that the emission intensity of BAM is 100 for a 146-nm emission.

3.3. Heat-stable properties

Although the blue phosphor of BAM:Eu^{2+} shows good VUV luminescence properties, it presents the serious drawback of thermal degradation during heat processing for panel

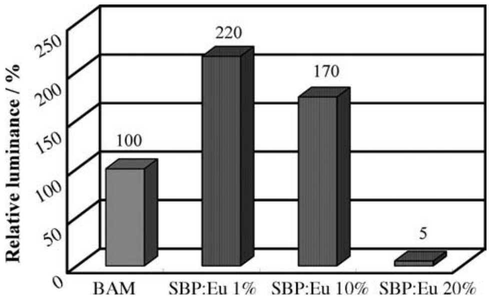

Fig. 6. Relative luminance intensity of SBP:Eu^{2+} and BAM:Eu^{2+}.

fabrication [3]. In this study, a preliminary examination of the thermal stability was performed for the SBP:Eu^{2+} phosphor. Luminescence intensities measured before and after heating were unchanged when the SBP sample was heated at 773 K for 30 min (heating and cooling rates were both 1 K/min). The rigid framework of SBP may be protective against heat attack, allowing no thermal degradation (BAM luminance usually decreases at about 20% after 773 K heat treatment).

4. Conclusion

A new VUV phosphor of $Sr_6BP_5O_{20}$:Eu^{2+} was synthesized using a conventional solid-state reaction, then characterized. The phosphor, under UV and VUV excitation, showed a strong light-blue luminescence. The SBP luminance was about 2.2 times higher than that of a commercial blue phosphor of BAM:Eu^{2+}. Furthermore, the phosphor showed excellent characteristic heat-stability properties in comparison with the BAM phosphor.

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