

## Synthesis of Eu, Dy co-doped SrAl<sub>2</sub>O<sub>4</sub> phosphors by using liquid phase precursor process

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SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup>s are well-known as persistent luminescence phosphors with high brightness and long afterglow. They have been widely commercialized for afterglow applications such as security signs, emergency route signage, identification markers, and also bio-image in vivo. The persistent researches of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor have been widely studied during the past decades. In this study, the properties of SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor were studied with wide range firing temperature and different annealing conditions. Synthesis of persistent phosphorescence in Eu<sup>2+</sup> and Dy<sup>3+</sup> ions co-doped SrAl<sub>2</sub>O<sub>4</sub> phosphors fired at 1100-1300 °C was conducted by using the cellulose assisted liquid phase precursor (LPP) process under reducing atmosphere. The SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup> showed a typically broad emission band at 512 nm under excitation of UV range and Dy<sup>3+</sup> considerably enhanced the persistent luminescence intensity. Europium ions substituted for the two different Sr sites in the phosphor's the monoclinic of host lattice resulting in greenish emission. The obtained phosphors were measured and analyzed by X-ray diffraction (XRD), scanning electron microscope (FE-SEM) and photoluminescence spectra (PL).

**Key words:** Phosphor, LPP method, Photoluminescence.

### Introduction

Phosphorescent materials have a great potential for various device applications and have been widely studied by many researchers. In the past, the ZnS-based phosphors had been extensively applied to many displays. However, the sulfide compound has a short durability because the compound is very unstable to moisture or carbon dioxide in the atmosphere. Hence these conventional sulfide phosphors are not sufficiently bright or long-lasting for actual application if radioisotopes are not added.

Compared with the alkaline earth sulfides, alkaline earth aluminates are chemically stable in an ambient environment, and are used as new host materials in recent years [1]. Europium and dysprosium co-doped strontium aluminate (SrAl<sub>2</sub>O<sub>4</sub>:Eu and SrAl<sub>2</sub>O<sub>4</sub>:Eu, Dy) phosphors have been recrystallized to exhibit high brightness and long-lasting phosphorescence without radioactive materials, and available for a wide range of applications [2-4].

Since the discovery in 1996 of SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> as a new persistent luminescent compound by Matsuzawa *et al.*, a number of researchers have developed techniques for their preparation, including sol-gel methods, hydrothermal synthesis, chemical precipitation, laser synthesis and solid state reaction.

In previous reports, SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors

were synthesized by high temperature solid-state reaction process, which requires quite long reaction time (4-10 hrs) in a high temperature (i.e., 1400-1600 °C) [5-7]. As a result, the obtained particles have a large particle size which is impractical for printing applications, in which particles < 10 μm are required.

On the other hands, liquid phase precursor (LPP) process which is the new synthesis method leads to achieve easily the deaggregated and nano-sized particles. This method is the low temperature synthesis caused by liquid medium such like sol-gel method. Unlike the sol gel process, however, this method can control distribution of the particles by using impregnation to cellulose homogeneously. We propose LPP process to achieve clear single phase of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor at low temperature, and has high luminescence properties.

### Experimental Procedure

Sr<sub>1.7-x-y</sub>Al<sub>2</sub>O<sub>4</sub>: Eu<sub>x</sub><sup>2+</sup>, Dy<sub>y</sub><sup>3+</sup> (x = 0.8000, y = 0.0500) particles were synthesized using solution reaction. The raw materials strontium nitrate, aluminum nitrate, europium chloride and dysprosium nitrate were dissolved in deionized water, mixed solution were stirred for few minutes and then impregnated onto the cellulose precursor by 1 : 1 weight ratio. The sample was rapid fired at 600 °C to burn out the organics and raise the temperature to 1000 °C to form the SrAl<sub>2</sub>O<sub>4</sub> phase in an alumina crucible for 3 hrs. Afterward boron oxide is added as a flux to the obtained powders. Finally due to dope Eu<sup>2+</sup> selectively on SrAl<sub>2</sub>O<sub>4</sub>, the sample was fired at 1300 °C in H<sub>2</sub>/N<sub>2</sub> atmosphere and

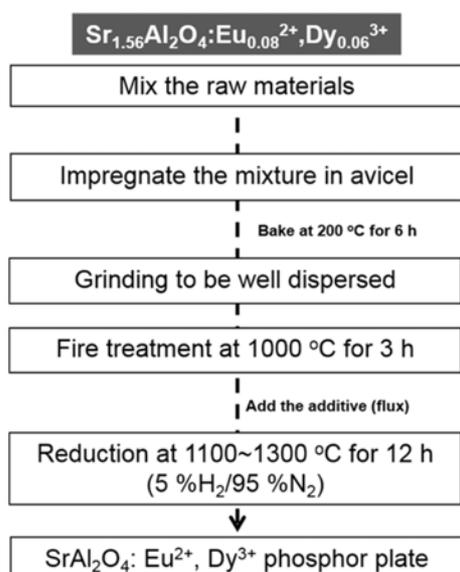
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**Fig. 1.** Scheme of experiment process.

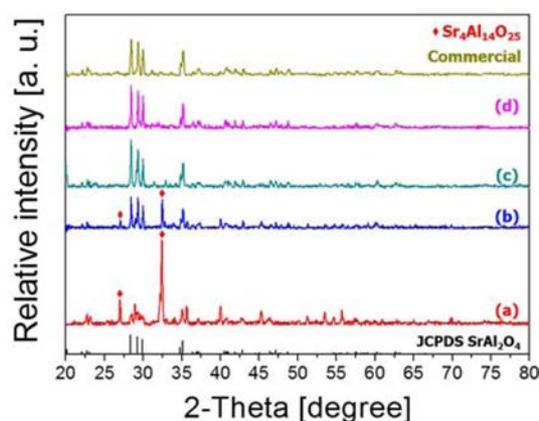
this process improve their luminescence. A schematic diagram of the experimental process were shown in Fig. 1.

The synthesized powders were identified by an X-ray diffractometer with Cu-K $\alpha$  radiation. The scan speed was 6 °/min and range covered was between  $2\theta = 20^\circ$  and  $90^\circ$ . The morphology of the powders was observed by scanning electron microscopy (SEM, FE-SEM XL-30, Philips). Photoluminescence spectrometer with a pulse a Xe lamp. The luminescent properties of the Eu<sup>2+</sup>-activated silicate phosphor were examined by measuring the PL using a Darsa PRO 5300 PL system (PSI Trading Co., Ltd., Korea) with xenon lamp (500 W). The measurements were carried out at an excitation wavelength of 390 nm. Excitation was performed with a wavelength of 200-450 nm. The PLE spectra were corrected by dividing the measured emission spectra by the observed spectrum of a xenon lamp source.

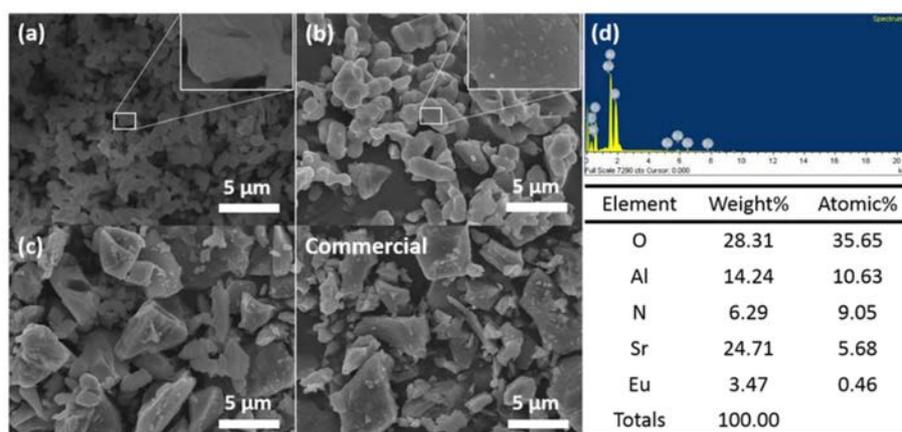
## Results and Discussion

In order to optimize the PL properties of a SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphor, the firing temperature was the variable considered. The phosphor was synthesized at various temperatures ranging from 1100 to 1300 °C.

Fig. 2 shows the XRD patterns of SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> with different temperatures and atmosphere. The samples annealed at (a) 1100 °C, (b) 1200 °C and (c) 1300 °C under N<sub>2</sub>/H<sub>2</sub> atmosphere, and another sample (d) annealed 1300 °C under Ar-H<sub>2</sub> atmosphere. The SrAl<sub>2</sub>O<sub>4</sub> crystal is known as a monoclinic lattice. In case of (a), the annealing temperature is too low to form a clear SrAl<sub>2</sub>O<sub>4</sub> single phase. The secondary phase, Sr<sub>4</sub>Al<sub>14</sub>O<sub>25</sub>, is observed which were attributed to the characteristic lack of energy homogeneity during the combustion. The SrAl<sub>2</sub>O<sub>4</sub> phase appeared at lower temperature in the strontium oxide-aluminum oxide (SrO-Al<sub>2</sub>O<sub>3</sub>) system than in the SrAl<sub>2</sub>O<sub>4</sub> phase. The secondary phase was going to weak with increase of the temperature. The samples fired at 1300 °C were



**Fig. 2.** XRD patterns of the Sr<sub>1.56</sub>Al<sub>2</sub>O<sub>4</sub>:Eu<sub>0.08</sub>Dy<sub>0.06</sub> phosphor fired at (a) 1100 °C, (b) 1200 ° and (c) 1300 °C under H<sub>2</sub>/N<sub>2</sub> reduction atmosphere and fired at (d) 1300 °C under H<sub>2</sub>/Ar atmosphere.



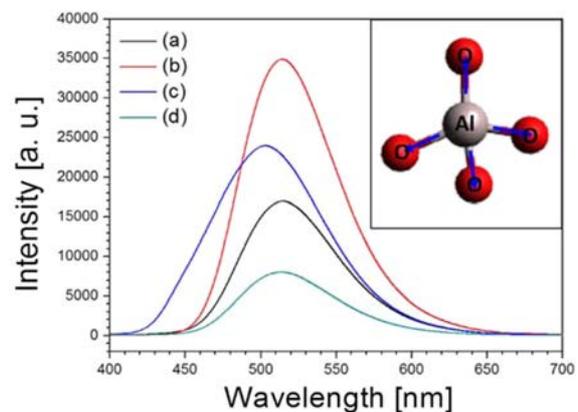
**Fig. 3.** SEM images and EDS analysis of Sr fired at (a) 1200 °C and 1300 °C under H<sub>2</sub>/N<sub>2</sub> atmosphere; (c) 1300 °C under H<sub>2</sub>/Ar atmosphere (d) EDS analysis at the area of sample (b).

formed completely clear single phase as shown Figs. 2(c) and 2(d). Therefore a reduction temperature range was associated with the stability of forming single phase.

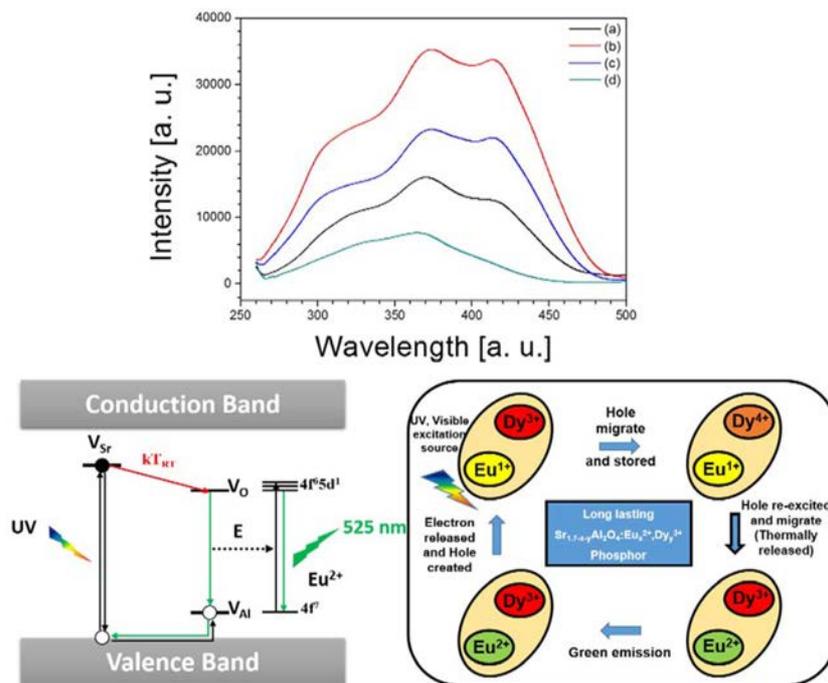
The FE-SEM micrographs and EDS analysis results shown in Figs. 3(a-d), illustrate the morphology and particle size distribution of the  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$ . In Figs. 3(a-b) it is seen that the  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}, \text{Dy}^{3+}$  samples had the ball-like particles. With the reduced temperature increasing, the grain growth was appeared. But even when the sintering temperature reach  $1300^\circ\text{C}$ , the average grain size is less than  $100\text{ nm}$ , suggesting that the luminescent powder is nanometer grade while the average grain size of commercial sample was is about  $4000\text{ nm}$ . In addition, the sample can be observed impurities on the particle surface, it may be caused by Al-N bonding compounds as shown EDS results (Fig. 3(d)). During reduction firing, nitrogen gas which ruled reduction valance gas reacted with samples. This reaction occur easily, because the sample may contain the carbon could not be vaporized during calcine the cellulose. The carbon has high reactivity thus can aid the reaction with  $\text{N}_2$ . A sample fired at  $1300^\circ\text{C}$  under  $\text{H}_2/\text{Ar}$  reduction atmosphere was obtained irregular shape particles such as a commercial sample shown in Fig. 3(c).

The luminescence properties of  $\text{SrAl}_2\text{O}_4 : \text{Eu}^{2+}$  were discovered in 1968 [8-9]. Poort *et al.* [10] suggested that the  $520\text{ nm}$  emission band originate from the  $4f^65d^1 \rightarrow 4f^7(^8S_{7/2})$  transition of  $\text{Eu}^{2+}$  located at the two different crystallographic strontium sites. The emission spectrum at room temperature is shown in Fig. 4. It

displays a broad band with a maximum at  $515\text{ nm}$ . Leading to the green luminescence of the materials under normal conditions. The intensity of sample fired at  $1300^\circ\text{C}$  under  $\text{H}_2/\text{Ar}$  atmosphere is higher than the others including commercial sample. When the temperature is  $1300^\circ\text{C}$  under  $\text{H}_2/\text{N}_2$ , a clear blue shift occurs in the emission spectra of which the peak of the emission spectra is  $500\text{ nm}$  respectively as shown in Fig. 4(c). The brightness is also greatly reduced, even if it is same temperature with (b). There were two reasons on this phenomenon. Firstly, Al-N bonding leads to blue shift emission. Another reason is effect of crystal field. According to the previous researches [11], when the grain size reaches nanometer grade, the



**Fig. 4.** Emission spectra of the  $\text{Sr}_{1.56}\text{Al}_2\text{O}_4 : \text{Eu}_{0.8}\text{Dy}_{0.06}$  (a) commercial powders and samples fired at (b)  $1200^\circ\text{C}$  and (c)  $1300^\circ\text{C}$  under  $\text{H}_2/\text{N}_2$  reduction atmosphere and fired at (d)  $1300^\circ\text{C}$  under  $\text{H}_2/\text{Ar}$  atmosphere. Besides is the atomic structure of  $\text{AlO}_4^-$ .



**Fig. 5.** Excitation spectra of the  $\text{Sr}_{1.56}\text{Al}_2\text{O}_4 : \text{Eu}_{0.8}\text{Dy}_{0.06}$  (a) commercial powders and samples fired at (b)  $1200^\circ\text{C}$  and (c)  $1300^\circ\text{C}$  under  $\text{H}_2/\text{N}_2$  reduction atmosphere and fired at (d)  $1300^\circ\text{C}$  under  $\text{H}_2/\text{Ar}$  atmosphere. Below is the scheme of mechanism of emission and trap system.

luminescent materials shows the blue shift of emission spectra. It leads to two phenomenon. One is to increase the surface energy rapidly resulting in a distortion of the atomic structure. In result crystal field strength of surrounding Eu<sup>2+</sup> ion is change. Another is ionic radii of the atoms. The  $\beta$ -tridymite type monoclinic structure of SrAl<sub>2</sub>O<sub>4</sub> consists of AlO<sub>4</sub> tetrahedral formed by a 3D framework of oxygen ion surrounded by M<sup>2+</sup> ions [12]. The means that smaller particle is that smaller crystal field strength. The 4f electrons in Eu<sup>2+</sup> are well shielded by the outer shell, but the 5d electrons are viable to splitting by the action of crystal field strength. Since the excited 4f<sup>6</sup> → 5d configurations of Eu<sup>2+</sup> ion is extremely sensitive to the change in the lattice environment, the 5d electron may couple strongly to the lattice [13]. Hence, the mixed states of 4f and 5d configuration are splitted by the crystal field, which may lead to the blue shift of its emission peak.

Fig. 5 shows the excitation spectra with different reduction conditions. There were three excited levels. Two shoulders are observed at 300 and 425 nm in addition to the maximum at 370 nm on the excitation spectrum of the commercial sample as shown in Fig. 5(a). The intense absorption of other samples fired at 1300 °C were observed at nearly same position shown figure (b) and (c). These broad band absorption are attributed to the parity allowed transition of Eu<sup>2+</sup>. The phosphorescence mechanism of SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> is involved in the direct excitation of Eu<sup>2+</sup> due to the 4f → 5d transition occurs upon UV irradiation [25]. When SrAl<sub>2</sub>O<sub>4</sub>: Eu<sup>2+</sup>, Dy<sup>3+</sup> absorbs UV, Eu<sup>2+</sup> 4f → 5d charge transfer forms, the recombination of electron-hole pairs can be pressed.

## Conclusions

SrAl<sub>2</sub>O<sub>4</sub>:Eu<sup>2+</sup>, Dy<sup>3+</sup> phosphors fired at 1300 °C were formed completely clear single phase. The sintering temperature reach 1300 °C, nevertheless, the average grain size is less than 100 nm, while the average grain size of commercial sample. In case of sample fired 1300 °C under N<sub>2</sub>/H<sub>2</sub>, blue shift occurred in the emission spectra of which the peak of the emission

spectra is 500 nm. The intensity of sample fired at 1300 °C under H<sub>2</sub>/Ar atmosphere had nearly two times emission intensity as compared to the commercial sample. The excitation spectrum of the commercial sample has a broad absorption band peaking at 370 nm and two additional shoulders at 300 nm and 415 nm following previous researches. It leads to raise the optical properties such as emission intensities and persistent properties.

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