Suggestions for Future Research Work

i) Luminescence study of the $Sr_3Al_2O_6$ material under influence of variation in concentration of the different impurities is highly essential to find good phosphors for their applications in lamp and radiation dose estimation.

ii) The study concerning the effect of change in relative concentrations of impurities on luminescence behaviors will definitely throw more light on the selection and the use of the material in both the fields undertaken in the present work.

iii) Generally, one selects, Blue-, Green-, and Red-emitting three different phosphors to obtain required CRI for getting white light. The present work indicates the possibility of getting all the three required emissions through same host, $Sr_3Al_2O_6$ by incorporating suitable multi activators with proper concentrations. This also prevents the chemical reactions expected in the lamp at operating temperature amongst the three different phosphors used to get White light emissions. Therefore, this is one of the important out come of the work. Research program must be undertaken in future to investigate these facts.

iv) The thermoluminescence dosimetric application of this phosphor has to be studied in detail by making pellets of $Sr_3Al_2O_6:Tb^{3+}$ phosphor. Also the TL dosimetric properties of $Sr_3Al_2O_6:Tb^{3+},Ce^{3+}$ phosphor is to be studied in lamps for accidental radiation monitoring.

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Synthesis, characterization and luminescence of $Sr_3Al_2O_6$ phosphor with trivalent rare earth dopant

Pallavi Page, Rahul Ghildiyal, K.V.R. Murthy *

Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara 390001, India

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Abstract

The luminescent properties of $Sr_3Al_2O_6$ doped and co-doped with the rare earths ($Ln^{3+} = Eu^{3+}$, Dy^{3+}, Eu^{3+} and Dy^{3+}) have been studied. The material was synthesized by reflux method and fired up to 900 °C for 16 h. The X-ray diffraction pattern confirms that the synthesized material consists of $Sr_3Al_2O_6$ as main phase. The photoluminescence study gives a clear evidence of europium stabilizing in trivalent form and surprisingly with no presence of europium in the divalent state. The addition of Dy^{3+} as co-dopant in the $Sr_3Al_2O_6$:Eu^{3+} matrix shows the quenching effect in the photoluminescence (PL) spectra. The photoluminescence intensity of Eu^{3+} falls gradually on increasing the concentration of the co-dopant in the range from 0.1 mole% to 2.0 mole%. The significantly intense thermoluminescence (TL) glow peak was obtained for $Sr_3Al_2O_6$:Eu^{3+}, Dy^{3+} (1% and 0.1%) at around 194 °C when irradiated with 10 kGy dose from Sr-90 β source.

Keywords: A. Optical materials; B. Chemical synthesis; C. X-ray diffraction; D. Luminescence

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1. Introduction

Though the long afterglow of strontium aluminates has been studied extensively, much of the research is focused on the new promises which this material shows when doped with various rare earth compounds. The effect of calcining temperature on the phase stabilization of the strontium aluminate is very interesting from the point of view of its varied applications. The role of rare earths in this regard is very important considering the wide variety of application prospects it shows. In recent years, the different phases of strontium aluminate doped with the rare earths have been developed like $Sr_2Al_6O_{11}$:Eu^{2+}, $Sr_4Al_{14}O_{25}$:Eu^{2+} [1–3], $SrAl_2O_4$:Eu^{2+}, Dy^{3+} [4–6], $SrAl_{12}O_{19}$:Eu^{2+}, $SrAl_4O_7$:Eu^{2+} [7,8], etc. These phosphors are known as efficient green and blue emitters and for their long persistent properties. The nanocrystalline phosphor $SrAl_2O_4$:Ce^{3+}, Pr^{3+}, Tb^{3+} [9] has also been reported with rare earth dopant effect on the optical properties of this phosphor. The calcining temperature and time play an important role in different phase formations in strontium aluminate ($SrO–Al_2O_3$) system. Different studies on this aspect have already been carried out and reported, in the temperatures range from 750 °C to 1100 °C [10]. The phases reported are $Sr_3Al_2O_6$ along with $SrAl_2O_4$ and $SrAl_4O_7$. The new phase $Sr_3Al_2O_6$ [11] is also seen but Akiyama et al. [12] have reported this phase at

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* Corresponding author. Tel.: +91 9327225568; fax: +91 2652710377.
E-mail address: drmurthykvr@yahoo.com (K.V.R. Murthy).

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1300 °C. Most of the literature have mentioned that the pure phase $SrAl_2O_4$, $Sr_4Al_{14}O_{25}$ and $SrAl_{12}O_{19}$ are found at temperature as high as 1300 °C. Capron and Douy [7] have reported that the monoaluminate phase ($SrO–Al_2O_3$) was not achieved even at 1400 °C but was found at above 1500 °C; further, as the temperature was increased to 1800 °C, the compound became unstable and the two phases $SrAl_2O_4$ and $SrAl_4O_7$ were found. Thus, a lot of discrepancy in the literature exists over the calcining temperature and the corresponding phase formations. As our interest is centered around developing a very strongly emitting phosphor rather than on temperature-dependent phase transformation, we have concentrated on this aspect in the present paper.

Europium doped strontium aluminate is mostly reported to have characteristic emission of europium in the divalent state; however, some of the papers also report the presence of europium in divalent as well as trivalent state when calcined up to 750–900 °C [10,11]. In the present paper, we report on the preparation and the characterization of $Sr_3Al_2O_6:Eu^{3+}$, $Sr_3Al_2O_6:Dy^{3+}$ and $Sr_3Al_2O_6:Eu^{3+}, Dy^{3+}$, their luminescence properties and the influence of co-dopants on the photoluminescence (PL) intensity of these phosphors.

2. Experimental

All the phosphor samples were prepared by the reflux method. The starting materials taken were strontium nitrate, aluminium nitrate and the rare earths in the nitrate form. All of them were acquired from S.D. Fine Chemicals with rare earths of purity 99.9%. The first set of the samples was prepared by doping the europium nitrate in the host matrix. The powders were weighed according to the nominal composition of $Sr(NO_3)_2 + Al(NO_3)_3{\cdot}9H_2O + xEu(NO_3)_3$ ($x = 0\%$, 1%, 1.5% and 2%). Second set of samples was prepared with dysprosium as dopant with composition as $Sr(NO_3)_2 + Al(NO_3)_3{\cdot}9H_2O + yDy(NO_3)_3$ ($y = 0\%$, 0.025%, 0.5%, 1%, 1.5% and 2%). Also a third set of samples was prepared doped and co-doped with europium and dysprosium, respectively, i.e. $Sr(NO_3)_2 + Al(NO_3)_3{\cdot}9H_2O + 1\%$ $Eu(NO_3)_3 + yDy(NO_3)_3$ ($y = 0\%$, 0.1%, 0.2%, 0.3%, 0.5% and 2%).

The starting materials strontium and aluminium nitrates were taken in 1:2 proportions and dissolved in the appropriate amount of distilled water and kept for stirring. Thereafter the rare earths compounds with different concentrations were mixed to the above solution. Citric acid and ethylene glycol were added to the solution after 1 h of constant stirring. The resulting gel was set for refluxing at 100 °C for 3 h. The gel thus obtained was kept for drying in an oven maintained at 100 °C for 10 h. The yellowish gel then transformed into a fluffy material. It was then kept for firing at a temperature maintained at 900 °C in a furnace for 16 h in air. The white powder obtained on firing was ground using an agate mortar and pestle and was then subjected to various characterizations.

Phase identification of the powders was carried out by the X-ray powder diffraction using Rigaku D'MAX III Diffractometer having Cu Kα radiation. The photoluminescence (emission and excitation spectra) was recorded at room temperature using spectrofluorophotometer RF-5301 PC of Shimadzu make. The thermoluminescence (TL) glow curves of all the samples were recorded using Nucleonix make TL reader with a heating rate of 7.5 °C/s. For measuring the thermoluminescence glow curve all the samples were first irradiated with β-rays from a Sr-90 source of 50 mCi strength.

3. Results and discussion

3.1. X-ray diffraction studies

In order to determine the crystal structure, phase purity, chemical nature and homogeneity of the phosphors, X-ray diffraction (XRD) analysis was carried out. Fig. 1 shows X-ray diffraction pattern of the $Sr_3Al_2O_6:Eu^{3+}(1\%)$, $Dy^{3+}(0.1\%)$ phosphor. From the XRD pattern analysis it was found that the prominent phase formed is $Sr_3Al_2O_6$. The $Sr_3Al_2O_6$ phase belongs to the space group *pa*3 having a cubic crystalline structure (JCPDS card no. 24-1187). Where few $SrAl_4O_7$ peaks were also observed, the peaks representing $SrAl_2O_4$ were very weak. All the samples followed the same XRD pattern.

3.2. Photoluminescence characteristics

The excitation and emission spectra of $Sr_3Al_2O_6:xEu$ (where $x = 0\%$, 1%, 1.5% and 2%) were measured at room temperature and are shown in Figs. 2–4, respectively. The emission spectra were recorded for all the phosphors after

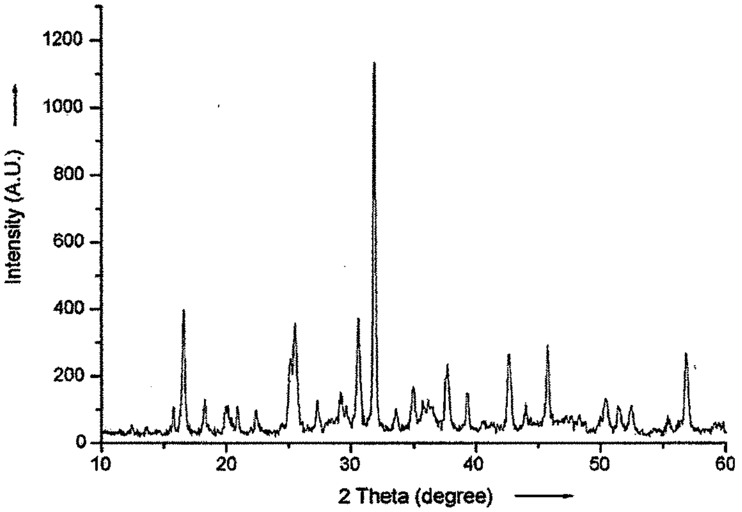

Fig. 1. X-ray diffraction pattern of $Sr_3Al_2O_6$:Eu^{3+} (1%), Dy^{3+} (0.1%).

exciting them with 254 nm wavelength. The undoped $Sr_3Al_2O_6$ material does not show any luminescence but the emission spectra of europium doped material show luminescence in the wavelength range from 580 nm to 620 nm. The $Sr_3Al_2O_6$:Eu^{3+} phosphor exhibits narrow emission at 580 nm, 592 nm, 595 nm, 613 nm and 617 nm instead of characteristic 520 nm emission which is the case for divalent europium. One can also observe from Fig. 3 that as the europium concentration increased from 1% to 2% the intensity of the lines at the respective wavelengths also goes on increasing. Such unexpected trivalent emission from $Sr_3Al_2O_6$:Eu^{3+} materials was also observed by Song et al. [10], wherein they considered $Sr_3Al_2O_6$ to be an intermediate phase at 900 °C along with the presence of $SrAl_2O_4$ and $SrAl_4O_7$. As the temperature was increased above 1200 °C the $Sr_3Al_2O_6$ and $SrAl_4O_7$ transform into $SrAl_2O_4$. Song et al. also stated that the Eu^{3+} ions stabilized at the $Sr_3Al_2O_6$ sites only. At the elevated temperatures along with the transformation of $Sr_3Al_2O_6$ into $SrAl_2O_4$ the trivalent europium (Eu^{3+}) also was converted into divalent (Eu^{2+}) form. This observation of trivalent europium (Eu^{3+}) emission along with divalent europium (Eu^{2+}) is also reported by Liu

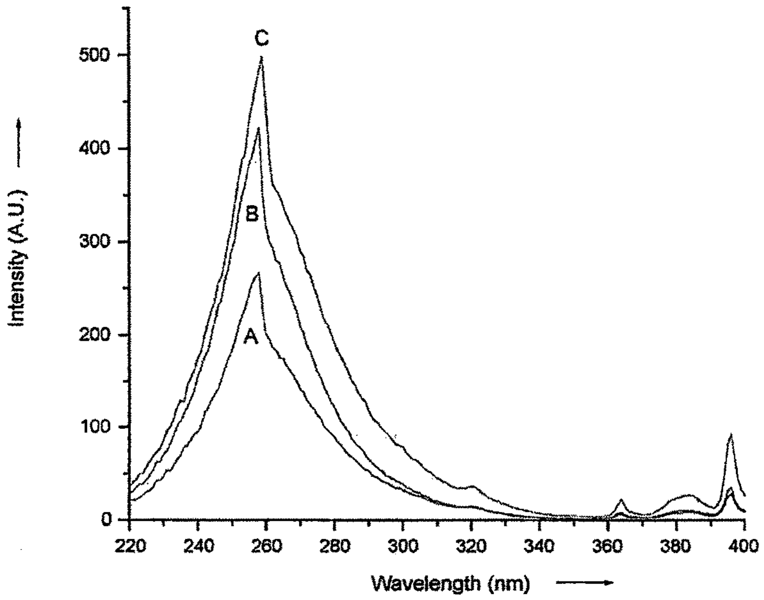

Fig. 2. Excitation spectra of $Sr_3Al_2O_6$:Eu^{3+} monitored at 613 nm, where (A) $Sr_3Al_2O_6$:1% Eu; (B) $Sr_3Al_2O_6$:1.5% Eu; (C) $Sr_3Al_2O_6$:2% Eu.

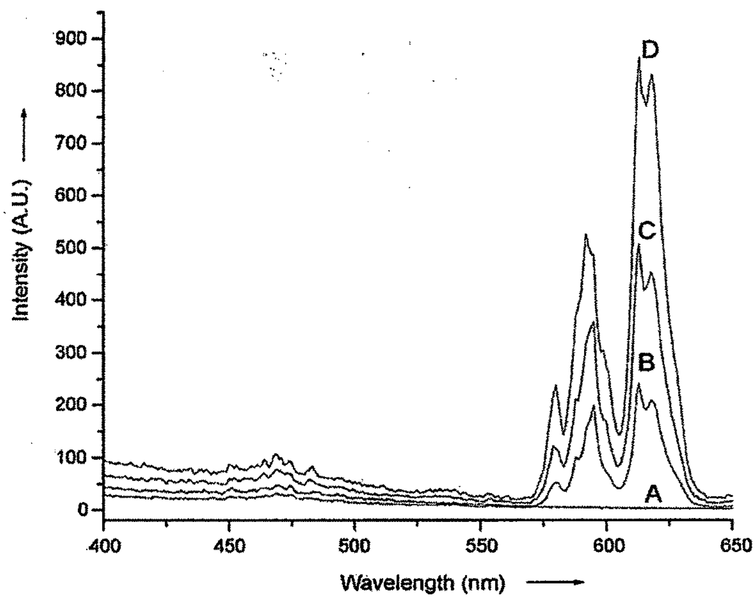

Fig. 3. Emission spectra of $Sr_3Al_2O_6:Eu^{3+}$ monitored at 254 nm excitation, where (A) $Sr_3Al_2O_6$:0% Eu; (B) $Sr_3Al_2O_6$:1% Eu; (C) $Sr_3Al_2O_6$:1.5% Eu; (D) $Sr_3Al_2O_6$:2% Eu.

and Xu [11] at 750–1000 °C. The authors have further reported that the host $Sr_3Al_2O_6$ was not responsible for the emission from trivalent europium but it was $SrAl_2O_4$ that was responsible for the emission due to the lack of inversion symmetry.

Fig. 3 shows very intense emission spectra of trivalent europium ion. Further the high intensity ratio for the two fluorescence transitions mainly $^5D_0 \rightarrow {}^7F_2$ and $^5D_0 \rightarrow {}^7F_1$ indicates that the Eu^{3+} site is closer to the inversion symmetry [13–15] and is also attributed to $Sr_3Al_2O_6$ host lattice as there is no evidence of $SrAl_2O_4$ being present. We are at variance with the observations of Liu et al., on this point as our XRD pattern clearly shows the $Sr_3Al_2O_6$ as the prominent phase and our results are in agreement with those reported by Song et al. [10]. Moreover, the highly intense emission of the europium in the $Sr_3Al_2O_6$ is clearly seen in Fig. 3 resulting transitions from $^5D_0 \rightarrow {}^7F_J$ (J = 0–2) and no transition is observed which could be due to the characteristic of divalent europium (Eu^{2+}), i.e. from $^4F_6{}^5D_1 \rightarrow {}^4F_7$.

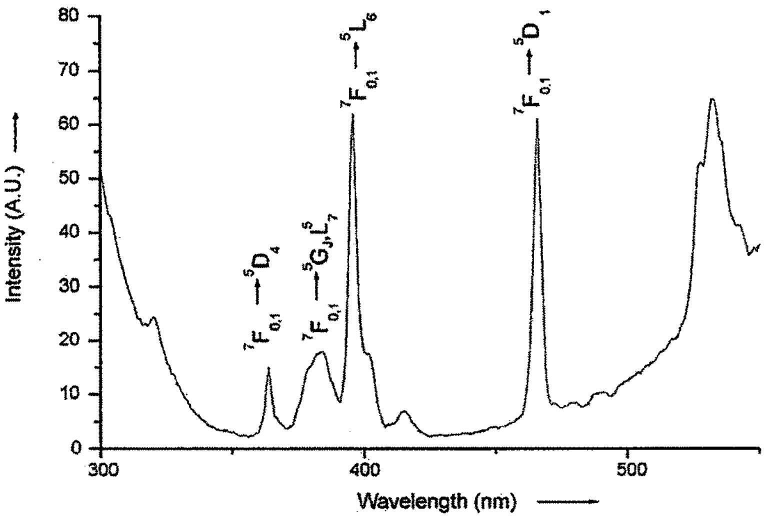

Fig. 4. Excitation spectra of $Sr_3Al_2O_6:Eu^{3+}$ in the range 300–550 nm at room temperature, the wavelength is monitored at 613 nm.

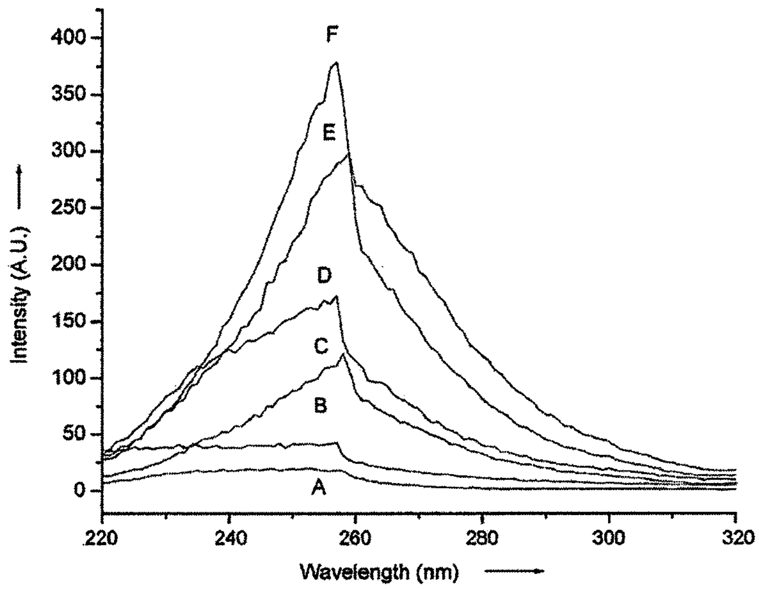

Fig. 5. Excitation spectra of $Sr_3Al_2O_6$:Eu^{3+}, Dy^{3+} monitored at 613 nm, where (A) $Sr_3Al_2O_6$:1% Eu, 2% Dy; (B) $Sr_3Al_2O_6$:0% Eu, 0.5% Dy; (C) $Sr_3Al_2O_6$:1% Eu, 0.5% Dy; (D) $Sr_3Al_2O_6$:1% Eu, 0.3% Dy; (E) $Sr_3Al_2O_6$:1% Eu, 0.2% Dy; (F) $Sr_3Al_2O_6$:1% Eu, 0.1% Dy.

Fig. 4 shows the excitation spectra of $Sr_3Al_2O_6$:1% Eu^{3+} phosphor in the 300–550 nm range. The emission wavelength at 613 nm shows sharp lines in the spectra corresponding to the direct excitation of the Eu^{3+} ground state to higher levels of the ^4F-manifold. The transitions at the $^7F_{0,1} \rightarrow {}^5D_2$ are clearly seen at 466 nm. These lines were also reported in the Eu^{3+}doped $LaPO_4$ material by Wang [13]. We observed the $^7F_{0,1} \rightarrow {}^5D_4$, $^7F_{0,1} \rightarrow {}^5G_J$, $^5L_7$ and $^7F_{0,1} \rightarrow {}^5L_6$ along with $^7F_{0,1} \rightarrow {}^5D_1$ transitions at 364 nm, 384 nm, 396 nm and 533 nm, respectively.

Figs. 5 and 6 show the excitation and emission spectra of the $Sr_3Al_2O_6$:Eu^{3+}, Dy^{3+} phosphors. Curve A in Fig. 6 represents the emission spectra of $Sr_3Al_2O_6$:0.5% Dy^{3+} phosphor, surprisingly dysprosium doping in the $Sr_3Al_2O_6$ has

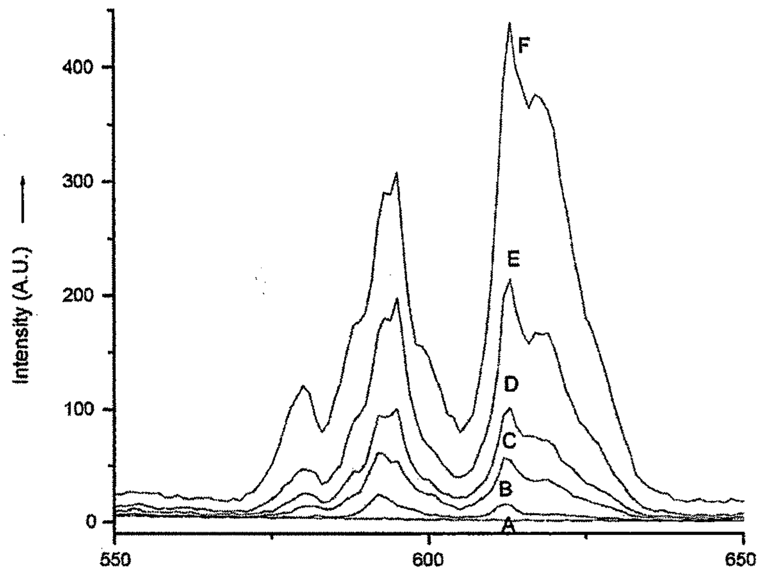

Fig. 6. Emission spectra of $Sr_3Al_2O_6$:Eu^{3+}, Dy^{3+} is monitored at 254 nm excitation, where (A) $Sr_3Al_2O_6$:0% Eu, 0.5% Dy; (B) $Sr_3Al_2O_6$:1% Eu, 2% Dy; (C) $Sr_3Al_2O_6$:1% Eu, 0.5% Dy; (D) $Sr_3Al_2O_6$:1% Eu, 0.3% Dy; (E) $Sr_3Al_2O_6$:1% Eu, 0.2% Dy; (F) $Sr_3Al_2O_6$:1% Eu, 0.1% Dy.

Table 1
Various concentrations of the rare earth elements in the $Sr_3Al_2O_6$ matrix

S. no.	Sample name	Percentage of europium	Percentage of dysprosium
1	$Sr_3Al_2O_6$ (Fig. 6, curve A)	0	0.5
2	$Sr_3Al_2O_6$ (Fig. 6, curve B)	1	0.1
3	$Sr_3Al_2O_6$ (Fig. 6, curve C)	1	0.2
4	$Sr_3Al_2O_6$ (Fig. 6, curve D)	1	0.3
5	$Sr_3Al_2O_6$ (Fig. 6, curve E)	1	0.5
6	$Sr_3Al_2O_6$ (Fig. 6, curve F)	1	2

not yielded any luminescence. Up till now $SrAl_2O_4:Eu^{2+}$, Dy^{3+} has been reported as an excellent long persistent phosphor [4–6], on the other hand $Sr_3Al_2O_6:Eu^{2+}$, Dy^{3+} phosphor has been reported as an excellent mechanoluminescent phosphor emitting green light [12,16]. Table 1 depicts the doping and co-doping concentrations in all the samples. On doping Dy^{3+} in $Sr_3Al_2O_6:Eu^{3+}$ we got the emission in the red region of the visible spectrum. As the concentration of Dy^{3+} was increased from 0.1% to 2% the emission intensity in the red region decreased. The significant decrease is correlated to the presence of the major phase of $Sr_3Al_2O_6$ in the host material rather than that of $SrAl_2O_4$ thereby showing the quenching effect due to addition of Dy^{3+}. This is due to the fact that $Sr_3Al_2O_6$ is the prominent phase observed in the present studies, and the red emission observed with excitation by 254 nm in the europium doped and dysprosium co-doped systems may be ascribed to the stabilization of Eu^{3+} ions in $Sr_3Al_2O_6$ host lattice and subsequent energy transfer (quenching of Eu^{3+} emission) to Dy^{3+} ions does not result in any significant Dy^{3+} ion emission.

3.3. Thermally Stimulated Luminescence characteristics

The phosphors were subjected to the Thermally Stimulated Luminescence (TSL) study to ascertain the defects present in the synthesized compounds. The thermoluminescence glow curve of the $Sr_3Al_2O_6$, $Sr_3Al_2O_6:Eu^{3+}$ (1%) and $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and 0.1%) samples were obtained in the temperature range between room temperature and 450 °C. A test dose of 10 kGy from a β-source (Sr-90) of 50 mCi strength was given to all the samples. The thermoluminescence glow curves were measured for heating rate of 7.5 °C/s. Fig. 7 shows the TL glow curves of β-irradiated $Sr_3Al_2O_6$, $Sr_3Al_2O_6:Eu^{3+}$ (1%) and $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and 0.1%) phosphors.

The host lattice, viz. $Sr_3Al_2O_6$ (Fig. 7, curve A), did not show any glow peaks while $Sr_3Al_2O_6:Eu^{3+}$ (1%) (Fig. 7, curve B) sample showed a very weak glow peak at around 194 °C. The glow curve for $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and

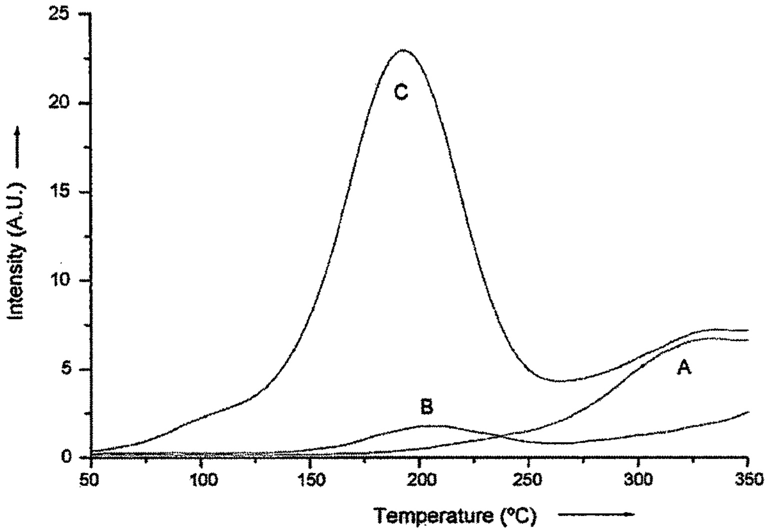

Fig. 7. TL glow curve of the samples, where (A) $Sr_3Al_2O_6$; (B) $Sr_3Al_2O_6:Eu^{3+}$ (1%); (C) $Sr_3Al_2O_6:Eu^{3+}$ (1%), Dy^{3+} (0.1%).

0.1%) (Fig. 7, curve C) however showed an intense glow peak at the same temperature of 194 °C. As the host lattice alone and the doped systems have all shown a continuously increasing trend in intensity of the glow curve beyond 300 °C without any specific peak appearance it is thought to be the onset of Kanthal strip glow (black body radiation). Thus, it is not considered to be a genuine glow peak for Thermally Stimulated Luminescence and all measurements were restricted to the 194 °C peak only. The traps in the $Sr_3Al_2O_6$ and $Sr_3Al_2O_6:Eu^{3+}$ seem to be very low due to lack of trapping levels present in the compound but on the doping of dysprosium in $Sr_3Al_2O_6:Eu^{3+}$ the electron concentration increases and the traps are formed, though at deep levels. The $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and 0.1%) material was also illuminated with a UV lamp of 365 nm wavelength for 30 min, but no thermoluminescence was observed. The trap depth of the β-irradiated $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and 0.1%) (Fig. 7, curve C) sample was calculated by Hoogenstraten equation and also by Chen's equation. We found that the trap depth calculated by Hoogenstraten equation [6,11] was 0.17 eV and by Chen's equation [17] was 0.87 eV. The significantly large difference in the values of trap depth is attributed to the Hoogenstraten equation being very approximate in estimating the trap depth value. The calculated trap depth in the $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} (1% and 0.1%) is too deep to give phosphorescence at room temperature. This could be the main reason for the absence of long afterglow even after UV illumination. The TL glow curve of $Sr_3Al_2O_6:Eu^{2+}$, Dy^{3+} was also studied by Akiyama et al. [16] in the temperature ranging from room temperature to 250 °C and they found it to be very weak compared to the $SrAl_2O_4:Eu^{2+}$, Dy^{3+} and $SrAl_4O_7:Eu^{2+}$, Dy^{3+}.

4. Conclusions

The $Sr_3Al_2O_6$, $Sr_3Al_2O_6:Eu^{3+}$ and $Sr_3Al_2O_6:Eu^{3+}$, Dy^{3+} have been successfully synthesized and the mechanism of the luminescence is due to stabilization of europium in the trivalent state. It was also observed that the dysprosium acts as a quencher in the $Sr_3Al_2O_6:Eu^{3+}$ matrix. The optical properties of this material lead us to state that it may serve as a promising material for use as lamp phosphor in the red region.

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Photoluminescence and thermoluminescence properties of $Sr_3Al_2O_6$:Tb^{3+}

Pallavi Page [1], Rahul Ghildiyal [1], K.V.R. Murthy *

Display Materials Laboratory, Applied Physics Department, Faculty of Technology and Engineering, The M.S. University of Baroda, Vadodara 390001, India

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Abstract

Photoluminescence and thermoluminescence characteristics of the SrO–Al_2O_3 system doped with terbium have been studied and reported here. The phosphor was synthesized by a reflux sol–gel technique. With a view to study the dosimetric properties, the effect of beta irradiation has been studied in detail; further, concentration quenching effects observed in the emission of various terbium doped phosphors have led to optimization of dopant content. A case is made to project the phosphor as an efficient green light emitting material with good dosimetric properties.

Keywords: A. Optical materials; B. Chemical synthesis; C. X-ray diffraction; D. Luminescence

1. Introduction

Recently, great emphasis has been placed on the dosimetric properties of the phosphor materials and the use of a phosphor as an accidental dosemeter [1,2]. This has opened up new challenges to the researchers in this field. Accidental dosimetry has its applications in protecting humans as well as for the environment as a whole. Until today the dosimetric materials mainly used for this purpose are $CaSO_4$:Dy and LiF:Mg but a great deal of research has aided the development of phosphors doped with other rare earths as well as the application of the lamp phosphors as dosimeters, such as the work by Rosa and coworkers [3–5] and Liu et al. [6]. They have studied many of these phosphors by elaborating on the thermoluminescence properties and their applications as dosimeters. The dual nature of some of the phosphors has also been studied by Murthy et al. [7,8]. Strontium aluminate, due to its long light persistence property is one such material that has been studied extensively for almost a decade now [9,10]. In our earlier work, we have reported the photoluminescence and thermoluminescence properties of rare earth doped $Sr_3Al_2O_6$ phosphor [11]. Not much has been reported on the $Sr_3Al_2O_6$ phase and its optical and thermoluminescent properties except its applicability as a mechanoluminscent material [12]. In this article, we report the optical and thermoluminescent properties of this material doped with terbium. To study the effect of the beta irradiation on the nature and type of traps, and to understand the mechanism by which the radiative recombination is taking place, the

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* Corresponding author. Tel.: +919327225568; fax: +912652710377.

E-mail address: drmurthykvr@yahoo.com (K.V.R. Murthy).

[1] Both the authors have contributed equally to the manuscript.

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thermoluminescence glow curves were recorded. For any phosphor to be a potential candidate as a dosimeter it should satisfy some set of criteria such as fading, linearity, reproducibility etc. [8]. All these dosimetric properties of the $Sr_3Al_2O_6$:Tb have been studied and discussed in detail in the article. The dopant concentration in the system was varied and the effect of concentration quenching was studied. The trap parameters have been evaluated by using Chen's equation. This paper reports in length the analysis of the data and the effect of the beta irradiation on the terbium doped $Sr_3Al_2O_6$ phosphor.

2. Experimental

2.1. Sample preparation

The synthesis of the $Sr_3Al_2O_6$ doped with rare earths has been described in our previous paper [11]. The phosphor samples were prepared by the reflux method. The starting materials of strontium and aluminum nitrates were taken in stoichiometric ratio and dissolved in the appropriate amount of distilled water and kept for stirring. Thereafter the rare earth dopant (as an activator) with different concentrations in the range of 0.025–2.0 mol% was mixed into the above solution. Citric acid and ethylene glycol were added to the solution after 1 h of constant stirring. The resulting gel was set for refluxing at 80 °C for 6 h. The gel thus obtained, was dried in an oven maintained at 100 °C for 10 h. The yellowish gel then transformed into a fluffy material. It was then fired at 900 °C in a furnace for 16 h in air. The white powder obtained after firing, was ground using an agate mortar and pestle and was then subjected to various characterization tests.

2.2. X-ray diffraction, photoluminescence and thermoluminescence characterization

Phase identification of the powders was carried out by the X-ray powder diffraction using a RIGAKU D'MAX III Diffractometer having Cu Kα radiation. The photoluminescence (Emission and Excitation spectra) were recorded at room temperature using a spectrofluorophotometer (RF-5301 of SHIMADZU) with a xenon source. The slit width of both the excitation and the emission monochromator was kept at 1.5 nm and the sensitivity was kept high for all the samples. The thermoluminescence glow curve of all the samples were recorded using a Nucleonix-1009 make thermoluminescence reader at a constant heating rate of 2.0 °C/s. The amount of sample used for studying TL was 5 mg and was irradiated with Beta rays from a Sr-90 source of 50 mCi strength.

3. Result and discussion

3.1. X-ray diffraction studies

In order to determine the phase purity of the phosphors, X-ray diffraction (XRD) analysis was carried out. Fig. 1 shows X-ray diffraction (XRD) pattern of the $Sr_3Al_2O_6$:Tb^{3+} phosphor. From the XRD pattern analysis it was found

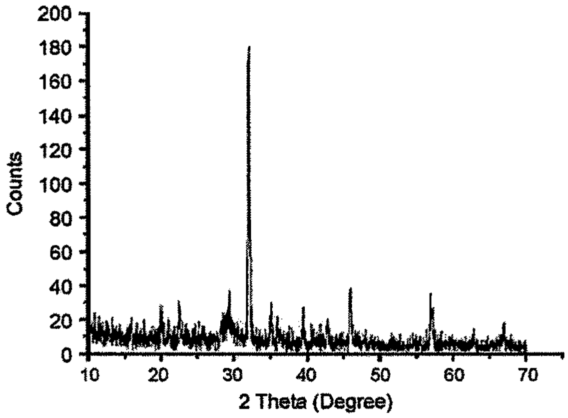

Fig. 1. The X-ray diffraction pattern of $Sr_3Al_2O_6$:Tb (1%).

that the prominent phase formed was $Sr_3Al_2O_6$. The $Sr_3Al_2O_6$ phase belongs to the cubic space group pa3 [13]. The traces of other phases of $SrO–Al_2O_3$ system were very weak. As the XRD patterns are similar for all the terbium concentrations, only one with 1% terbium has been shown and it matches very well with that reported by Kennedy and coworkers [14].

3.2. Photoluminescence (PL) characteristics

The emission and excitation spectra were recorded at room temperature for the $Sr_{3-x}Al_2O_6$: xTb (where $x = 0.025$, 0.1, 0.5, 1.0, 1.5 and 2.0 mol%) samples and are shown in Figs. 2 and 3, respectively. The emission spectra show the peaks mainly at 489, 545, 585 and 620 nm, respectively when excited with 254 nm. These have been identified as due to the transitions $^5D_4 \rightarrow {}^7F_{6,5,4\text{ and }3}$ trivalent terbium ions in the $Sr_3Al_2O_6$ phosphors. Of these, the green emission at 545 nm ($^5D_4 \rightarrow {}^7F_5$) is the most intense of all the transitions. This can also be attributed to the fact that even for higher concentration of terbium in the host matrix, the absence of blue emission was typical as the cross relaxation produces an increase in the population of the $^5D_4$ state at the expense of the $^5D_3$ state [15]. Moreover, we found that as the concentration of the terbium was increased in the host lattice, there was a significant increase in the intensity of all the terbium transitions and at 2.0 mol% terbium concentration the observed intensity for 545 nm peak $^5D_4 \rightarrow {}^7F_5$ was out of range of the measuring instrument. The excitation spectra show the peak at 254 nm when monitored for 545 nm emission. This is a broad band starting from 220 nm and ending at around 290 nm. The intensity of this band goes on increasing as the concentration increases from 0.025 mol% to 2.0 mol% and it was also recorded out of range of the

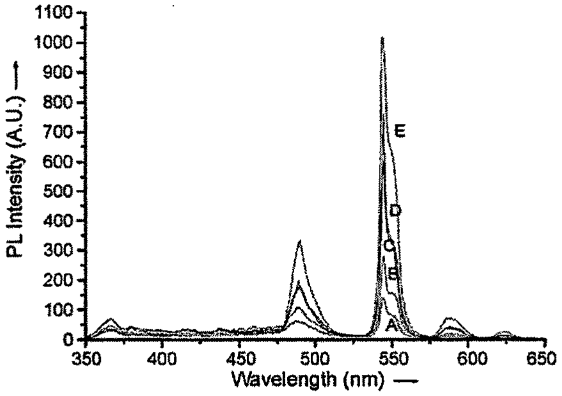

Fig. 2. The emission spectra of $Sr_3Al_2O_6$:Tb, where $A = 0.025\%$, $B = 0.1\%$, $C = 0.5\%$, $D = 1.0\%$, $E = 2.0\%$ mole concentration of Terbium.

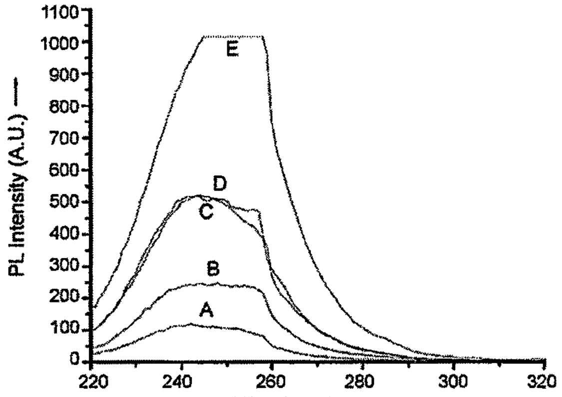

Fig. 3. The excitation spectra of $Sr_3Al_2O_6$:Tb, where $A = 0.025\%$, $B = 0.1\%$, $C = 0.5\%$, $D = 1.0\%$, $E = 2.0\%$ mole concentration of Terbium.

measuring instrument for the terbium concentration at 2.0 mol%. The excitation peak at 254 nm signifies that this has a potential to be used as a green emitting phosphor in lamps as it coincides with 254 nm of mercury emission.

3.3. Thermoluminescence (TL) characteristics

The thermoluminescence response of the terbium doped $Sr_3Al_2O_6$ phosphor has been studied above room temperature. Until now, the TL study of the SrO–Al_2O_3 system was done only to find out the kinetic parameters of the phosphor so as to know the trap depth responsible for the thermoluminescence of the phosphor. As per our knowledge the application of the SrO–Al_2O_3 system as a dosimeter is a new concept and has not been studied yet in detail. The TL measurements of $Sr_3Al_2O_6$: Tb (1%) were carried out to ascertain the defects present in the synthesized compound. The thermoluminescence glow curve of the $Sr_3Al_2O_6$:Tb^{3+} (1%) sample was obtained in the temperature range between room temperature to 450 °C. By considering the high radiation field during a nuclear disaster, a test dose of 100 Gy from a beta source (Sr-90) was given to the samples. The TL glow curve of the $Sr_3Al_2O_6$:Tb^{3+} (1%) phosphor is shown in Fig. 4. The first peak at 124 °C along with a hump at around 163 °C and a second peak at around 350 °C was observed. To isolate the peaks of the glow curve the "Tstop" technique [16] was applied. To separate the hump from the 124 °C peak, a fresh sample was exposed to beta rays to accumulate equal dose. The irradiated material was then heated upto 122 °C to bleach the 124 °C peak. After heating the material, TL was again recorded under the same conditions. The hump at 163 °C turned into a single peak. To find out if more peaks exist above this temperature, the procedure of thermal cleaning was repeated after every 10 °C. But no other peak was observed except the peak at 350 °C.

The analysis of all the three isolated glow peaks was done using the peak shape method [17], as this is the most widely used and accepted for the glow curve analysis. The order of kinetics of all the glow curves was calculated by measuring the symmetry (geometrical) factor:

$$\mu_g = \frac{\delta}{\omega} \tag{1}$$

The values of the δ, ω and τ were calculated as follows: $\delta = T_2 - T_m$, the high-temperature half width of the glow curve; $\omega = T_2 - T_1$, the full width of the glow peak at its half height; $\tau = T_m - T_1$, the low-temperature half width of the glow curve.

From the values of the geometrical factor it is clear that all the three peaks obey General Order Kinetics. The trap depth or the activation energy was calculated using the Chen's equation [17]:

$$E_\alpha = c_\alpha\left(\frac{kT_m^2}{\alpha}\right) - b_\alpha(2kT_m) \tag{2}$$

Where k = Boltzmann constant and T_m = peak temperature.

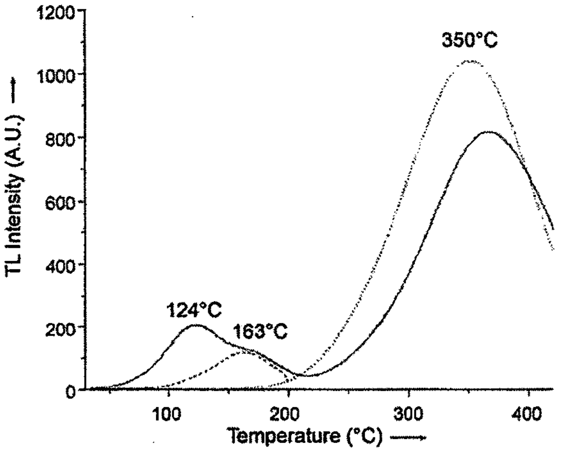

Fig. 4. The Thermoluminescence spectra of $Sr_3Al_2O_6$:Tb(1.0%) exposed to 100 Gy beta dose. The dashes (- - -) and dots (· · ·) line shows the isolated peaks after the T_{stop} method was applied.

Table 1
The values of the activation energy as calculated by Chen's equation

Peak temperature T_m (°C)	Geometrical factor (μg)	E_t (eV)	E_α (eV)	E_δ (eV)	Mean E (eV)
124	0.55	0.75	0.75	0.746	0.748
163	0.5	0.77	0.79	0.81	0.79

The values of the constants, c_α and b_α were calculated by the Chen's Equation for the General Order Kinetics where α was replaced by δ, ω or τ as the case may be.

The calculated values by the Chen's equation are listed in Table 1. The mean activation energy for the temperature region at 124 °C comes out to be 0.748 eV and for the 163 °C it comes out to be 0.79 eV. The addition of the terbium as activator produces deep traps at temperature around 120–350 °C which could be useful for dosimetric purpose due to their thermal stability and low fading. The role of the dopant in the host matrix is to increase overall oxygen vacancies and in consequence number of trapped charge carriers that in turn, induce an increment of the TL signal intensity. The TL glow pattern of the phosphor indicates that the presence of the terbium ions increases the TL efficiency. This increase may be due to enhancement of the charge carriers and the radiative recombination efficiency of those freed electrons or holes by thermally stimulating them. Evidently, the concentration of dopant ion increases the defect formation that promotes the trapping and recombination processes [5]. To observe the effect of the activator concentration on the TL glow curve of $Sr_3Al_2O_6:Tb^{3+}$ phosphor, the TL of the samples of different terbium concentration under the same dose were recorded and are presented in Fig. 5. The increase in the intensity of peaks with respect to concentration of terbium up to 0.5 mol%, is an indication that the corresponding charge carrier traps are produced by the oxygen vacancies [4]; similarly the decrease in the TL intensity above 0.5 mol% of terbium concentration is attributed to the reduction of oxygen vacancies, i.e. no additional traps were created at higher concentration [5]. The shapes of all the glow peaks remain constant in the concentration range studied. As shown in the inset of the Fig. 5, the TL output of the sample first increases with increasing concentration of terbium from 0.025 up to 0.5 mol%, reaches the maximum value at 0.5 mol% and then gradually decreases from 1 mol% to 2 mol%. This is a well known concentration quenching phenomena and is also reported for $Ba_2Ca(BO_3)_2$:Tb [6] and $CaSO_4$:Dy [18].

The high fading effect of beta irradiated sample is due to the recombination of the trapped electrons released at room temperature. After initial fading the sample becomes stable and new recombination can occur only by heating the sample at elevated temperature. To study the fading effect, the phosphor $Sr_3Al_2O_6:Tb^{3+}$(1%) was given the test dose of 100 Gy from Sr-90 β source and the TL signal was recorded at different interval of days for nearly two months. Fig. 6 shows the plot of TL intensity versus number of days after exposure. Strong fading was observed after 10 days of

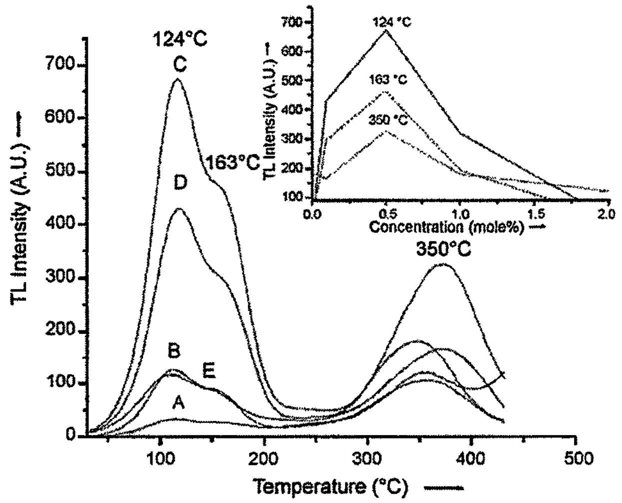

Fig. 5. TL glow curves of $Sr_3Al_2O_6$:Tb Phosphor with different Tb^{3+} concentrations irradiated with a 100 Gy beta dose at room temperature, where $A = 0.025\%$, $B = 0.1\%$, $C = 0.5\%$, $D = 1.0\%$, $E = 2.0\%$. The inset shows the dependence of TL response on Tb^{3+} concentration.

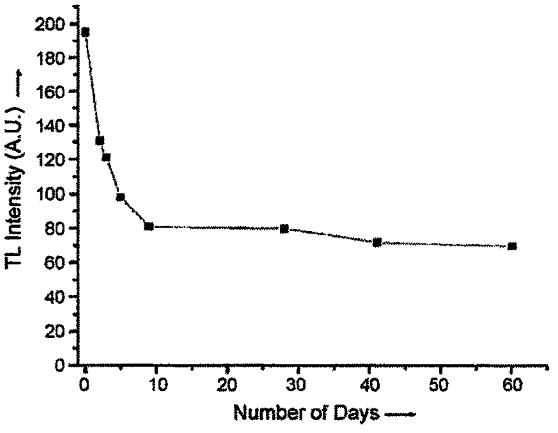

Fig. 6. The TL Fading of $Sr_3Al_2O_6$:Tb(1.0%) exposed to 100 Gy of beta irradiation for a period of 60 days.

irradiation, as the phosphor $Sr_3Al_2O_6:Tb^{3+}$(1%) lost around 59% of the TL signal when compared with the intensity observed immediately on irradiation. But after this, the decay is quite slow and finally stabilizes after 30 days. The 41% remnant TL signal is high enough to be considered for dosimetric applications [3]. The 124 °C peak slowly disappeared after one day and the hump at 163 °C turned into a well-defined peak; hence, for dosimetric purpose the peak at 163 °C was taken into consideration and studied. The activation energy for both the traps are very similar to each other (from Table 1) so the chances of the charge transfer from the lower to higher temperature region, i.e. at 163 °C are high, thereby increasing the population of the active charges at the higher region. Another desirable property of a TL dosimeter is that it should exhibit a linear relationship with TL intensity and absorbed dose. The dose response of beta irradiated samples was investigated by plotting the TL intensity as a function of irradiation dose and is shown in the Fig. 7. The TL intensity of the samples follows the linearity with the increasing dose from 1 Gy to 450 Gy and is shown in the inset of Fig. 7. It can be observed that the phosphor does not loose its linearity even at high beta dose.

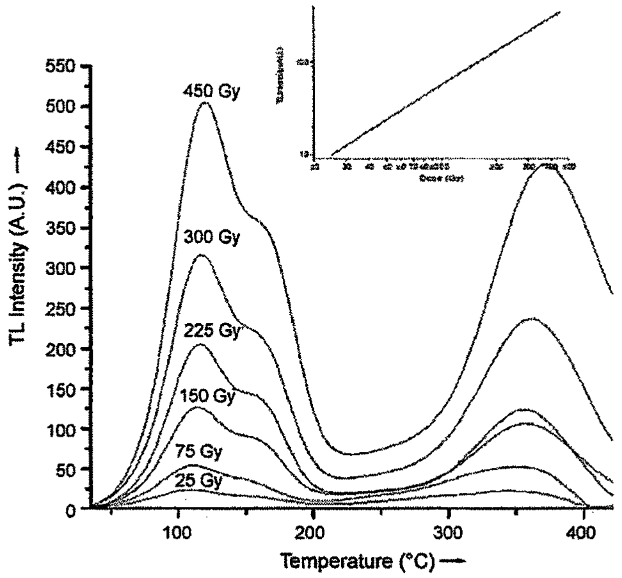

Fig. 7. TL glow curves of $Sr_3Al_2O_6$:Tb(1.0%) exposed to different doses of beta irradiation. The inset shows the dose response with respect to TL intensity for 163 °C peak in the log scale.

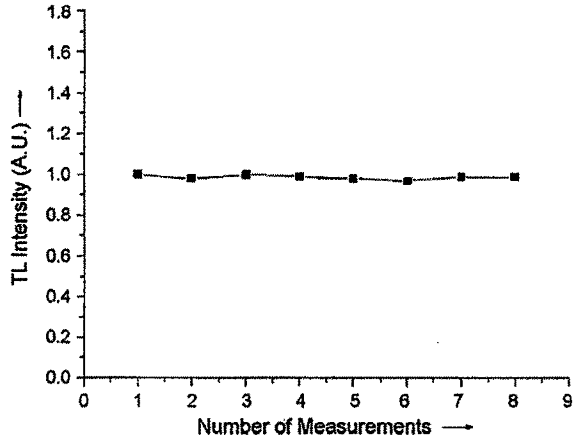

Fig. 8. The reproducibility of the TL signal from $Sr_3Al_2O_6$:Tb(1.0%) phosphor over a eight repeated cycles of annealing-irradiation-readout.

The peak at around 350 °C was related to the phenomenon known as spurious TL, i.e. glow which does not result from the irradiation of the specimen. There are many possibilities for such spurious glow such as [16]:

(i) The transfer of charge from the deep trap to the dosimetry traps during exposure to light.
(ii) Tribothermoluminescence, where the trapping of the charge in the TL traps following mechanical disturbance of the specimen (friction, grinding, etc.).
(iii) Chemiluminescence produced during the read out (probably due to the oxidation of the surface impurities).

The presence of this spurious signal does not show any effect on the dosimetric peak at 163 °C. There can also be a possibility of the role of impurity present in the sample at ppm level and also due to the high temperature synthesis similar to that observed by Chatterjee et al. for Gd_2O_2S: Tb phosphor [19]. The third peak at 350 °C was in high temperature region so the activation energy for it was not calculated and emphasis was given only to the other two peaks at 124 °C and 163 °C.

The reusability is another desirable property for a dosimetric phosphor. If the sensitivity of the sample does not change after several cycles of exposure and readouts, then it is considered to be as a good dosimetric phosphor. The $Sr_3Al_2O_6$:Tb^{3+}(1%) was also tested for its reusability. The sample was exposed to beta dose of 100Gy and the TL glow curve was recorded from room temperature to 450 °C. It was then quickly cooled to room temperature and exposed to 100 Gy from Sr-90 source again to accumulate the dose. The glow curve was again recorded for the second time; several such cycles of exposures and glow curve recordings were performed and are shown in Fig. 8. No significant change in the TL intensity of both the 120 °C and 164 °C peaks was observed. Excellent reusability is thus seen in the present sample and mainly for the dosimetric peak under consideration at 164 °C.

4. Conclusion

The photoluminescence characteristics of the phosphor $Sr_3Al_2O_6$:Tb^{3+} shows highly fluorescent transitions at $^5D_4 \rightarrow {}^7F_5$. The thermoluminescence characteristics of the phosphor and the glow recorded for the 124 °C and 163 °C show that the traps levels are close to each other so the charge transfer is taking place between the levels. The values of the activation energy were calculated by Chen's equation of the peak shape method and the mean of those was calculated as 0.749 eV and 0.79 eV for the 124 °C and 163 °C, respectively. The terbium concentration effect on the phosphor has been discussed at length and was found to give highest intensity for the 0.5 mol%. The effect of the beta irradiation on the $Sr_3Al_2O_6$: Tb^{3+}(1%) was studied in detail and found that the response of the glow peak at the 163 °C was very much suitable for the dosimetric applications. The reusability and the fading of the same were studied. It can thus be concluded that the phosphor could be used for the dual purpose of the dosimetry as well as an efficient green emitter in the lamps.

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