Research Article

Giant Improvement on the Afterglow of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ Phosphor by Systematic Investigation on Various Parameters

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Received 28 November 2012; Accepted 22 January 2013

Academic Editor: Necmettin Maraşlı

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Highly intense, long persistent $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}$ blue-green phosphor with different B^{3+} , Eu^{2+} , Dy^{3+} , and Ag^{+} contents was prepared by solid-phase reaction at various temperatures in reductive atmosphere of 10% H_2 in N_2 . The effects of synthesis parameters like calcination temperature and time, calcination environment, effect of stoichiometry of the host composition, and additives like addition of boron and rare earth ions (Eu, Dy) were studied in detail. Results revealed that the phosphor containing ~40 mol% H_3BO_3 showed dense and pure $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase with higher emission intensity, but in the samples containing less than 20 mol% H_3BO_3 mixed phases consisting of Al_2O_3 , $\text{SrAl}_{12}\text{O}_{19}$ and SrAl_2O_4 were observed, while in higher H_3BO_3 content, $\text{SrAl}_2\text{B}_2\text{O}_7$ phases predominated. When the stoichiometry of Al/Sr was 3.7, the best phosphorescence and afterglow were noted. The phosphor containing 4 at.% of Eu and 8 at.% of Dy, and 3 at.% Ag exhibited the maximum initial intensity of $5170 \text{ mcd}\cdot\text{m}^{-2}$ and the longest persistency of greater than 30 hours over the value of $5 \text{ mcd}\cdot\text{m}^{-2}$, higher than the commercial products and applicable for various display applications involving indoor as well as outdoor uses.

1. Introduction

Phosphor materials with long afterglow is a kind of energy storing materials that can absorb UV-visible light from sun light, and gradually release the absorbed energy in the darkness at a certain wavelength [1]. Among the various phosphors, ZnS-based materials doped with Cu or Mn ions were first prepared and applied for various fields [2]; however, the luminescent intensity of these phosphors are not bright enough and the afterglow time is short. Therefore, some radio-active elements such as Co and Pm had to be codoped into the ZnS-matrix so as to prolong the afterglow time. Compared to sulfide-based phosphors, oxide-based phosphors have been recognized as the efficient host materials because of their high quantum efficiency [3], chemical stability, no radio-active radiations, environmental capability, and long persistence of phosphorescence [4].

As far as the development of phosphor is concerned, Eu^{2+} ions were used frequently as an activator ion for various host lattices. This occurs because the $4f^7$ electron configuration of the Eu^{2+} ion shows efficient luminescence

owing to the $4f \rightarrow 5d$ transition, and the luminescence colors or wavelengths change widely from near UV to red regions depending on the nature of host lattice [5]. As a new phosphor, strontium aluminates doped with Eu divalent ion (SAE) have been investigated as an efficient phosphor that has high quantum efficiency and good stability, indicating their good practical prospects [4–8]. These phosphors have decay time ranging from nanosecond to tens of seconds and were used as important constituents of light emitting devices, fluorescent lamps, plasma display panels, and lamps for medical applications [9]. However, for specific dark vision applications involving signage, blackouts, emergency rescue guidance systems, and luminous watches, the phosphors with appreciable brightness and long persistent time of more than 5 h are fundamental requisites [7].

In order to improve the phosphorescence characteristics, Dy^{3+} is added to SAE and fabrication conditions have been examined [9–15]. For specific dark vision applications, the existing brightness and afterglow phosphorescence have been improved but are not enough and needed more improvements. Fascinated by the techno-commercial applications,

many researchers started exploring the dependence of various physico-chemical parameters such as thermal parameters [10], addition of flux [1, 7, 11–15], and effect of compositions [15, 16] on the luminescence and long persistent behavior of these phosphors. But detailed study on the composition of Al/Sr, effects of flux, composition of rare earth ions, charge compensator ions, and heating temperature and time are not well revealed for $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphor. Thus, in this paper, the systematic examination regarding composition of starting materials, rare earth ions (Eu^{2+} , Dy^{3+}), flux (H_3BO_3), charge compensator ions, reduction temperatures/time, and reduction atmosphere on the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphor have been explained in detail.

2. Experimental

Strontium aluminates doped with Eu^{2+} and Dy^{3+} were prepared by the reaction between strontium carbonate (SrCO_3 ; Aldrich, 99.9%), aluminium oxide (Al_2O_3 , BaikaloX, AR), europium oxide ($x\text{Eu}_2\text{O}_3$; Aldrich, 99.99%), dysprosium oxide ($y\text{Dy}_2\text{O}_3$; Aldrich, 99.99%), and boric acid ($x\text{H}_3\text{BO}_3$; Aldrich, 99%) in a reducing atmosphere of $\text{H}_2/\text{N}_2 = 1/9$ (20 mL H_2 /180 mL N_2) at various temperatures (1100–1400°C) for different time periods (4–6 h). The powders were weighed according to the chemical composition of $(4-x-y)\text{SrCO}_3 + 7\text{Al}_2\text{O}_3 + x \text{ at. \% Eu (as } \text{Eu}_2\text{O}_3) + y \text{ at. \% Dy (as } \text{Dy}_2\text{O}_3) + (0, 20, 40 \text{ and } 100) \text{ mol \% B (as } \text{H}_3\text{BO}_3)$. The appropriate amounts of the starting materials according to the derived compositions were mixed thoroughly in a mortar and pestle with the help of ethanol. The mixture was allowed to dry to form powder and prepared in the form of pellets of ($\varnothing$ 13 mm $\times$ 3 mm) dimension applying pressure of $650 \text{ kg}\cdot\text{cm}^{-2}$ for 3 minutes. Then, these pellets were preheated in air atmosphere at 800, 900, and 1000°C for 4 h at heating rate $150^\circ\text{C}/\text{h}$. After pulverization, pellets ($\varnothing$ 13 mm $\times$ 3 mm) were prepared. The pellets were heated in reducing atmosphere of $\text{H}_2/\text{N}_2 = 1/9$ flowing H_2 -20 mL/min and N_2 -180 mL/min. The products obtained after reduction were gritty solids which were pulverized to get fine powder.

Phase identification was carried out using a Shimadzu-610D X-ray diffractometer with $\text{Cu-K}\alpha$ radiation. Thermogravimetric (TG) and differential thermal analyses (DTA) were carried with a SEIKO-6300TG/DTA instrument. Scanning electron microscopy (SEM) observations were carried out using a Hitachi S-3000N scanning electron microscope. EDS coupled with SEM were used to observe the elemental mapping images of Eu and Dy in various samples. Elemental mapping of all samples were carried out for elapsed time of 100 seconds. Bulk area ($\varnothing$ 10 mm) EDAX measurements were carried out using Rayny EDX-800HS energy dispersive X-ray fluorescence spectrometer. Photoluminescence (PL) emission spectra were recorded using USB 4000-UV-VIS-NIR fiber optic spectrometer (Ocean optics). PL excitation spectra were measured using Hamamatsu Quantaurus QY absolute quantum yield measurement instrument. The decay curves were recorded using a brightness meter (Konica Minolta LS-100) equipped with RS232C Comm and fitted using Microsoft program solver. Before afterglow and decay

FIGURE 1: TG-DTA curves of $4\text{SrCO}_3\cdot 7\text{Al}_2\text{O}_3$ mixture containing different amount of boric acid as flux showing the reaction process during calcinations.

curves measurements, each sample was exposed to 15 W normal D65 fluorescent lamps for 5 minutes. All measurements were carried out at room temperatures.

3. Result and Discussion

To understand the thermal behavior of the raw materials and mixtures during raising temperature, it is necessary to observe TG and DTA. The TG and DTA measurements were carried out for representative samples $\text{S}_4\text{A}_7\text{B}_0$ (0 mol% H_3BO_3), $\text{S}_4\text{A}_7\text{B}_{0.2}$ (20 mol% H_3BO_3), and $\text{S}_4\text{A}_7\text{B}_{0.4}$ (40 mol% H_3BO_3) with 4 at.% Eu and 8 at.% Dy, and the results are depicted in Figure 1. The weight loss below 300°C indicates the dehydration of boric acid and γ -alumina used as raw powder. For $\text{S}_4\text{A}_7\text{B}_0$ mixture, ~3 wt% loss was due to dehydration of γ -alumina. The weight loss of $\text{S}_4\text{A}_7\text{B}_{0.2}$ and $\text{S}_4\text{A}_7\text{B}_{0.4}$ mixture below 300°C were 3.4 and 3.8%, respectively, that came from the weight loss in γ -alumina as well as the decomposition of boric acid present in the mixture. The total weight loss of 17.26%, 17.34%, and 18.84% was analogous to the theoretical values of 17.1%, 17.4%, and 17.7% for the $\text{S}_4\text{A}_7\text{B}_0$, $\text{S}_4\text{A}_7\text{B}_{0.2}$, and $\text{S}_4\text{A}_7\text{B}_{0.4}$, respectively. The endothermic peak on TG and DTA at $700\text{--}900^\circ\text{C}$ indicated the decomposition of SrCO_3 to form SrO, and it clearly suggested that SrCO_3 decomposed at relatively lower temperature in case of boric acid containing mixtures than without boric acid containing mixture.

Figures 2(a)–2(d) show the XRD patterns of strontium aluminate phosphors containing 0, 20, 40, and 100 mol% H_3BO_3 , respectively, prepared at 1300°C for 5 h. XRD patterns showed that in the phosphor without H_3BO_3 ($\text{S}_4\text{A}_7\text{B}_0$), SrAl_2O_4 (JCPDS; 34-0379), and $\text{SrAl}_{12}\text{O}_{19}$ (JCPDS; 26-0976) were appeared as main phases along with some residual alumina (JCPDS; 46-1212). On increasing H_3BO_3 content to 20 mol% ($\text{S}_4\text{A}_7\text{B}_{0.2}$), these SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$ phases decreased, and at the same time $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase appeared

as a major phase. The phosphor obtained by adding 40 mol% H_3BO_3 ($\text{S}_4\text{A}_7\text{B}_{0.4}$) showed single-phase $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ having orthorhombic crystal structure with $Pm\bar{m}a$ space group which is in good agreement with the JCPDS data (52-1876) and the results of others [16–18]. It suggests that $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase is formed by the reaction between $\text{SrAl}_{12}\text{O}_{19}$ and SrAl_2O_4 in presence of boron oxide that accelerates the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase formation acting as high temperature solvent. As boron content increased to 100 mol% ($\text{S}_4\text{A}_7\text{B}_{1.0}$), there appeared some crystalline aluminoborates $\text{SrAl}_2\text{B}_2\text{O}_7$ (JCPDS; 47-0182) along with glassy phases. So at higher H_3BO_3 concentrations, B_2O_3 (formed by decomposition of H_3BO_3) not only acts as high temperature solvent, but actively participates in chemical reaction with the aluminates to form aluminoborates as in Figure 2(d). Thus, formation of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ involves complex chemical reaction process in which SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$ are formed as intermediate phases [18]. The whole synthesis process can be expressed by the following chemical reactions:

The proposed reaction scheme is supported by TG results in Figure 1, and direct XRD patterns of the intermediate reaction products given in Figure 3. At very low reaction temperature of 800–900°C, there appeared SrAl_2O_4 and unreacted residual alumina. As reaction temperature increased to 1000°C, there appeared a new phase $\text{SrAl}_{12}\text{O}_{19}$ along with the SrAl_2O_4 phase. As in (5), SrAl_2O_4 reacts with residual alumina to form $\text{SrAl}_{12}\text{O}_{19}$ phase. Further, increase of temperature to 1200°C, a new metastable phase $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ appeared slightly. However, at reaction temperature of 1300°C, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ single phase was observed (Figure 3(d)). Thus, it is generalized that at higher temperatures SrAl_2O_4 reacts with $\text{SrAl}_{12}\text{O}_{19}$ in the presence of liquid boron oxide flux to generate metastable $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase as in (6). However, if boron oxide flux concentration is very high (>40 mol%), at higher temperature it actively participates in reaction with the products and forms aluminoborates and other glassy phases. We also conducted experiments at

FIGURE 2: XRD patterns of strontium aluminates phosphors: (a) $\text{S}_4\text{A}_7\text{B}_0$, (b) $\text{S}_4\text{A}_7\text{B}_{0.2}$, (c) $\text{S}_4\text{A}_7\text{B}_{0.4}$, and (d) $\text{S}_4\text{A}_7\text{B}_{1.0}$ sintered at 1300°C for 5 h.

FIGURE 3: The effect of preheating temperature on the phase formation of strontium aluminate phosphors.

higher temperature (1400°C, 1450°C, and 1500°C) keeping the flux concentration constant, but we observed the same phase $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$. However, if temperature is increased to 1600°C, $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase decomposes to form SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$ which are stable at higher temperatures.

The change in the grain morphology and the surface microstructure of the phosphors was examined by SEM observations. Figures 4(a)–4(d) represent the SEM micrograph of strontium aluminate phosphors containing 0, 20, 40, and 100 mol% H_3BO_3 , respectively. It is clear from Figure 4(a) that in the absence of H_3BO_3 irregular to round shaped, tinny ($\varnothing$ 0.2 to 0.5 μm) grains connected with each other were formed. Due to spherical particle shape, micropores were observed in the microstructure of the ceramics. When the H_3BO_3 concentration was increased to 20 mol% (Figure 4(b)), hexagonal to angular particles with increased particle size ($\sim 1 \times 1 \mu\text{m}$) were observed. The microstructure

FIGURE 4: SEM microstructures of the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphors prepared by adding different H_3BO_3 contents: (a) 0 mol%, (b) 20 mol%, (c) 40 mol%, and (d) 100 mol%.

was not smooth throughout indicating the presence of other phases or glasses on the surface [1]. It is well known that H_3BO_3 is a good glass former at higher temperature, the rough microstructure seen in the SEM images in Figures 4(b) and 4(d) was glass which was also supported by the XRD profile in Figure 2(b). In XRD patterns, the mountain like part from 2θ value of 18° to 30° is due to the presence of glassy phase. Due to the crystal growth, the micropores as observed in the ceramics without H_3BO_3 were reduced. As H_3BO_3 concentration increased to 40 mol%, fine and regular particles grew with increased particles size of $\sim 2 \times 2 \mu\text{m}$ (Figure 4(c)). The particles distribution was almost homogeneous throughout the surface. These angular shaped phosphor particles might have been formed by dissolution precipitation process from SrAl_2O_4 in the presence of molten B_2O_3 . But in Figure 4(d), at high B_2O_3 content, very big and irregular shaped particles with smooth corner and round holes were observed. At higher B content, large amount of glass was formed and completely covered the surface of the phosphor particles making the ceramics rough. The particle size distribution was wide ranging between 5 and $10 \mu\text{m}$. These results are also supported by the previously published works [11–15]. Thus, it might be suggested that at high temperature, the B_2O_3 acts as liquid medium flux and accelerates the grain growth of the particles generating highly crystalline and dense $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase at optimum

concentration but at higher concentration it generates the glasses and crystalline aluminoborates.

Figure 5 shows the excitation and emission spectra of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphors prepared at 1300°C . These samples can be excited by a wide range of UV to visible light ($<250 \text{ nm}$ to 450 nm wave length, $\lambda_{\text{max}} = 262 \text{ nm}$) showing wide applications. All the samples exhibited emission centered at 497 nm with blue-green color except $\text{Sr}_4\text{Al}_7\text{B}_0$ sample, but their intensity varied significantly with B contents. In the case of $\text{Sr}_4\text{Al}_7\text{B}_0$ sample, a significant amount of SrAl_2O_4 phase appeared which exhibits emission centered at 520 nm [13]. As a result, the emission peak is shifted to about 505 nm . All other samples contain $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ as a major phase which exhibits emission centered at about 495 nm . At the same time, increasing H_3BO_3 concentrations the phosphorescence intensity increased and reached the maximum at $\sim 40 \text{ mol\%}$ H_3BO_3 and above 40 mol% again decreased as in Figure 6. It may be explained as, in $\text{Sr}_4\text{Al}_7\text{B}_0$ phosphor, mixed phases of SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$ were existed, the later is nonweak emissive [13]. But increasing B concentration to $\sim 40 \text{ mol\%}$, highly crystalline, dense, single phase $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ was formed which produced higher PL intensity. It is the flux that can properly facilitate the entry of activator ions into the crystal lattice and aids in the formation of luminescent centers [19]. Due to liquid boron oxide as high temperature flux, distribution of the rare ions becomes random and deep

FIGURE 5: Excitation (dotted lines) and emission (solid lines) spectra of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+}, \text{Dy}^{3+}, x \text{ mol\% } \text{H}_3\text{BO}_3$ phosphor. Inset shows the digital micrograph of 40 mol% B contained phosphor in black light.

throughout the lattice, as well as, the flux enforce the Eu and Dy ions to replace the Sr site in the lattice. This increases the Eu and Dy contents in the lattice and causes steep increase in the PL properties. Further, to prove the increment of activator in the strontium aluminates host, EDAX experiments on samples containing 0, 20, 40, and 100 mol% B with same amount of Eu (4 at.%) and Dy (8 at.%) in the starting mixture were carried out, and the results were presented in Table 1. As shown in Table 1, the incorporated amount of Eu and Dy in the strontium aluminates host increased with the increase of the B content as flux, consequently increasing the PL and AGL intensity. The decrease in the PL intensity at higher content of B ($\text{S}_4\text{A}_7\text{B}_{1.0}$) might be due to the formation of nonemitting phase $\text{SrAl}_2\text{B}_2\text{O}_7$ and glasses as observed in XRD profiles that covers the emitting surface. Further, the EDS elemental mapping images of Eu and Dy in the phosphor containing 0, 40, and 100 mol% H_3BO_3 were shown in Figure 7. From the mapping images, it was clear that the surface concentration of Eu and Dy increased on increasing the H_3BO_3 concentrations.

Figure 6 depicts the persistent afterglow pattern of the phosphor samples containing 0, 20, 40, and 100 mol% H_3BO_3 with 4 at.% Eu and 8 at.% Dy. The afterglow data were recorded 10 seconds after the excitation source was switched off. It was found that the persistent time from B free phosphor was the least. As the amount of B increased, the initial phosphorescence intensity and the afterglow duration increased and reached the maximum at 40 mol% ($\text{S}_4\text{A}_7\text{B}_{0.4}$), above that it again decreased. The liquid phase sintering aided by H_3BO_3 facilitates the grain growth of the strontium aluminates and increases the penetration of trap centers in the phosphor that enhances the phosphorescence properties [20]. Further, the dissolved B^{3+} ions substitute Al^{3+} ions at tetrahedral positions [21]. This substitution result in the shrinkage of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$

FIGURE 6: Variation of afterglow intensities of strontium aluminate phosphor with different flux (H_3BO_3) concentrations.

lattice and enhance the hole trapping ability of Dy^{3+} ions that further increases the phosphorescence afterglow [22, 23]. The decrease of afterglow on increasing the B content ($\text{S}_4\text{A}_7\text{B}_{1.0}$) might be due to presence of glasses which covers the emissive surface of the phosphor.

The phosphorescence intensity and durability increased on increasing the preheating temperature from 800°C to 1000°C . The 800°C and 900°C preheated mixture showed some peaks of alumina and $\text{SrAl}_{12}\text{O}_{19}$ phase in XRD profiles (Figure 3). As temperature increased to 1000°C , alumina peaks completely disappeared, and $\text{SrAl}_{12}\text{O}_{19}$ peaks increased. As in reaction described above these two phases, namely, $\text{SrAl}_{12}\text{O}_{19}$ and SrAl_2O_4 reacts with each other in presence of boron oxide to generate $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phase. The higher PL intensity in case of 1000°C preheated and 1300°C reduced sample might be due to existence of dense, highly crystalline, single phase $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ as described earlier.

Figure 8 shows the variation of PL properties as a function of heating temperature and time. We observed that the phosphor prepared at 1300°C for 5 h in reducing atmosphere showed higher PL intensity and persistency. As reduction temperature increased above 1300°C and reduction time increased more than 5 h, the increase in emission intensity was incremental, indicating that 1300°C heating for 5 h was the sufficient temperature and time to get good PL properties. To get better PL properties, the phosphor should be prepared under slightly reduced atmosphere so as to reduce Eu^{3+} to Eu^{2+} . When the phosphor was prepared on air atmosphere, the PL intensity as well as durability was negligible. The negligible Eu^{2+} emission in the sample prepared in air comes from the self reduced Eu^{2+} in the Sr^{2+} sites as explained by Peng et al. [24].

Figure 9 shows the decay curves of afterglow phosphorescence of the phosphor specimens with various Al/Sr ratios (R). Keeping Al concentration constant, we monitored the Sr concentrations. While increasing the value of R from

FIGURE 7: EDS mapping of Eu ((a), (c), and (e)) and Dy ((b), (d), and (f)) in strontium aluminate phosphors prepared with different H_3BO_3 concentrations: ((a), (b)) 0 mol%, ((c), (d)) 40 mol%, and ((e), (f)) 100 mol%.

TABLE 1: The list of samples with various B contents and Eu^{2+} and Dy^{3+} values obtained from EDAX studies correlated with emission intensities.

Samples	Emission maximum (nm)	Phases	Amount of Eu^{2+} wt%	Amount of Dy^{3+} wt%	AGL intensity ($\text{cd}\cdot\text{m}^{-2}$)
$\text{S}_4\text{A}_7\text{B}_0$ (boron free)	505	SrAl_2O_4 and $\text{SrAl}_{12}\text{O}_{19}$	0.125%	0.5%	0.18
$\text{S}_4\text{A}_7\text{B}_{0.2}$ (20 mol% B)	498	SrAl_2O_4 and $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$	0.134%	0.69%	3.09
$\text{S}_4\text{A}_7\text{B}_{0.4}$ (40 mol% B)	495	$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$	0.146%	0.89%	3.31
$\text{S}_4\text{A}_7\text{B}_{1.0}$ (100 mol% B)	493	$\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ and $\text{SrAl}_2\text{B}_2\text{O}_7$	0.156%	0.92%	1.81

FIGURE 8: Variation of phosphorescence intensities as a function of heating temperature and time.

FIGURE 9: Afterglow decay curves of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphor with different Al/Sr ratio. Inset shows the Phosphorescence intensity of the corresponding phosphors just after switching off excitation source.

3.4 to 4.0, the initial intensity (inserted in Figure 9) and the afterglow duration of the phosphors first increased, attained the maximum at R equals 3.7, and then decreased when the R value was increased above 3.7. Similar results were observed by Yuan et al. [17] and explained on the basis of decay time (τ) values obtained by curve fitting and thermoluminescence measurements using TSL parameters. According to them, slightly Sr deficit samples exhibits large number of traps which is suitable for the brighter afterglow and longer afterglow time.

All the phosphors doped with different amount of Eu and Dy showed the main emission peak centered at ~ 497 nm as shown in the inserted curve in Figure 10. Further, the phosphor samples with lower concentration of Eu showed two emission peaks; one pronounced emission peak at

FIGURE 10: Phosphorescence decay curves of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphors with various Eu concentrations. Inserted figure shows the effect of Eu at.% on the PL intensity.

497 nm and another weak peak at about 407 nm. The weak peak at 407 nm decreased continuously on increasing Eu concentration while at the same time the main peak at 497 nm increased till it reached saturation. According to Li et al. [25] there are two Eu^{2+} sites in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ matrix due to existence of two different types of Sr^{2+} ions; one surrounded by 6 oxygen atoms and another surrounded by eight oxygen atoms in the oxygen polyhedra. However, with the increase of Eu concentration energy transfer from higher energetic Eu site to lower energy Eu site predominates, and emission band at 407 nm gradually decreased while at 497 nm increased. On increasing the Eu concentration, the initial phosphorescence intensity goes on increasing, attain maximum at 4 at.% Eu, and above it starts decreasing. It means 4 at.% Eu may be the critical quenching concentration [26]. When the doped Eu concentration is above 4 at.%, the nearby Eu ions in the lattice interacts with each other because the critical distance, assumed to be 40 nm [9], overcame above 4 at.% Eu concentration. So, the optimum doped amount of Eu^{2+} is 4 at.% in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ phosphor.

From the decay curves as shown in Figure 10, it is clear that the decay speed of the persistency of phosphors changed with the amount of Dy^{3+} concentration too. The codoped Dy acts as trap centers [2, 27] that trap the holes generated during the exposure of phosphor to excitation source. To monitor the variation of phosphorescence intensity according to Dy concentration, we kept the doped amount of Eu at 4 at.% and changed the codoped amount of Dy. On increasing Dy concentrations, the phosphorescence intensity increased as shown in Figure 10. When the codoped amount of Dy was 8 at.%, the phosphor showed the longest persistency of greater than 20 h with intensity greater than $5 \text{ mcd}\cdot\text{m}^{-2}$. But as the concentration of Dy was above 8 at.%, the phosphorescence intensity and persistency decreased sharply. It can be assumed that small amount of Dy is insufficient to form enough trap defects in the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}$ matrix to trap sufficient holes.

FIGURE 11: Variation of phosphorescence intensity of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphor with some of the charge compensating ions, each additives being 4 at. %.

However, if the amount of doped Dy is greater than 8 at.%, it may cause the concentration quenching and reduce the emission intensity.

The mechanism of phosphorescence in aluminates phosphor has been explained by many researchers [1, 2, 4, 11, 13, 28–30] and might be explained in detail as: upon exposure to excitation source, an electron of Eu^{2+} ($4f^7$) is promoted to the $4f^65d^1$ band followed by either direct or phonon assisted escape of the electron from Eu^{2+} to the host conduction band. The lattice defects (especially, oxygen vacancies) close to the bottom of the host conduction band traps the electrons. Large numbers of electrons are trapped by the Dy^{3+} or Dy^{3+} -borate complex assisted traps at various depths [28–30] making an important role of Dy^{3+} during the persistent afterglow. When the excitation source is removed, the captured electrons near the host conduction band released to the conduction band with thermal energy and consequent recombination of them with the emitting $\text{Eu}^{2+}/\text{Eu}^{3+}$ centers lead the persistent afterglow. Thus, the important point for the persistent afterglow is the number of electrons captured in the traps and its depths from the bottom of the host conduction band. The afterglow intensity of the persistent phosphor, thus, depends on the densities of the traps/captured electrons, while the afterglow duration depends on the depth of the captured electrons. The number of captured electrons, in turn, depends on the concentration of oxygen vacancies/ Dy^{3+}/Dy -borate complexes and the trap depth of it. Under the suitable trap depth, the trap concentration is directly proportional to the Dy ions or the concentration of Dy-borate complex. Hence, optimum Dy concentration produces the longer afterglow duration with higher intensity. Further, the factors which stabilize the traps or increase its density definitely increased the afterglow intensity and its duration.

FIGURE 12: Effect of Ag^+ ions doping on the afterglow emission of the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphor.

FIGURE 13: TL glow curves of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:$ 4 at.% Eu, 8 at.% Dy with and without B and Ag doping.

Figure 11 shows the effect of various charge compensators on the PL emission intensity of the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphor. The Li^+ , Na^+ , Ca^{2+} and Ag^+ ions doping increased the PL intensity while the Si^{4+} , W^{6+} , Ba^{2+} , and Mg^{2+} doping decreased the PL intensity on the increasing order. Since the Ag^+ doping increased the PL intensity the most, the effect of concentration of the Ag^+ ions on the PL emission of the phosphor was studied and expressed in Figure 12. It was observed that doping 3 mol% Ag^+ on the $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:$ 4 at.% Eu^{2+} , 8 at.% Dy^{3+} phosphor increased both the PL and AGL intensity more than 1.5-fold exhibiting most intense PL and longest afterglow duration. Similar results were observed by Suriyamurthy and Panigrahi [31]. According to them the

TABLE 2: TSL parameters of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+}$ phosphors.

Samples	Glow peak (°C)	Glow peak shape parameters				TSL parameters	
		δ	τ	ω	μ_g	E_T	n_o
S ₄ A ₇ B ₀	97	70	130	200	0.35	0.446	1.34×10^6
S ₄ A ₇ B _{0.4}	111	79	154	233	0.34	0.641	1.87×10^6
S ₄ A ₇ B _{0.4} , Ag _{0.03}	113	78	158	236	0.33	0.645	2.77×10^6

FIGURE 14: Comparison of PL excitation and PL emission intensity of $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+},\text{Ag}^+$ phosphor with the commercial Nemoto BGL300M.

enhanced afterglow intensity and lifetime by Ag^+ doping is due to the increased number of traps in the Ag^+ doped sample. It is speculated that the addition of Dy^{3+} ions into the Sr^{2+} sites produces stress due to charge imbalance which is reduced by the Ag^+ ions doping due to charge neutrality. We measured the TSL parameters of samples with and without Ag^+ ions doping as shown in Figure 13, and various TSL parameters are presented in Table 2. It is clear that addition B^{3+} not only increased the trap density but also deepened the traps making the phosphor persist for longer periods. But the addition of Ag^+ ions did not shift the peak positions, but the trap densities were drastically increased. The increased number of traps is responsible for the enhancement of the afterglow intensity.

The phosphor was also compared with the commercially available product from Nemoto and Co. LTD (BGL300M) in term of PL and decay parameters and expressed in Figure 14. It clearly suggests that our product is much more superior to BGL300M (the best one among commercially available blue-green persistent phosphor) and possess superior applications.

4. Conclusions

$\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+},\text{Ag}^+$ phosphor with high brightness and long persistent luminescence was prepared by the solid-phase reaction method at 1300°C . The broadband

UV-visible excited luminescence of the orthorhombic $\text{Sr}_4\text{Al}_{14}\text{O}_{25}:\text{Eu}^{2+},\text{Dy}^{3+},\text{Ag}^+$ was observed in the blue-green region ($\lambda_{\text{max}} = 497 \text{ nm}$) due to transitions from $4f^65d^1$ to $4f^7$ configuration of the Eu^{2+} ion. Well crystallized, regular shaped phosphor particles were obtained by the addition of small amount of H_3BO_3 as flux. The phosphorescent characteristics are highly influenced by the addition of small amount of H_3BO_3 in the starting mixture, and the maximum PL intensity was observed by adding 40 mol% H_3BO_3 . When the ratio of Al/Sr was 3.7, and the Eu and Dy concentrations were 4 at.% and 8 at.%, respectively, the phosphor exhibited a higher emission intensity and longer afterglow duration. The addition of Ag^+ ions has better effect on the PL emission and AGL intensity and duration of the phosphor due to the stabilization of the Dy^{3+} into the host and consequently increasing the traps responsible for the afterglow. The phosphor was compared with the commercial product and found to be much superior than the existing one.

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