

Effects of Adding B_2O_3 as a Flux on Phosphorescent Properties in Synthesis of $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ Phosphor

Yeon-Tae Yu[†] and Byoung-Gyu Kim

Minerals and Materials Processing Division, Korea Institute of Geoscience and Mineral Resources,
30 Gajeong, Yuseong, Daejeon 305-350, Korea

(Received 12 June 2003 • accepted 1 August 2003)

Abstract— $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ phosphor was prepared by solid state reaction. B_2O_3 as a flux was added in $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ in order to accelerate a solid state reaction. In this paper, the effects of B_2O_3 on the crystal structure and the phosphorescent properties of the material have been evaluated. The synthesized phosphor exhibited a broad band emission spectrum peaking at 520 nm, and the spectrum peak showed little effect by the B_2O_3 contents. The maximum afterglow intensity of the $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ phosphor was obtained at the B_2O_3 content of 5%. Adding the B_2O_3 caused uniform distortion to the crystal structure of the phosphor and resulted in reducing the lengths of a and c axes and β angle of the $SrAl_2O_4$ crystal. The uniform distortion was accompanied with crystal defects which can trap the holes generated by the excitation of Eu^{2+} ions. The afterglow characteristic of the $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ phosphor was thus enhanced.

Key words: Phosphorescent Phosphor, Strontium Aluminate, Stuffed Tridymite Structure

INTRODUCTION

The tridymite type $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ has been regarded as a useful green phosphor of the long persistent phosphorescence. The phosphor, which does not contain radioactive elements such as tritium (H-3) and promethium (Pm-147), can be used safely as phosphorescent pigments for luminous watches and electric applications [Matsuzawa et al., 1996; Takasaki et al., 1996].

The $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ phosphor (hereafter abbreviated as SAEDP) has an emission peak at 520 nm. Phosphorescence from the phosphor crystals has been considered due to the 5d-4f transition of the Eu^{2+} ions in the crystal. A mechanism to explain the long persistent phosphorescence from SAEDP has been proposed based on hole trapping by the Dy^{3+} ions added as an auxiliary activator. Holes generated by the excitation of Eu^{2+} were trapped by codoped Dy^{3+} ions and/or native defects. The holes trapped at Dy^{3+} and/or defects are released slowly, and then recombine with electrons from the Eu^{2+} ions. This process has been thought to be the origin of the long persistent phosphorescence from SAEDP [Katsumata et al., 1997; Victor, 1971; Ito et al., 1979]. However, the mechanism for long persistent phosphorescence is not still fully understood [Tanabe et al., 1996].

To improve the phosphorescence characteristics of SAEDP, many studies have mainly performed about synthetic methods, the composition effect for the phosphor crystals, or the effect of auxiliary activators, in particular such as various trivalent rare-earth elements [Matsuzawa et al., 1996; Takasaki et al., 1996; Kutty et al., 1990]. The effect of B_2O_3 , which is usually used as a flux [Murayama, 1997], has not been studied as much. And, to understand the mechanism of the very long phosphorescence, it is considered to be important to clarify the effects of a crystal defects on the phosphorescence

characteristics of SAEDP.

The present paper deals with the long phosphorescence characteristics of SAEDP with various B_2O_3 contents, and examines the crystal defects in the phosphors in detail.

EXPERIMENTAL

The $SrAl_2O_4 : (Eu^{2+}, Dy^{3+})$ phosphors were prepared by the solid state reaction method. Starting materials used in the preparation of phosphors were pure powders of such as Al_2O_3 (4 N, amorphous), $SrCO_3$ (3 N), Dy_2O_3 (3 N), Eu_2O_3 (4 N) and B_2O_3 (4 N), which were supplied by Aldrich Chemical Co., Inc. The composition of the samples prepared was shown as $Sr_{0.985}Al_2O_4 : (Eu_{0.005}^{2+}, Dy_{0.01}^{3+})$, and the concentration of B_2O_3 ranged from 0% to 10% of the total sample weight. Preweighed materials were perfectly mixed in a ball mill with ethanol for 24 h, and then dried at 130 °C for about 12 h to evaporate ethanol. Phosphors were formed by firing in the appropriate gas mixtures of 2% H_2 -Ar at 1,300 °C for 3 h.

Products were examined by the X-ray diffraction (XRD) using $Cu K_{\alpha 1}$ radiation ($\lambda = 1.5405 \text{ \AA}$). On the photoluminescence (PL) emission, the excitation and the afterglow spectra of powder samples were obtained by means of the SLM Instrument Inc. Model-1800 luminescence spectrometer. Each sample was excited with 365 nm radiation from a pulsed xenon discharged lamp. The emission spectrum was scanned over the range of wavelengths from 300 nm to 800 nm. The afterglow spectrum was measured after the samples were excited with a mercury lamp for 10 minutes. B_2O_3 contents were considered to be as starting composition of the synthesized mixtures, because the B_2O_3 contents of products were not analyzed.

RESULTS

Fig. 1 shows the emission spectra from SAEDP with various B_2O_3

[†]To whom correspondence should be addressed.

E-mail: yytae@kigam.re.kr

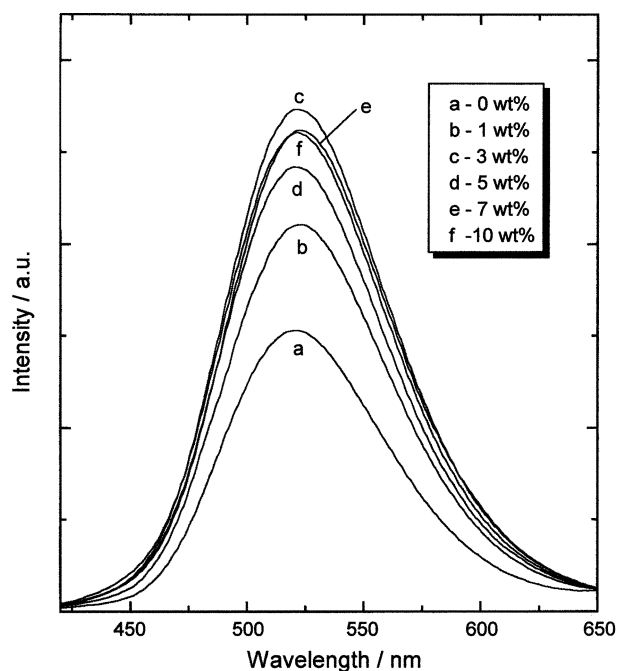


Fig. 1. Emission spectra of SAEDP with various B_2O_3 content.

content. The specimens exhibit broad band emission spectra peaking at $\lambda=520$ nm and show the typical spectrum of green phosphor of the $SrO-Al_2O_3:(Eu^{2+}, Dy^{3+})$ system. From the figure, the peak wavelengths of the emission spectra are found invariable with the B_2O_3 content. This implies that the crystal field, which affects the 5d electron states of Eu^{2+} ions, remains unchanged by the variations of B_2O_3 content.

Fig. 2 shows the afterglow characteristics of the phosphorescence from SAEDP with various B_2O_3 content. The persistent duration of phosphorescence from the phosphors varies dramatically with B_2O_3 content. The results show that SAEDP with 5% B_2O_3 has relatively high phosphorescence intensity, as compared with the other

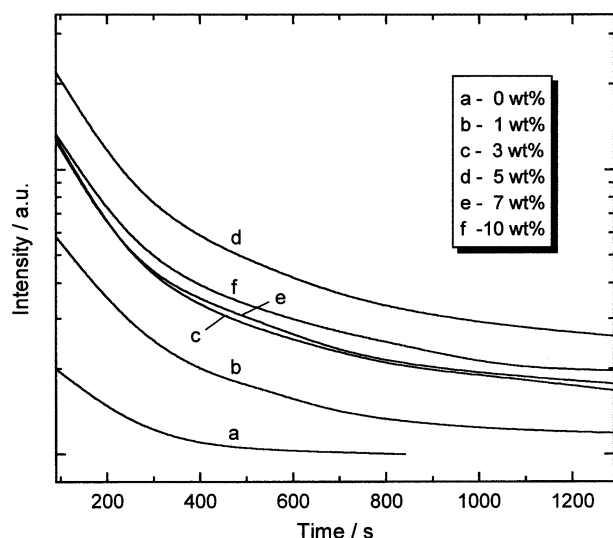


Fig. 2. Afterglow characteristics of phosphorescence from SAEDP with various B_2O_3 content.

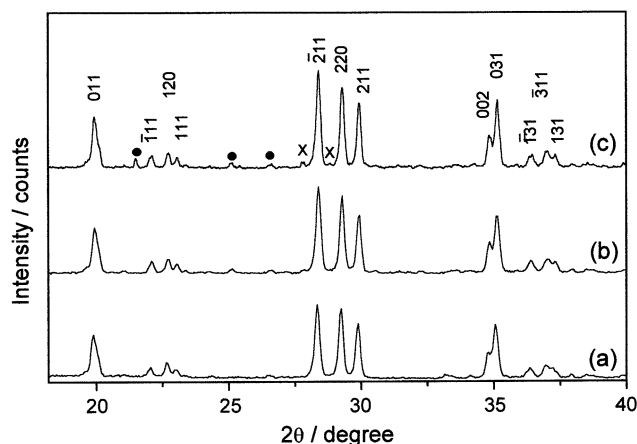


Fig. 3. XRD patterns of SAEDP with various B_2O_3 content as starting compositions.

(a) 0 wt%, (b) 5 wt%, (c) 10 wt%. ●: SrB_2O_4 , X: unknown

samples. But the phosphorescence intensity decreases remarkably at the content over 7% as discussed in next sections.

Fig. 3 shows X-ray diffraction patterns of SAEDP powders with various B_2O_3 content. Despite the coexistence of the B_2O_3 flux, all of the samples show the typical X-ray patterns of $SrAl_2O_4$ crystal phase of the monoclinic structure. Peaks from SrB_2O_4 phase are observed at about $2\theta=21.5^\circ$ and 25.1° in the sample at the B_2O_3 content of 5%, and these peaks obviously appear at the samples above 7% B_2O_3 . Small peaks from new products other than those of SrB_2O_4 phase are found in the X-ray diffraction pattern of the sample with the B_2O_3 content of 10%, as shown in Fig. 3(c). Although small peaks are considered due to another type of strontium aluminate phase such as $SrAl_2O_7$ or $Sr_2Al_2O_7$, they cannot be assigned because of their small intensities. Fig. 2 shows that the phosphorescence intensity of the phosphors with the B_2O_3 content over 7% is lower than that of the sample with 5% B_2O_3 .

From the above observations, adding B_2O_3 causes some changes in the crystal structure of SAEDP, and these changes affect the afterglow characteristics. We therefore tried to examine the lattice strains of the SAEDP crystals to clarify the relationship between the long persistent luminescence and lattice defects.

There are generally two kinds of strains in a crystal: a heterogeneous strain (micro strain) and a uniform strain (macro strain). The heterogeneous strain means that lattice parameters vary from place to place in the crystal. The existence of the strain can be evaluated by XRD's peak broadening analysis. The uniform strain means that all of crystal lattice is uniformly distorted by a stress, and can be evaluated from peak shift analysis [Cullity, 1997].

The peak broadening analysis proposed by Hall was applied to the three diffraction peaks such as 011, $\bar{2}11$ and 031 for two samples with B_2O_3 content of 0% and 5% [Harada et al., 1981; Ohsima et al., 1981]. The correction for instrumental broadening was made by using the pattern from a KCl powder sample, the crystalline size of which was large enough to eliminate peak broadening. Fig. 4 shows the Hall's plots of $\beta \cos \theta / \lambda$ vs. $\sin \theta / \lambda$, where β is the integral width, θ is the Bragg angle and λ is the X-ray wavelength. The straight lines show results of the least squares fittings. According to Hall's theory, the slope of the straight line indicates the exis-

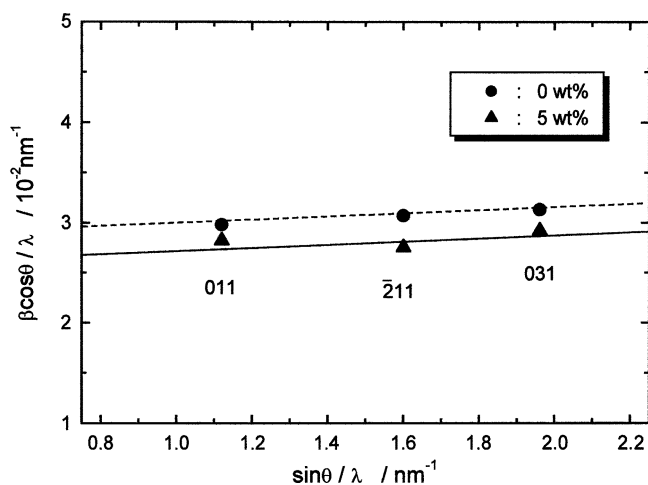


Fig. 4. Hall's plots for analysis of X-ray diffraction profiles from SAEDP with 0 wt% and 5 wt% of B₂O₃.

tence of heterogeneous strain in the crystal. Fig. 4 shows, however, that the inclination of the slopes is nearly zero; besides, the line obtained from the sample with 5% B₂O₃ is almost parallel to that from the sample with 0% B₂O₃. And thus the change of heterogeneous strain in SAEDP crystals by addition of B₂O₃ is thought to be ig-

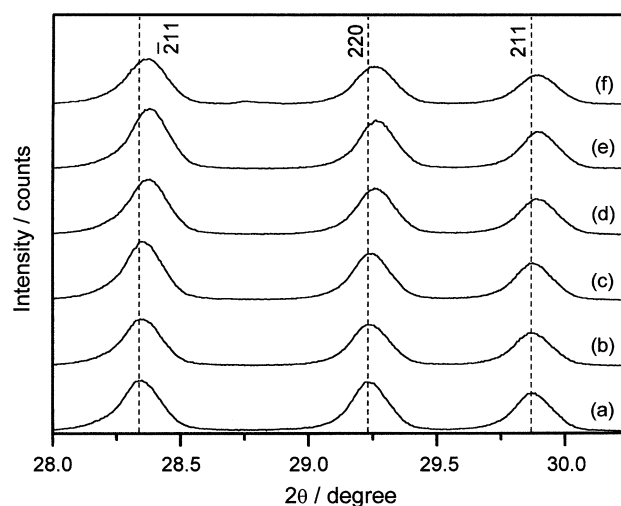
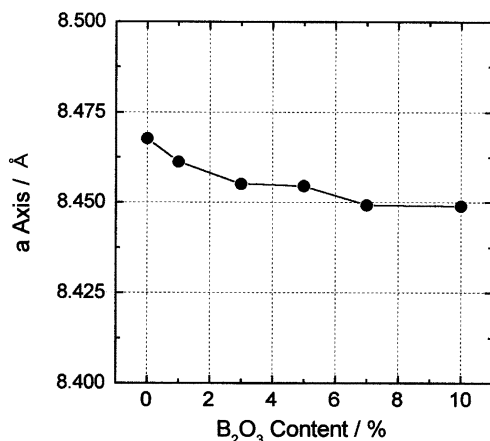


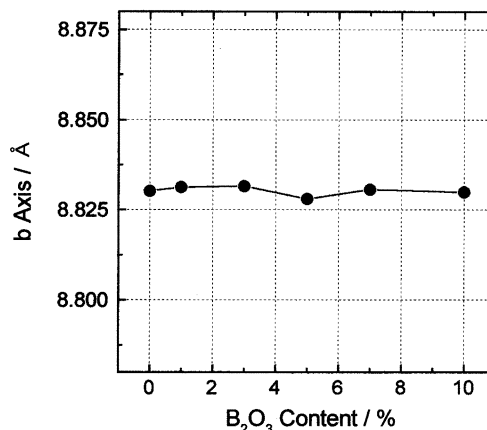
Fig. 5. XRD patterns of SAEDP with various B₂O₃ content as starting compositions.

(a) 0 wt%, (b) 1 wt%, (c) 3 wt%, (d) 5 wt%, (e) 7 wt%, (f) 10 wt%

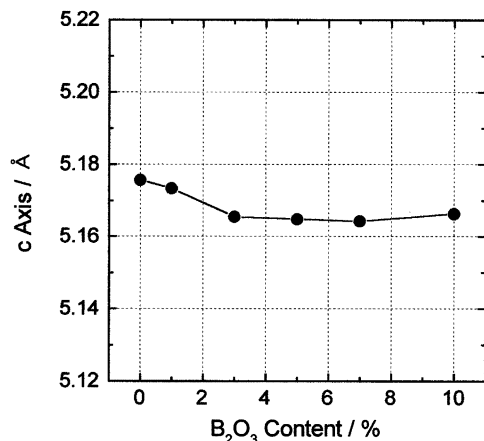
nored. The intercept at $\sin\theta/\lambda=0$ gives the inverse of the average crystalline size. The average crystalline sizes are 34 nm and 37 nm



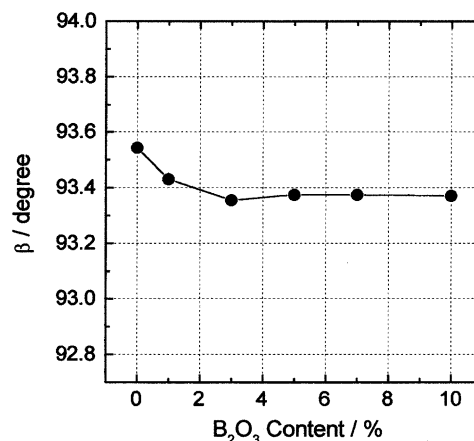
(a)



(b)



(c)



(d)

Fig. 6. Change of lattice parameters for SAEDP with various B₂O₃ content as starting compositions.

for 0% B₂O₃ and 5% B₂O₃ samples, respectively.

We also analyzed the peak shift of the X-ray diffraction patterns in order to certify the nature of the uniform strain in crystals. Fig. 5 shows the X-ray diffraction patterns at $\bar{2}11$, 220 and 211 of SAEDP crystals with various B₂O₃ content. Each diffraction peak shift was found to be a higher angle with increasing B₂O₃ content. This results in lattice contraction according to the increase of B₂O₃ content.

Fig. 6 shows the contraction of a, c and β lattice parameters of SAEDP crystals with increasing B₂O₃ content, whereas b remains rather constant. The a-length decreased up to the B₂O₃ content of 7%, and the c-length and the β angle value reduced up to the B₂O₃ content of 3%.

DISCUSSION

X-ray diffraction analysis of SAEDP showed that the increase of B₂O₃ content caused the uniform distortion in the phosphor crystal to about 5%. Further addition of B₂O₃ formed other compounds such as SrB₂O₄, SrAl₄O₇ or Sr₂Al₂O₇ in SAEDP crystal (Fig. 3). The relative intensity in phosphorescence from SAEDP showed the maximum value at the B₂O₃ content of 5% (Fig. 2).

These facts indicate that the B₂O₃ component in the phosphor makes a solid solution ranging to 5%, and plays a role as a source of uniform distortion in SAEDP crystal. The distortion generates crystal defects which can trap the holes generated by the excitation of Eu²⁺ ions. It is thought that the afterglow characteristics of SAEDP are enhanced by adding the B₂O₃ up to its content of about 5%. These results support that the defects act as a hole trapped center. Hosono et al. had identified that an Al-O hole center had been generated by irradiating ultraviolet light on crystals in the CaO-Al₂O₃ system. The guest compound such as SrB₂O₄ was found in SAEDP crystal synthesized at a B₂O₃ content above 7%, which indicates the fatal limit of reserving the tridymite structure of SrAl₂O₄. The afterglow characteristic of the SAEDP sample is therefore decreased at the higher content of B₂O₃.

CONCLUSIONS

The synthesized SAEDP exhibited a broad band emission spectrum peaking at 520 nm, and the spectrum peaks were stable with variation of the B₂O₃ content. The maximum afterglow intensity of SAEDP was obtained at the B₂O₃ content of 5%. Adding B₂O₃ as a flux changes the lattice parameters of SAEDP crystal. The lattice parameters of the phosphor crystal were decreased with the B₂O₃

content up to 3-5%, but no further variation in the B₂O₃ content above 7%, where the guest compounds such as SrB₂O₄ was found. This indicates the compositional limit for B₂O₃ content of the phosphor crystal. The afterglow characteristic of SAEDP was decreased with B₂O₃ content above 7%. B₂O₃ contained is considered to generate crystal defects that trap the holes generated by the excitation of Eu²⁺ ions. The afterglow characteristic of SAEDP is enhanced by adding the B₂O₃ up to 5%.

REFERENCES

- Cullity, B. D., "Elements of X-ray Diffraction," Addison-Wesley Publishing Company Inc., Reading, Massachusetts, U.S.A., 375 (1977).
- Harada, J., Yao, S. and Ichimiya, A., "X-ray Diffraction Study of Fine Gole Particles Prepared by Gas Evaporation Technique," *J. Phys. Soc. Japan*, **48**, 1625 (1981).
- Hosono, H., Yamazaki, K. and Abe, Y., "Long Lasting Phosphorescence Properties of Eu-activated Strontium Aluminate Glasses," *J. Am. Ceram. Soc.*, **70**, 867 (1987).
- Ito, S., Banno, S., Suzuki, K. and Inagaki, M., "Solid Solubilities in the Alkaline-earth Metal Aluminates," *Yogyo-Kyokai-Shi*, **87**, 344 (1979).
- Katsumata, T., Nabae, T., Sasajima, K., Komuro, S. and Morikawa, T., "Effects of Composition on the Long Phosphorescent SrAl₂O₄ : Eu²⁺, Dy³⁺ Phosphor Crystals," *J. Electrochem. Soc.*, **144**, L243 (1997).
- Kutty, T. R. N., Jarannathan, R. and Rao, R. P., "Luminescence of Eu²⁺ in Strontium Aluminates Prepared by the Hydrothermal Method," *Mat. Res. Bull.*, **25**, 1355 (1990).
- Matsuzawa, T., Aoki, Y., Takeuchi, N. and Murayama, Y., "A New Long Phosphorescent Phosphor with High Brightness, SrAl₂O₄ : Eu²⁺, Dy³⁺," *J. Electrochem. Soc.*, **143**, 2670 (1996).
- Murayama, Y., "Long Phosphorescent Materials," *Ceramics Japan*, **32**, 40 (1997).
- Ohshima, K., Yatsuya, S. and Harada, J., "Characterization of Ultra Fine Palladium Particles with the Mean Size of 20 Å by X-ray Diffraction," *J. Phys. Soc. Japan*, **50**, 3071 (1981).
- Takasaki, H., Tanabe, S. and Hanada, T., "Long-lasting Afterglow Characteristics of Eu, Dy Codoped SrO-Al₂O₃ Phosphor," *J. Ceram. Soc. Japan*, **104**, 322 (1996).
- Tanabe, S. and Hanada, T., "Appearance of Light-storage Rare Earth Aluminate Phosphors and Their Optical Properties," *New Ceramics*, **10**, 27 (1996).
- Victor, A., "Optical and Electrical Properties of SrAl₂O₄ : Eu²⁺," *J. Electrochem. Soc.*, **118**, 930 (1971).