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# Effect of Al/Sr ratio on the luminescence properties of $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ phosphors

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**Abstract**

Recent studies have brought out many phosphors like $Eu^{2+}$, $Dy^{3+}$-doped alkaline earth aluminates. The trivalent $Dy^{3+}$ ions as co-dopants greatly enhance the duration and intensity of persistent luminescence. These phosphors show excellent properties, such as high quantum efficiency, long persistence of phosphorescence, good stability and suitable color emission.

In this work the effect of Al/Sr ratio on the afterglow and phosphorescence decay properties of $Eu^{2+}$ and $Dy^{3+}$ co-activated strontium aluminates synthesized by a solid-state process has been investigated. The luminescence properties of samples were investigated by means of excitation spectra, emission spectra and X-ray diffraction analysis.

A variety of strontium aluminates, such as $SrAl_2O_4$, $Sr_4Al_2O_7$, $Sr_3Al_2O_6$, $Sr_3Al_2(Eu, Dy, Y)O_{7.5}$, $Al_5(Eu, Dy, Y)O_{12}$, $Sr_4Al_{14}O_{25}$, $SrAl_{12}O_{19}$ and $(Eu, Dy, Y)AlO_3$ have been identified in the samples prepared from starting precursors with Al/Sr mole ratios ranging from 0.44 to 5. The afterglow decay rate was found to be the fastest for sample with Al/Sr ratio of 4.18, in which $SrAl_4O_7$ phase was dominant. The afterglow decay rate for phosphor with Al/Sr ratio of 2, in which $SrAl_2O_4$ phase was dominant, was detected to be slow. Moreover, the emission spectra of the samples shift to yellow-green long wavelength from bluish-green-ultraviolet short wave with the increase of Al/Sr ratios resulting from the change in the composition.

*Keywords:* Long persistence phosphorescence; Strontium aluminates; Al/Sr ratio; Crystal

## 1. Introduction

In general, a phosphor is a solid that converts certain types of energy into electromagnetic radiation over and above the thermal radiation. The term luminescence, which includes both fluorescence and phosphorescence, is defined as a phenomenon, in which the electronic states of substance is excited by some kind of external energy and the excitation energy is given off as light of various wavelengths [1]. In 1990s, Matsuzawa reported a new type of long persistent phosphor, $SrAl_2O_4$:$Eu^{2+}$/$Dy^{3+}$, with a strong emission centered at 520 nm (green). The persistent time of this $SrAl_2O_4$:$Eu^{2+}$/$Dy^{3+}$ phosphor was found to be longer than 16 h [2–4]. Double oxides containing strontium and aluminum have become of interest in material science since they exhibit excellent properties, such as high quantum efficiency, long persistence of phosphorescence, safety and good stability when compared with classical sulfide phosphorescent phosphors. Based on these properties, some strontium aluminates have found themselves many application fields [5–9].

The Al/Sr ratio in the strontium aluminates phosphors can affect the long duration phosphorescence [10]. In $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$, the long duration phosphorescence was also reported to be affected by chemical composition [11,12]. However, the compositional variation of $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ in terms of phosphorescence is not so drastic. So, its effects on the long duration phosphorescence have, therefore, not been fully understood. In order to clarify this effect on the long duration phosphorescence, one must conduct researches on the crystals with wider variation in composition. Sakai et al. reported such effects in $BaAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$. They indicated that the Al/Ba ratio has great influence on the long afterglow properties of the phosphors since Al-rich compounds have much better phosphorescence properties than Ba-rich compounds [13,14].

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In the present study, $SrAl_2O_4$ was used as the matrix materials, and doped with $Eu^{2+}$, $Dy^{3+}$, and $B3^{+}$ as the main activator, co-activator and fluxing agent, respectively. Phosphor samples containing SrO, $Al_2O_3$, $Eu_2O_3$, $Dy_2O_3$, $Y_2O_3$ and $B_2O_3$ were prepared by solid-state reaction. The effect of Al/Sr ratio on the luminescent properties was investigated. XRD data, phosphorescence spectra, afterglow decay rates of the synthesized phosphors with Al/Sr ratio ranging from 0.44 to 5.02 as functions of excitation wavelengths and host compositions were reported here.

## 2. Experimental procedures

$SrCO_3$ (99.5%), $Al_2O_3$ (99.99%), $Eu_2O_3$ (99.99%), $Dy_2O_3$ (99.9%), $Y_2O_3$ (99.0%) and $H_3BO_3$ were employed as starting materials. The phosphor powders were prepared with varying amounts of $Al_2O_3$ and SrO. The Al/Sr ratio changed from 0.44 to 5.02. $Y_2O_3$ was added to the recipes to enhance the luminescence properties. $H_3BO_3$ was evaluated as fluxing agent. In all recipes 0.006 mole $Eu^{2+}$, 0.003 mole $Dy^{3+}$ and 0.02 mole $B_2O_3$ were input to the composition. For this purpose 8 different recipes were prepared and coded as Al1 (Al/Sr: 0.44), Al3 (Al/Sr: 1.3), Al4 (Al/Sr: 2), Al6 (Al/Sr: 2.62), Al8 (Al/Sr: 3.34), Al10 (Al/Sr: 3.48), Al12 (Al/Sr: 4.18) and Al14 (Al/Sr: 5.02). The batches were preciously weighed and thoroughly mixed by wet-milling with zirconia balls in zirconia bowls at 200 rpm for 1 h. After being dried at 75 °C for 1 day, the final luminescence powders were obtained by calcining the raw mixtures at 1450 °C for 2 h in a reducing environment of 97% $N_2$ + 3% $H_2$. The products obtained after reduction in all the cases were in the form of hard aggregates, which were then ground to powder by agate mortar and sieved under 60 μm.

Phase identification of the powders was carried out by X-ray powder diffraction 40 kV and 30 mA with Rigaku Rint 2000 using Cu Kα radiation). The samples particle sizes were analyzed by the Malvern Instruments Mastersizer Hydro 2000G laser particle size analyzer. SEM images were taken on a Zeiss EVO 55 scanning electron microscopy. The PL spectra and decay rates were obtained by a Perkin-Elmer LS55 fluorescence spectrometer at room temperature with xenon lamp as the light source. To obtain decay rates, the samples were irradiated by sunlight for 20 min and then were directly analyzed by spectrometer.

## 3. Results

Figs. 1–8 indicate powder X-ray diffraction (XRD) patterns of phosphors with different Al/Sr ratios.

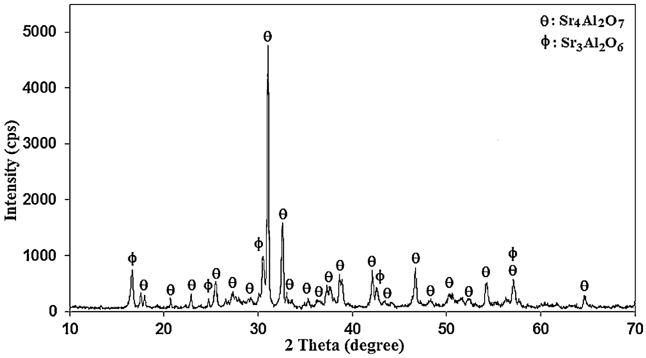

Fig. 1. XRD pattern of Al1 (Al/Sr: 0.44) coded phosphor.

If XRD graphs are examined, when Al/Sr ratio is 0.44, it can be clearly seen that strontium rich phases formed such $Sr_4Al_2O_7$ as the main and $Sr_3Al_2O_6$ as the secondary phase. The main phase converts to $Sr_3Al_2O_6$ with the increase in Al/Sr ratio to 1.3 and also $SrAl_2O_4$ crystal forms. When Al/Sr ratio is 2, $SrAl_2O_4$ phase desired to obtain as the main crystal phase in the phosphorescent pigment composition is present in the structure. There are very little amounts of intermediate phases, such as $SrAl_4O_7$, $Sr_3Al_2O_6$, $Sr_3Al_2(Eu, Dy, Y)O_{7.5}$, $Al_5(Eu, Dy, Y)O_{12}$, $Sr_4Al_{14}O_{25}$ and (Eu, Dy, Y)$AlO_3$ in the recipe coded Al4. The stoichiometric ratio needed to obtain $SrAl_2O_4$ phase is achieved by this recipe, in which $Al_2O_3/SrCO_3$ mole ratio is 1.

It is determined that $SrAl_{12}O_{19}$, as well as $SrAl_2O_4$ forms in the composition having 2.62 Al/Sr mole ratio. It is obvious that the main phase occurred in 4 samples (Al8, Al10, Al12, Al14) having Al/Sr mole ratio of 3.34 and over is $SrAl_4O_7$ rich in alumina and also $SrAl_2O_4$ phase appears in the structure.

After XRD analyses, the excitation and emission wavelength and intensity of powders were measured by phosphorescence spectrophotometer.

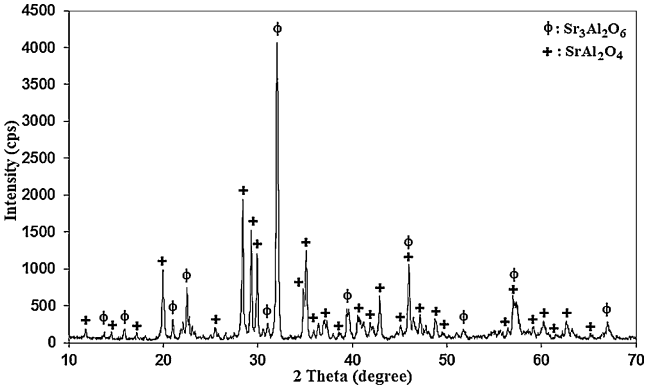

Fig. 2. XRD pattern of Al3 (Al/Sr: 1.3) coded phosphor.

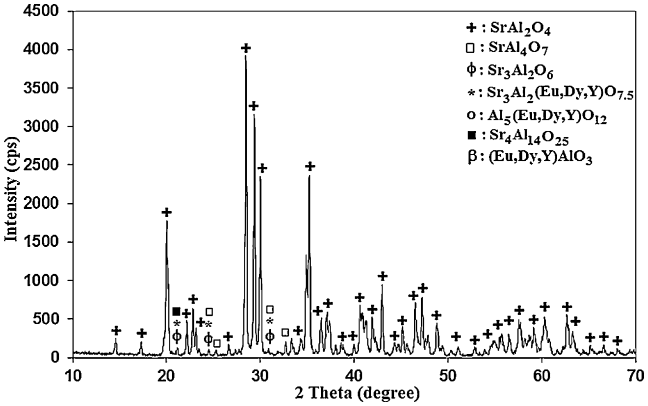

Fig. 3. XRD pattern of Al4 (Al/Sr: 2) coded phosphor.

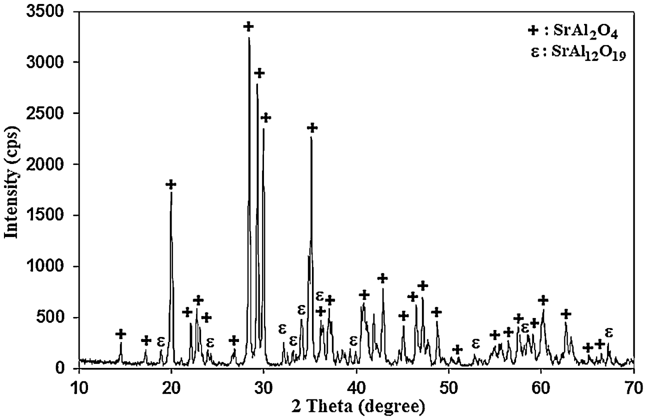

Fig. 4. XRD pattern of Al6 (Al/Sr: 2.62) coded phosphor.

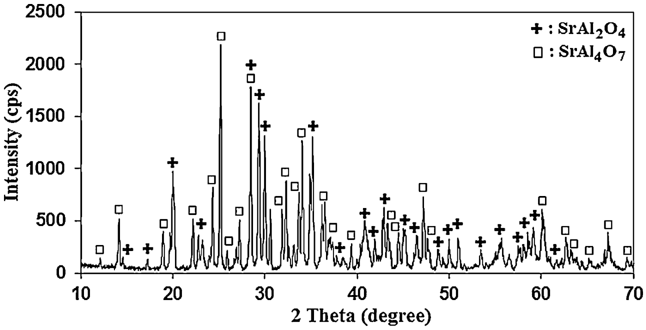

Fig. 5. XRD pattern of Al8 (Al/Sr: 3.34) coded phosphor.

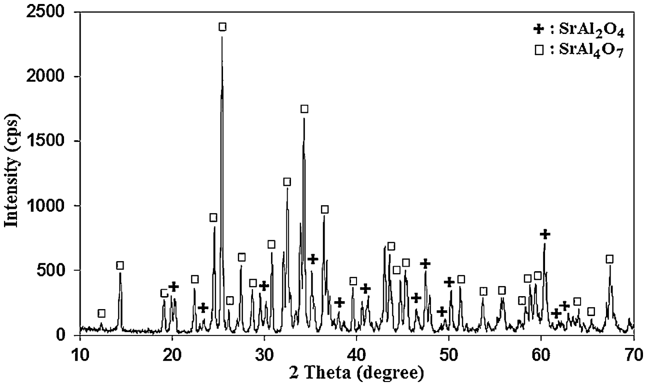

Fig. 7. XRD pattern of Al12 (Al/Sr: 4.18) coded phosphor.

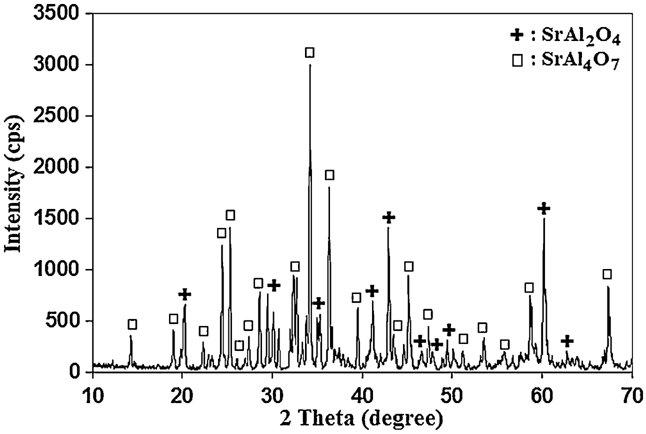

Fig. 8. XRD pattern of Al14 (Al/Sr: 5.02) coded phosphor.

The emission wavelength and intensity values obtained under 260 nm excitation for phosphors by spectroscopic measurements (Table 1). A non-stoichiometric composition may result in either enhancement or quenching of the luminescence of the phosphor even though the exact cause of such a phenomenon is not well understood [15]. According to the excitation/emission results, the maximum intensity is given by A14 coded pigment having Al/Sr ratio of 2 at 519 nm. This result matches up with that of Al coded one, in which $SrAl_2O_4$ was obtained, having potential of emission in green region shown by XRD graphs as main crystal (Fig. 3). The emission of $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ systems at near 515 nm indicate why the emission wavelength shifts to green region [16].

In long afterglow phosphors, optical excitation energy is stored in the lattice by trapping of photo excited charge carriers. The most prominent example is $SrAl_2O_4$:Eu, Dy after optical excitation of $Eu^{2+}$, $Eu^{2+}$ is oxidized to $Eu^{3+}$ and $Dy^{3+}$ is reduced to $Dy^{2+}$. Thermal excitation of $Dy^{2+}$ to $Dy^{3+}$, followed by capture of the electron by $Eu^{3+}$ and subsequent $Eu^{2+}$ emission, results in time-delayed $Eu^{2+}$ emission [17]. Emission wavelength of $Eu^{2+}$ ions can be converted from blue to red depending on host lattice because of crystal field effect [18]. It can be said

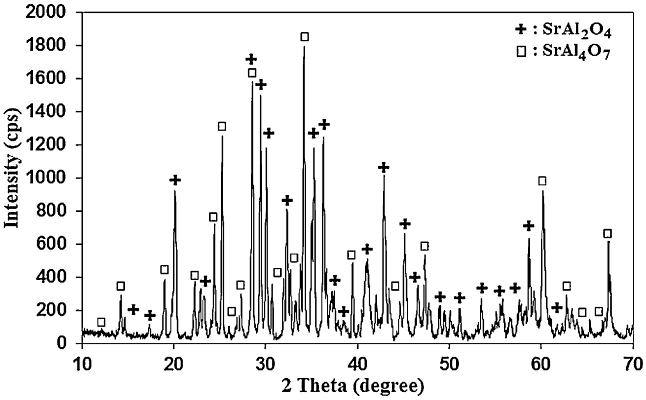

Fig. 6. XRD pattern of Al10 (Al/Sr: 3.48) coded phosphor.

Table 1
The excitation/emission wavelength and intensity values of samples with different Al/Sr ratios.

| Sample | Emission (under 260 nm excitation) | |
|---|---|---|
| | Wavelengths (nm) | Intensity (a.u.) |
| Al1 | 490 | 6.71 |
| Al3 | 518.01 | 69.67 |
| Al4 | 519.47 | 71.37 |
| Al6 | 518.04 | 66.90 |
| Al8 | 518.55 | 67.05 |
| Al10 | 537 | 4.52 |
| Al12 | 536 | 6.33 |
| Al14 | 544 | 5.58 |

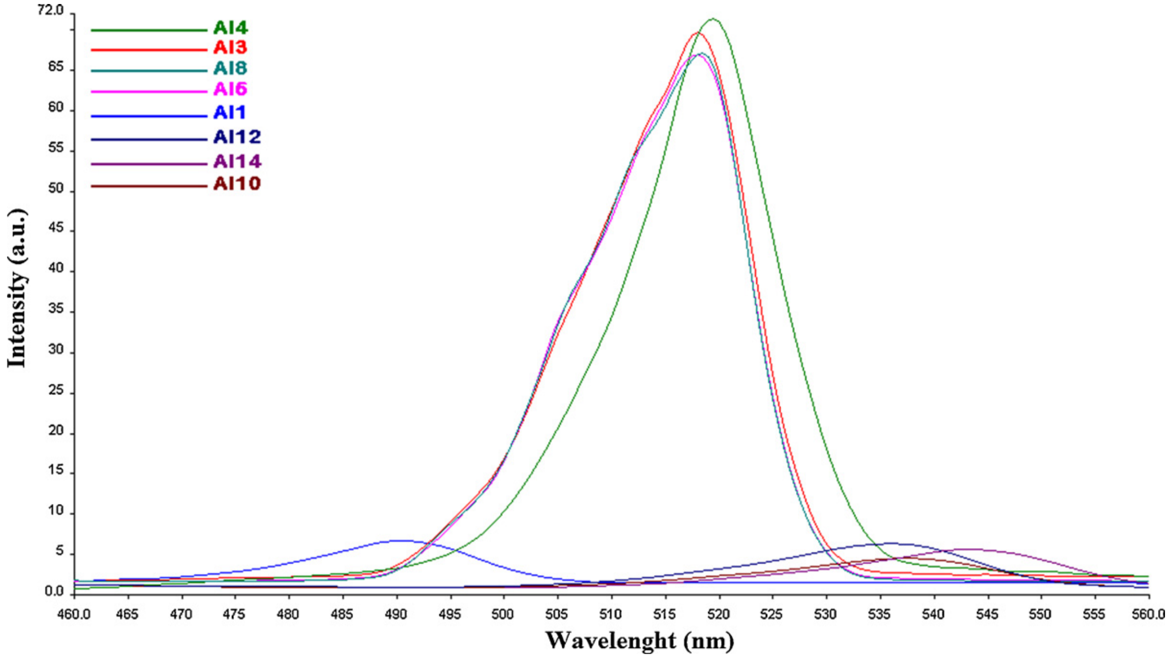

Fig. 9. The emission curves of yellowish-green phosphorescence pigment having different $Al_2O_3$ contents.

from this point that pigment emission wavelength can be changed with respect to primary and secondary phases formed in the system. Moreover, it is clear that secondary phases decrease luminescence intensity [19].

Fig. 9 shows emission graphs of yellowish-green phosphorescent pigment having different amount $Al_2O_3$. If spectrophotometer analyses are examined, it can be noticed that the emission wavelength is shifted from blue-green (~490 nm) to green region (~520 nm) with the increase of $Al_2O_3$ ratio in the composition. The emission intensity decreases significantly for the molar ratio of Al/Sr is equal or more than 3.48 (Table 1). This is probably due to $SrAl_4O_7$ being the main phase rather than $SrAl_2O_4$ having green-band emission (Figs. 6–8) [20,21]. It is known that $SrAl_4O_7$:$Eu^{2+}$ phosphor has an emission in red region at 612 nm under UV excitation [22]. The observed diversity may be attributed to the phase distribution in the phosphor powder series or the fraction of long-lasting phosphorescent $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$ present in different strontium aluminate phases described above. In addition, $Eu^{2+}$ ion was considered to distribute randomly in the host lattice of miscellaneous strontium aluminate phases (i.e., $SrAl_2O_4$, $SrAl_{12}O_{19}$, and $Sr_3Al_2O_6$) and, thus, the luminescence attributed to $Eu^{2+}$ is the result of interaction in different crystal fields. Furthermore, the hole traps ascribed to $Sr^{2+}$ vacancies and defects present in the $SrAl_2O_4$ lattice are commonly generated and stabilized by charge compensation with doping of the $Dy^{3+}$ as an auxiliary activator. Thus, the intensity of afterglow is expected to be highly dependent on the content or relative fraction of $SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$, $SrAl_4O_7$:$Eu^{2+}$, $Dy^{3+}$ and $SrAl_{12}O_{19}$:$Eu^{2+}$, $Dy^{3+}$ phases [23,24].

The decay curves (afterglow) of phosphorescent pigments are presented in Fig. 10. From graphs it can be followed that the samples coded by Al4 and Al6 have higher initial emission intensity and decay time. Chen et al. [23] have reported that the effect of the host composition on the afterglow and phosphorescence decay properties of strontium aluminates co-activated with Eu and Dy, synthesized by a sol–gel process by varying the molar ratio of Al/Sr (from 1 to 12) and concluded that the afterglow decay rate is the fastest for

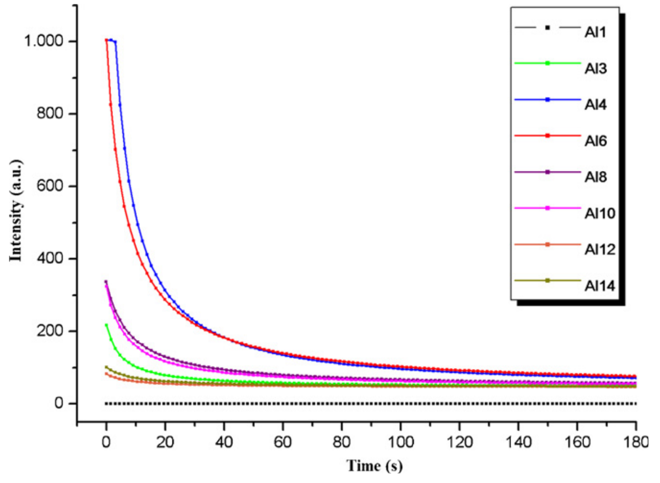

Fig. 10. The decay curves of yellowish-green phosphorescence pigment having different $Al_2O_3$ contents.

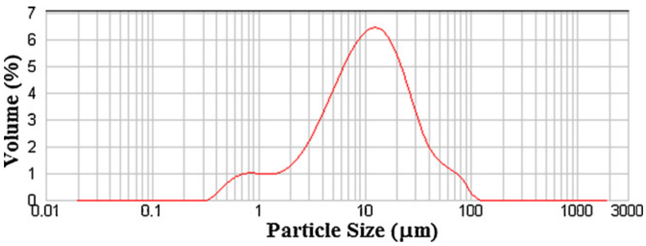

Fig. 11. The particle size distribution curve of Al4 coded phosphor powder.

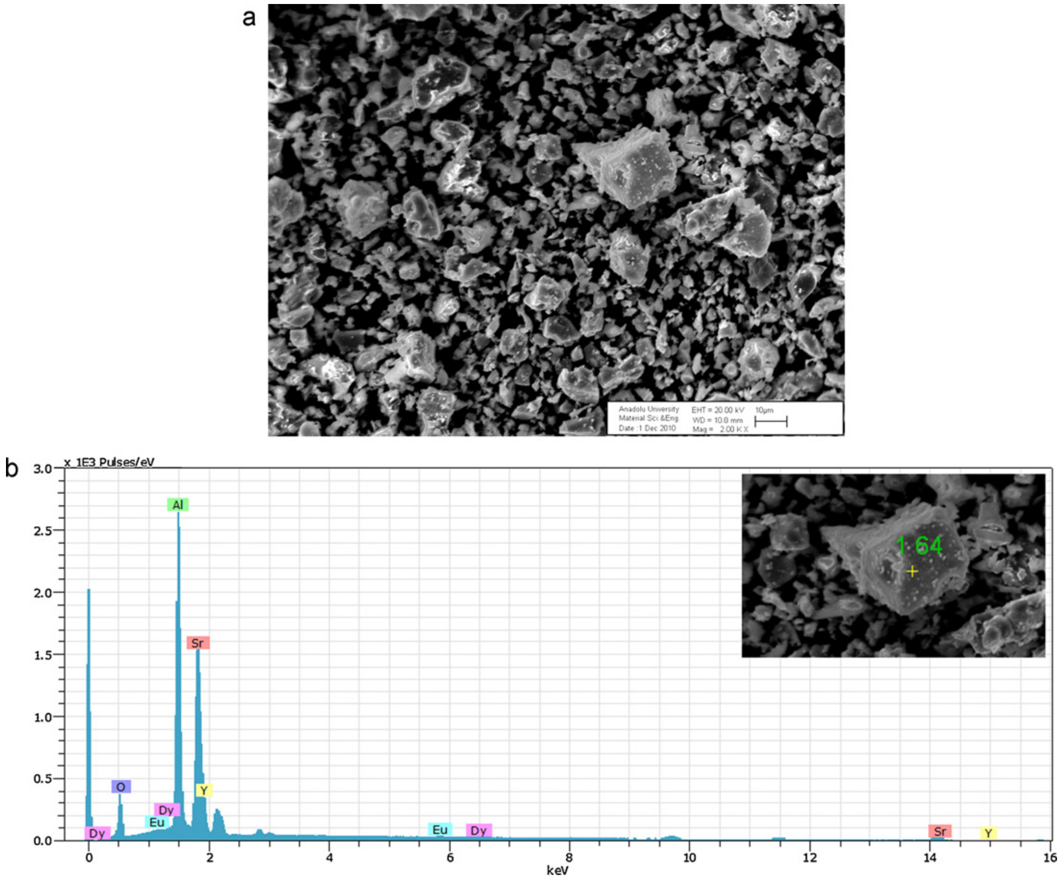

Fig. 12. SEM image (a) and EDX result (b) of Al4 coded phosphorescent pigment (having $SrAl_2O_4$ as the main phase).

samples with Al/Sr ratio 1:1 and the slowest for samples with Al/Sr ratio of 2:1 to 12:1.

In the light of all these results, phosphor composition coded A14 with 2 Al/Sr mole ratio is designated as the optimum recipe by which $SrAl_2O_4$ phase having maximum emission intensity is obtained as the main phase. The particle size distribution of this phosphor is given in Fig. 11.

According to the analysis result seen in Fig. 11, the particle size distribution of yellowish-green phosphorescent pigments produced is determined as $d(0.1)$: 2.535 μm, $d(0.5)$: 11.390 μm and $d(0.9)$: 33.256 μm. The SEM and EDX results of Al4 coded phosphorescent powder are depicted in Fig. 12.

With EDX analysis, it is determined that the pigment analyzed has Al and Sr elements basically and little amounts of rare earth elements such as Eu, Dy, etc.

## 4. Conclusions

$SrAl_2O_4$:$Eu^{2+}$, $Dy^{3+}$phosphors with different starting compositions were prepared successfully by solid reaction method. The phase composition and the excitation–emission spectrum were found to be influenced greatly by the composition of starting materials. Moreover, the afterglow characteristics were also changed with various compositions. The initial afterglow intensity for phosphor powders was found to vary with Al/Sr ratio (i.e., from 0.44 to 5.02). The better afterglow phosphorescence was observed in phosphors with the Al/Sr ratio is 2.

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