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# New Phosphors for Mercury-free Illumination

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Photoluminescence properties of new vacuum ultraviolet (VUV) excitable blue phosphor $Sr_6BP_5O_{20}:Eu^{2+}$ were investigated. $Sr_6BP_5O_{20}:Eu^{2+}$ showed a bright blue-green luminescence under VUV excitation. The composition, $(Sr_{0.99}Eu_{0.01})_6BP_5O_{20}$, shows its highest luminance under VUV excitation (147 nm), which corresponds to 216 % that of the commercial BAM phosphor as a reference. Therefore, this borophosphate phosphor is an attractive candidate for a new VUV phosphor for a mercury-free fluorescent lamp.

Key words: Mercury-free Lamp, Phosphor, Crystal Structure, Rare Earth, Vacuum Ultraviolet

## 1. INTRODUCTION

Present white fluorescent lamp contains poisonous mercury vapor, which gives serious damages to human and environment [1]. A discharge of Xe gas is promising candidate for the excitation of the white fluorescent lamp without the mercury. For application in plasma display panel (PDP) and mercury-free fluorescent lamp based on the Xe discharge, phosphors with a high quantum efficiency under Xe-based vacuum ultraviolet (VUV) excitation are required. The VUV light was produced by the discharge of Xe or Xe/Ne for both applications [2,3]. When a high VUV energy is absorbed in phosphor materials, the most suitable phosphor matrixes are oxide materials with a large bang gap. Blue $BaMgAl_{10}O_{17}:Eu^{2+}$, green $Zn_2SiO_4:Mn^{2+}$ and red $(Y,Gd)BO_3:Eu^{3+}$ as current VUV phosphors have strong absorption in the VUV region. Although the current PDP phosphors satisfied the requirements, there are some problems for practical applications.

For example, red $(Y,Gd)BO_3:Eu^{3+}$ show poor chromaticity [4] and green $Zn_2SiO_4:Mn^{2+}$ has a long decay time [5]. Blue $BaMgAl_{10}O_{17}:Eu^{2+}$ (BAM) has a thermal degradation after heating process in the PDP production [6]. In addition, BAM is vulnerable to continuous VUV irradiation. These are serious problems. The crystal structure of the BAM blue VUV phosphor is similar to the β - alumina ($NaAl_{11}O_{17}$) structure with high sodium ionic conductivity [7]. Goto et al. reported that BAM shows ionic conductivity at high temperature [8]. Therefore, BAM is essentially an unstable compound in high temperature and plasma. Therefore, new phosphors with a rigid crystal structure should be designed. In this study, we reported the luminescence properties under VUV excitation for new blue VUV phosphor, $Sr_6BP_5O_{20}:Eu^{2+}$ (SBP). Since the new phosphor has a relatively strong absorption band in a short wavelength region, the material is attractive candidate for new VUV phosphor for the PDP and the mercury-free fluorescent lamp.

## 2. EXPERIMENTAL

The phosphor $Sr_6BP_5O_{20}:Eu^{2+}$ (SBP) powders used in this study were synthesized by a conventional solid state reaction. Stoichiometric amount of high-purity powders ($SrCO_3$ (purity 99.9%), $H_3BO_3$ (purity 99.5%), $(NH_4)_2HPO_4$ (purity 99.0%) and $Eu_2O_3$ (purity 99.99%)) were used as starting materials. The mixture was pressed into disk-shape pellets of 15 mm in diameter and about 1 mm thick under a pressure of 30 MPa for 10 min. Calcinations were carried out for the pellets in reduction atmosphere ($Ar: H_2 = 95: 5$) at 1273 K for 1 h.

The phase purities of synthesized samples were characterized by a powder X-ray diffraction (XRD) analysis. The excitation and emission spectra in the UV range were measured on a powder sample using a JASCO FP-6500/6600. The photoluminescence spectra in VUV region were recorded under the VUV excitation (147 nm) by $D_2$ lamp. The relative luminance of the phosphors under the VUV excitation (lamp: USHIO UER20H-146VA) was recorded by TOPCON BM-7 luminance colorimeter [9].

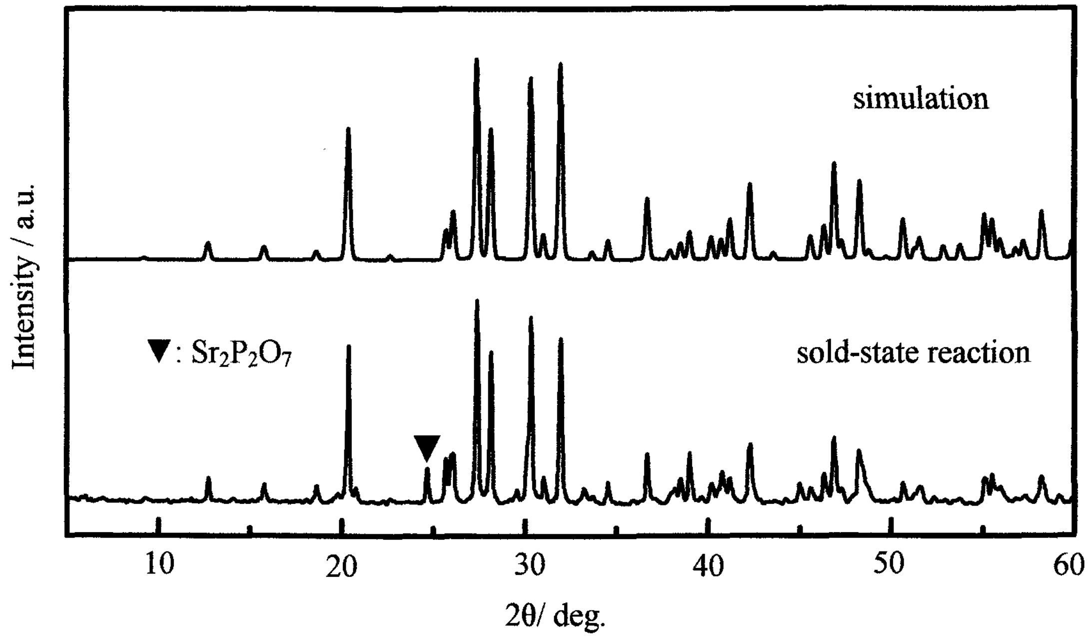

Fig. 1 X-ray diffraction patterns of SBP.

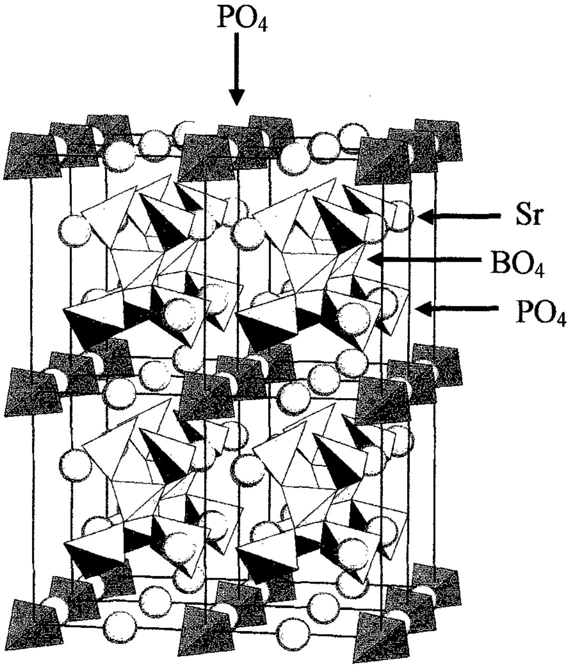

Fig. 2 Crystal structure of SBP.

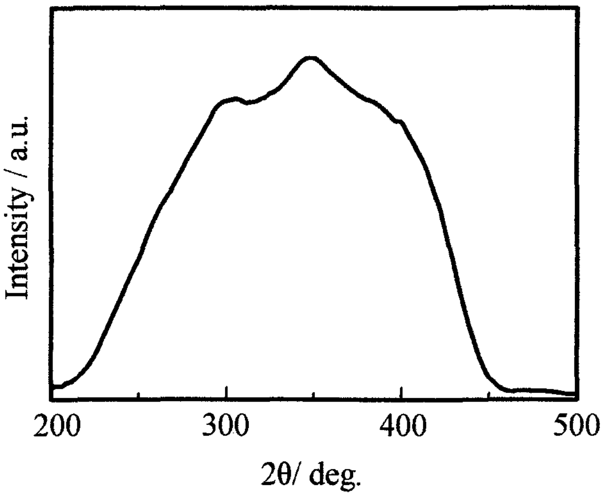

Fig. 3 UV excitation spectrum of SBP.

## 3. RESULTS AND DISCUSSION

The powder XRD pattern of the SBP was shown in Fig.1. The SBP contains small amount of the impurity phase. Figure 2 shows the crystal structure of the SBP. This compound crystallized in $Pb_6BAs_5O_{20}$-type structure [10]. The anion framework in this compound is complex: it resembles a propeller, with a central $[BO_4]$ tetrahedron surrounded by an array of four $[PO_4]$ tetrahedrons. The excitation energy is transferred from the surrounding propeller to the luminescence center $Eu^{2+}$ ion. This mechanism is similar to the antenna effect in luminescent complex between a rare-earth and an organic ligand [11].

The UV excitation spectra of SBP at room temperature were shown in Fig. 3. This compound shows a broad excitation band, corresponding to absorption of $Eu^{2+}$ center. Optimal excitation wavelength was 348 nm and it is extended to the visible region. This result indicates that the SBP has also promising potential practical LED phosphor applications [12]. The VUV excitation spectrum and the emission spectrum of the SBP are shown respectively in Figs. 4 and 5. The broad excitation absorption band around 147 nm and broad cyan emission (476 nm) were confirmed. The fundamental absorption band edge of the SBP is present around 180 nm. Therefore, the SBP efficiently absorbs the VUV photons. The composition, $(Sr_{0.99}Eu_{0.01})_6BP_5O_{20}$, shows its highest luminance under VUV excitation (147 nm), which corresponds to 216% that of the commercial BAM phosphor as a reference. Therefore, this borophosphate phosphor is an attractive candidate for a new VUV phosphor for a mercury-free fluorescent lamp.

Although the blue phosphor BAM shows good VUV luminescence properties, the thermal degradation after the baking process is serious problem in the PDP production. To estimate the thermal stability, the SBP was baked in air at 773 K for 30 min (heating rate, cooling rate: 1 K / 1 min). The luminescence intensities before and after heating were compared with those of BAM. After baking process, SBP had almost constant luminescence intensity (98-100 %). On the other hand, the intensity of BAM was significantly reduced after baking at 773K, corresponding to reduction of 20 %. Kunimoto et al. reported that the $CaMgSi_2O_6:Eu^{2+}$ (CMS) had a good thermal stability during baking process [13]. Im et al. conclude that high thermal stability is related to the rigid crystal structure of CMS [14]. The rigid framework structure maintains the divalent state of Eu ion in air even at high temperature. Since the BAM has an open layered structure with an ionic conduction plane, the oxidation of the $Eu^{2+}$ ion can easily occur in air. The new phosphor SBP has a rigid crystal structure because of the strong covalent characteristics of B-O and P-O bonds. Therefore, the SBP has also a good thermal stability during baking process.

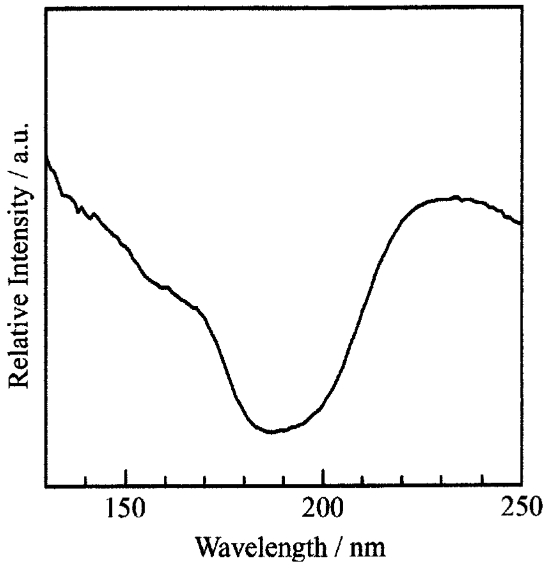

Fig. 4 VUV excitation spectrum of SBP.

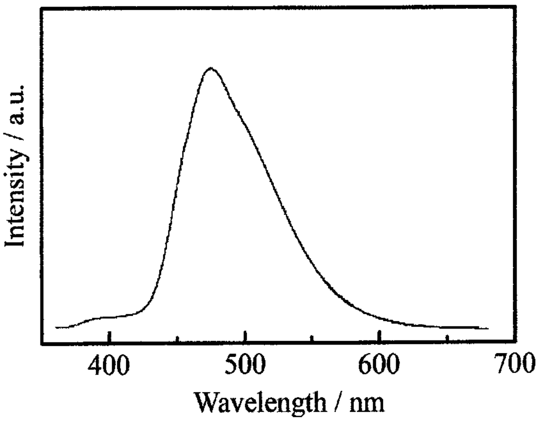

Fig. 5 Emission spectrum of SBP.

## 4. CONCLUSIONS

In this paper, new VUV excitable blue phosphor, $Sr_6BP_5O_{20}:Eu^{2+}$ (SBP), was synthesized by a conventional solid-state reaction. The SBP has a unique propeller-like framework and efficiently absorbs the VUV photons. The SBP is promising new candidate phosphor from the viewpoint of high luminance and thermal stability.

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