Effect of Sr on the luminescence properties of Eu\(^{3+}\) activated xZnO-(1-x) SrO-Al\(_2\)O\(_3\) phosphors

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Keywords: photoluminescence, thermoluminescence, mechanoluminescence, optically stimulated luminescence

Abstract

Europium-doped xZnO-SrO-Al\(_2\)O\(_3\) (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) phosphors were synthesized by the traditional Solid-State Reaction (SSR) method. The structure of the phosphors prepared was analysed with the x-ray diffraction technique. The xZnO-(1-x) SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.1 mol%) (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) exhibits varying PL intensity and is maximum for 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.4 mol%) and hence treated as the most prominent phosphor among these combinations. In the photoluminescence spectrum of the phosphors prepared, a sequence of emission bands were visible at various wavelengths viz., 576, 586, 620, 656 and 702 nm as a result of the transitions of Eu\(^{3+}\) ions [5D0 \(- 7Fj\) where (j = 0–4)] and an excitation spectrum at 620 nm. An efficient orange-red phosphor thus developed capable of yielding a quantum efficiency of about 12%. Studies revealed that the commercially available red phosphors having an efficiency of only 9.6% (\(\lambda_{ex} = 394\) nm) & 4.2% (\(\lambda_{ex} = 395\) nm). Hence the current sample could be an ideal alternative for an efficient phosphor near UV LEDs. The mechanoluminescence of the 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.4 mol%) phosphor was also measured. The phosphor composition was analysed using XPS. The present paper also reports the thermoluminescence and OSL properties of Europium doped Zinc Strontium Aluminate phosphor at different gamma-ray dosages. Peak shape method was employed to evaluate kinetic parameters like activation energy, frequency factor and symmetry factor.

1. Introduction

White LEDs are promising solid-state lighting (SSL) devices due to their superior performance in terms of efficiency, power consumption and lifetime making them practical substitute for incandescent and fluorescent lamps. Studies proved that the best method of developing efficient white LEDs is by creating a suitable template of RGB (red, green, blue) colour combinations [1–3]. Phosphors with RE-doped aluminates and silicates are widely used in display and signage applications due to their long-lasting afterglow and stability [4]. Among the aluminates and silicates, Eu\(^{3+}\) activated phosphors exhibit better characteristics, can be considered as an efficient red component for WLEDs [5]. Studies have proved that red phosphors are comparatively less efficient than its blue and green counterparts [6]. Hence it will be wiser to choose an alternative for lower efficient red phosphors. Studies are going on for the fabrication of white LED-excited by UV and near UV lights. Instead of resorting to less efficient red phosphors, a better alternative emerged from the studies is to utilize an orange-red phosphor that can be efficiently excited in the near UV region. Nowadays, RE based luminescent materials find applications in various fields like lighting, photosynthesis enhancement and photodynamic therapy in cancer treatment. Eu activated phosphors are undergoing intense studies because Eu\(^{3+}\) is a typical red-emitting activator [1]. Nowadays, spinel-type material (AB\(_2\)O\(_4\)) is becoming a focal point of interest due to their promising applications in the area of material science technology [7]. Spinel lattice comprises a divalent metal A-ion and a trivalent metal B-ion residing in the tetrahedral site and the octahedral site respectively [8].

Among the spinels, zinc aluminate (ZnAl\(_2\)O\(_4\)) has gained attention due to their multi-disciplinary interest. ZnAl\(_2\)O\(_4\), a direct wide gap semiconductor, a prototypical material in the metal aluminates family widely used as
electronic, ceramic and catalytic material [9]. The band gap value (optical) of the material is found to be 3.8 eV. It exhibits reflective property at wavelengths below 300 nm and transparency for wavelengths above 390 nm [10, 11]. Better efficiency and stability make zinc aluminate spinel a befitting host material. Since ZnAl₂O₄ is an earth-abundant host lattice, its usage as lanthanide emitter can reduce the cost of the material [8]. Researchers prefer alkaline earth aluminates than sulphides as ideal host material due to their chemical stability [12]. RE metal ions, when doped in the strontium aluminate based host material, results in intense luminescence in the blue to the green region having superior stability, efficiency and afterglow [13]. Strontium aluminates doped with europium are capable of producing significant phosphorescence and emission in the visible region [12]. Modification in luminescence properties of phosphors to obtain better and stable emissions are the current field of experimentation.

In this work, an attempt is made to enhance the luminescence property by varying the composition factor x in xZnO-(1-x)SrO-Al₂O₃:Eu³⁺ to exhibit orange-red component for white LED application. ZnAl₂O₄ and SrAl₂O₄ were chosen as a host matrix because of its excellent properties such as ease of preparation, strong absorption in the UV-region and to combine the excellent physical and chemical properties of the former and the significant phosphorescence of the latter. XZnO-(1-x)SrO-Al₂O₃ (x = 0.2, 0.4, 0.5, 0.6, 0.8) phosphors are prepared at different concentrations of Eu³⁺ ions. Conventional SSR method was employed to obtain orange-red emission when excited at 393 nm. The suitability of the sample phosphor for the desired luminescence properties was examined through CIE colour coordinate analysis. Photoluminescence study of Eu³⁺ doped xZnO-SrO-Al₂O₃ (x = 0.2, 0.4, 0.5, 0.6, 0.8) phosphor and its real-world applications is being documented for the first time.

2. Experimental method

The xZnO-(1-x) SrO-Al₂O₃ (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) phosphors doped with different concentration of Eu³⁺ was prepared by conventional SSR method. Stoichiometric weights of high purity ZnO, SrCO₃, Al₂O₃, Eu₂O₃ purchased from Sigma Aldrich (purity 99.99%) were taken as starting reagents. Reagents weights were measured using Shimadzu electronic balance and were mixed in an agate mortar with double distilled water as the medium. The slurry was then dried up, powdered and then calcined at 1200 °C for 5 h. The phase formation of the prepared sample was analysed using XRD [Model Bruker AXS D8 Advance]. The XPS (x-ray photoelectron spectroscopy) analysis of the 0.8ZnO-0.2SrO-Al₂O₃:Eu³⁺ (0.4 mol%) was taken using the Thermo Scientific ESCALAB Xi+ XPS system. The PL was recorded using Horiba Fluorolog fluorescence spectrometer with TCSPC (Model Fluorolog 3 TCSPC). Thermoluminescence and optically stimulated luminescence of the phosphor were measured using Nucleonix TL/OSL Research Reader (Model TL 1008).

3. Results and discussion

3.1. XRD analysis

Figure 1 represents the XRD patterns of xZnO-(1-x)SrO-Al₂O₃:Eu³⁺ to exhibit orange-red component for white LED application. Figures 1(a), (g) represents the SrAl₂O₄, Eu³⁺ (0.1 mol%), ZnAl₂O₄, Eu³⁺ (0.1 mol%) and (b-f) represents mixed phases of ZnAl₂O₄ (JCPDS card No.74-1138) and SrAl₂O₄ (JCPDS card No.74-0794). The diffraction peaks of 0.2ZnO-0.8 SrO-Al₂O₃ show a remarkable change when compared to the peaks of SrAl₂O₄. The peaks formed are clubbed together to form a single broad peak as depicted in Figure 1(b). As the composition of zinc increases the peak becomes sharp. The broadening of the peak of XRD is due to lattice strain or improper distribution of atoms in the lattice [14].

3.2. SEM analysis

Figures 2(a)–(c) shows the SEM micrographs of ZnAl₂O₄: Eu³⁺ (0.1 mol%), SrAl₂O₄:Eu³⁺ (0.1 mol%) and 0.8ZnO-0.2 SrO-Al₂O₃:Eu³⁺ (0.1 mol%). The SEM images show that the prepared phosphors consist of particles with different size distribution. The crystallite size varies from 1 μm to 10 μm.

3.3. X-ray photoelectron spectroscopy (XPS)

The figure 3 shows the Wide scan XPS spectra of 0.8ZnO-0.2 SrO-Al₂O₃:Eu³⁺ (0.4 mol%) in the range 0–1200 eV. In the XPS spectra, the presence of the elements Strontium (Sr 3d at 134 eV), Aluminium (Al 2p at 72 eV), and Oxygen (O 1 s at 530 eV) was detected. The peaks detected at 1142 and 1164 eV are due to core levels of Eu³⁺ (Eu 3d) [15, 16] and the peaks at 1022 eV and 1043 eV, are due to Zn (2P3/2 and 2P1/2) respectively [17].
3.4. Photoluminescence studies (PL)

Figure 4 depicts the PL spectra of ZnAl$_2$O$_4$: Eu$^{3+}$ (0.1 mol\%) and SrAl$_2$O$_4$:Eu$^{3+}$ (0.1 mol\%). Both ZnAl$_2$O$_4$ and SrAl$_2$O$_4$ are having the PL property and hence a series of combinations involving both of these, have been done to find out a more efficient PL material. The xZnO-(1-x) SrO-Al$_2$O$_3$ Eu$^{3+}$ (0.1 mol\%) phosphors were prepared with 0.1 molar concentration of Eu$^{3+}$ and analyzed with respect to the PL intensity and the colour purity.

Figure 5(a) represents the photoluminescence excitation spectrum of the prepared samples xZnO-(1-x) SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol\%) for x = 0.2, 0.4, 0.5, 0.6, 0.8 excited at 620 nm. It comprises a pattern of sharp bands ranging from 315 nm to 580 nm. These bands are due to the characteristic transition from the ground $^7$F$_0$ to excited levels $^5$L$_6$ (319 nm), $^5$D$_4$ (360 nm), $^5$L$_7$ (380 nm), $^5$L$_6$ (393 nm), $^5$D$_3$ (413 nm), $^5$D$_2$ (462 nm), $^5$D$_1$ (528 nm), $^5$D$_0$ (565 nm) [18]. Maximum intensity is visible for the transition $^7$F$_0$-$^5$L$_6$. The excitation intensity increases with and attains peak for 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol\%).

Figure 5(b) depicts the emission spectrum of xZnO-(1-x) SrO-Al$_2$O$_3$: Eu$^{3+}$ phosphor excited at 393 nm. The sharp lines in the PL spectra represent the transition from the excited states $^5$D$_{0}$ to the ground level $^7$F$_{j}$ (j = 0, 1, 2, 3). Europium ions can exist in divalent as well as trivalent oxidation states [19]. Eu$^{2+}$: ion exhibits a broad, structure-less emission in the blue or green region mainly due to dipole assisted transitions ($^4$F$_{0}$-$^4$F$_{j}$). Contrarily, Eu$^{3+}$: ion exhibits a series of narrow lines in the red region due to the forbidden electric dipole 4F-4F ($^5$D$_{0}$-$^5$F$_{j}$) transition. The emission spectra of Eu$^{3+}$: ions show sharp emission lines peaked at 450 nm, 576 nm, 586 nm, 602 nm, 610 nm, 620 nm, 656 nm, and 702 nm. The broad emission peak around 450 nm is due to host emission of ZnAl$_2$O$_4$. In ZnAl$_2$O$_4$, presence of oxygen vacancies ‘Vo’ which could be responsible for an emission without any dopant [20]. The most intensive emission observed at 620 nm corresponds to the forced electric dipole transitions ($^5$D$_{0}$-$^5$F$_{2}$) as by Judd ofelt selection rule. The intensity of this super sensitized transition highly depends on the neighbouring ligands [2, 21]. The weak emission lines in the PL emission spectra showing a maximum at 576 nm is associated with $^5$D$_{0}$-$^5$F$_{0}$ transitions of Eu$^{3+}$ ions and are forbidden in the inverse symmetry owing to the J-J mixing by the crystal gold effect [3]. It unveils that the trivalent Eu ions are occupying in octahedral low symmetry sites. Thus it is possible to assume that the local point group of Eu$^{3+}$ in the spinel structure is Cs, Cn or Cnv symmetry. At 586 nm, the intense emission observed due to the $^5$D$_{0}$-$^5$F$_{1}$ MD (magnetic dipole) transition. The intensity of this transition highly depends on the surroundings. The weak emission observed at 656 nm ($^5$D$_{0}$-$^5$F$_{2}$) is a forbidden ED transition [2]. At 702 nm, the strong emission is due to the $^5$D$_{0}$-$^5$F$_{2}$ electric dipole transition. The emission band at 620 nm is an ED transition (electric dipole), while the peak formed at 586 nm is an MD transition (magnetic dipole).

Usually, electric dipole transitions are affected by the variations in the chemical environment. The emission intensity of electric dipole is more prominent than that of a magnetic dipole, which discloses less symmetry around the Eu$^{3+}$ ions lacking an inversion centre [13]. The non-existence of symmetry centres causes mixing of 4f orbital with the opposite parity orbitals resulting in the occurrence of electric dipole transitions [22]. In the emission spectra, the transitions corresponding to electric dipole take the odd values of j while magnetic dipole transitions take the even values of j. Local symmetry influences electric dipole transitions, but it does not have any influence on magnetic dipole transitions. For Eu doped oxides, there is a potential of reducing valence state in some specific oxide hosts, e.g. Alkaline earth hosts. This is due to the increase of ionic radii of the alkaline earth
Figure 2. SEM images of (a) ZnAl$_2$O$_4$: Eu$^{3+}$ (0.1 mol%), (b) SrAl$_2$O$_4$: Eu$^{3+}$ (0.1 mol%), (c) 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol%).

Figure 3. XPS spectra of 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.4 mol%) phosphor.
in the host. The PL emission spectra show there is no evidence for the existence of Eu$^{2+}$ [23, 24]. The compositions $x$ZnO-(1-$x$) SrO-Al$_2$O$_3$ ($x = 0.2, 0.4, 0.5, 0.6, 0.8$) contain mixed phases of ZnAl$_2$O$_4$ and SrAl$_2$O$_4$. The PL intensity of 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol%) is 4 times greater than that of ZnAl$_2$O$_4$: Eu$^{3+}$ (0.1 mol%) and SrAl$_2$O$_4$:Eu$^{3+}$ (0.1 mol%). This is quite true for all other combinations except 0.5ZnO-0.5 SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol%).

Eu$^{3+}$ ions replace Al$^{3+}$ ions from the octahedral sites and Sr$^{2+}$ or Zn$^{2+}$ ions from tetrahedral sites. The strongest matrix luminescence was observed in 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ sample. Such a strong luminescence can be due to the lattice strain developed in the ZnAl$_2$O$_4$ and SrAl$_2$O$_4$ mixed phases or due to the variance in the atomic radii of Sr$^{2+}$ and Zn$^{2+}$. The ionic radius is a significant factor in the determination of dopant sites in the host. By comparing the ionic radii of Eu$^{3+}$ (1.09 Å), Zn$^{2+}$ (0.83 Å), Sr$^{2+}$ (1.21 Å), Al$^{3+}$ (0.67 Å), it reveals that Eu$^{3+}$ ions can more favourably replace Zn$^{2+}$ rather than Sr$^{2+}$ in the ZSA crystal structure.

However, since the Eu$^{3+}$ and Al$^{3+}$ have the same charge and octahedral co-ordination makes it suitable for replacing Al$^{3+}$ by Eu$^{3+}$ ion. The neighbouring ligands of the host materials largely influence the Eu$^{3+}$ emission. Hence the insertion of Zn ions modifies the Eu$^{3+}$ environment and the crystal structure; which results in the formation of different emission sites [25]. Even though the prepared phosphors $x$ZnO-(1-$x$) SrO-Al$_2$O$_3$: Eu$^{3+}$ ($x = 0.2, 0.4, 0.5, 0.6, 0.8$) are having mixed phases the XRD pattern shows a modification in the host material as evidenced by the broadening of the peaks. The broadening of the peaks can be associated with the lattice strain produced in the matrix. In phosphor having 80% Zinc content, this assumption seems to be true and that could be the reason for high PL intensity for 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.1 mol%). The excitation and emission exhibit a similar profile.

Figures 6(a) and (b) shows the excitation and emission intensity versus Eu$^{3+}$ ions concentration. The ideal concentration of activator (Eu$^{3+}$) ions was 0.4 mol%. As the Eu$^{3+}$ ions concentration increases, the separation between two adjacent activator ions gets shorter, and their interaction gets strengthened. As a result non-radiative transitions get enhanced with a subsequent decline in radiative transitions [1]. The energy transfer of non-radiative nature between dopant ions causes quenching concentration of Eu$^{3+}$ ions due to its exchange interaction and multipole-multipole interaction [26].

Mixed spinel materials generally contain highly disordered regions where the crystal field strength is high as a result of a distortion of the spinel host due to cell parameter mismatch. The presence of the highly disordered regions results in enhanced Eu$^{3+}$ emission in ZSA compound [2]. Since excitation by near UV is possible at around 393 nm, the prepared phosphor will be suitable for UV as well as NUV LEDs, revealing the immense potential for practical applications. Quantum efficiency is estimated with the help of integrating sphere attachment method. In the series of samples prepared i.e., ZnO-SrO-Al$_2$O$_3$: Eu$^{3+}$, the sample corresponds to $x = 0.8$ (0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$) exhibits superior PL intensity. The prepared sample 0.8ZnO-0.2SrO-Al$_2$O$_3$: Eu$^{3+}$ (0.4 mol%) has yielded a luminescence quantum efficiency of 11.83% (excited at 393 nm) at room temperature and is found to be greater than that of ZnAl$_2$O$_4$: Eu$^{3+}$ and
SrAl₂O₄:Eu³⁺. The yield is much higher when compared with the so far reported orange-red phosphor (SrSiO₃: Eu³⁺), which provides a better quantum efficiency of 10.2% [27]. When compared with the quantum yield of commercial red-emitting phosphors viz., Y₂O₃: Eu³⁺, Y₂O₂S: Eu³⁺ yielding 9.6% (λex = 394 nm) and 4.2% (λex = 395 nm) respectively, the quantum yield of 0.8ZnO-0.2SrO-Al₂O₃:Eu³⁺ (0.4 mol%) is far better [28, 29].

3.4.1. Phosphor characteristics

The chromaticity diagram CIE 1931 characterises the luminescence colour of the prepared phosphor excited at 393 nm. The photoluminescence emission spectrum of phosphor got transformed into the equivalent CIE 1931 chromaticity by clubbing the data from emission spectra and the CIE software. Figure 7 represents the CIE diagram of xZnO-(1-x)SrO-Al₂O₃:Eu³⁺. All- natural colours can be represented by (x, y) coordinates inside the chromatic shoe. The green emission of ZnAl₂O₄: Eu³⁺ is shifted to a long wavelength region for all other compositions of xZnO-(1-x)SrO-Al₂O₃: Eu³⁺. The luminescence colour of 0.8ZnO-0.2SrO-Al₂O₃: Eu³⁺ (0.4 mol%) is placed in the orange-red corner. The CIE coordinates influence the intensity of magnetic to electronic allowed transitions, termed as red/orange (R/O) ratio [8, 27]. The chromatic coordinates of the sample fall in the orange-red field and hence 0.8ZnO-0.2SrO-Al₂O₃: Eu³⁺ (0.4 mol%) phosphor is suitable in near UV based W-LEDs.

The analytical equation for computing the CCT (Correlated Colour Temperature) as proposed by Mc Camy is given by

![Figure 5](image-url)

**Figure 5.** (a) PL excitation spectra of xZnO-(1-x)SrO-Al₂O₃:Eu³⁺ (0.1 mol%) (x = 0.2, 0.4, 0.5, 0.6, 0.8) phosphors. (b) PL emission spectra of 0.8ZnO-0.2SrO-Al₂O₃:Eu³⁺ (0.1 mol%) (x = 0.2, 0.4, 0.5, 0.6, 0.8) phosphors.
Where \( n = (X - Xe)/(Y - Ye) \) represents the inverse slope of the line, \((Xe = 0.332, Ye = 0.186)\) represents the epicentre. CIE, CCT and colour purity of the prepared phosphors are listed in table 1. The value of CCT is within the admissible range and can be considered ‘warm’ in appearance. CIE, CCT and colour purity of the prepared phosphors are listed in table 1. As compared to that of ZnAl\(_2\)O\(_4\):Eu\(^{3+}\) and SrAl\(_2\)O\(_4\):Eu\(^{3+}\), the PL intensity and colour purity of 0.8ZnO-SrO-Al\(_2\)O\(_3\): Eu\(^{3+}\) (0.4 mol%) is determined to be higher.

### 3.4.2. Decay characteristics

The typical decay curve of 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\): Eu\(^{3+}\) (0.4 mol%) is depicted in figure 8, recorded with \( \lambda_{\text{ex}} = 393 \text{ nm} \) and \( \lambda_{\text{em}} = 620 \text{ nm} \). Curve fitting technique is used to calculate the decay time of the phosphor. The decay curves fitted by the summation of two exponential components have varying decay times.

\[
I = A_1 \exp \left( -\frac{t}{\tau_1} \right) + A_2 \exp \left( -\frac{t}{\tau_2} \right) 
\]

Where \( I \) denote the phosphorescence intensity, \( A1 \& A2 \) represent constants, \( t \) is the time, \( \tau_1 \) and \( \tau_2 \) represents the decay times (in sec.) for the exponential components. A bi-exponential decay curve was fitted by the equation (2). The fitting results indicate two regimes, with a primary component (75%) at \( \tau_1 = 2.16 \text{ ms} \) and a secondary component (25%) at \( \tau_2 = 1.30 \text{ ms} \).
Figure 7. CIE coordinates of $x\text{ZnO}-(1-x)\text{SrO-Al}_2\text{O}_3: \text{Eu}^{3+}(0.1 \text{ mol}%)$ ($x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1$) phosphors.

Figure 8. Lifetime decay curve of $0.8\text{ZnO-0.2SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.4 \text{ mol}%)$ phosphor.

Table 1. CIE, CCT and Colour purity of prepared samples.

| Sample | CIE coordinates | CCT (K) | Colourpurity (%) |
|--------|-----------------|---------|------------------|
| a. $\text{ZnAl}_2\text{O}_4: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.350, y = 0.410 | 1849 | 82 |
| b. $\text{SrAl}_2\text{O}_4: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.560, y = 0.420 | 1847 | 86 |
| c. $0.2\text{ZnO-0.8SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.565, y = 0.424 | 1842 | 87 |
| d. $0.4\text{ZnO-0.6SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.551, y = 0.412 | 1853 | 88 |
| e. $0.5\text{ZnO-0.5SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.547, y = 0.408 | 1854 | 85 |
| f. $0.6\text{ZnO-0.4SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.561, y = 0.422 | 1852 | 89 |
| g. $0.8\text{ZnO-0.2SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.1 \text{ mol}%)$ | x = 0.555, y = 0.421 | 1877 | 93 |
| h. $0.8\text{ZnO-0.2SrO-Al}_2\text{O}_3: \text{Eu}^{3+} \ (0.4 \text{ mol}%)$ | x = 0.586, y = 0.376 | 1736 | 96 |
3.5. TL studies of 0.8ZnO-0.2SrO-Al2O3: Eu³⁺ (0.4 mol%)

Due to various applications in the fields of dosimetry, dating and defect studies, TL glow curve analysis found to be a very useful tool. Rare earth activated aluminate phosphors exhibit a better TL response. The glow curve was recorded at a heating rate of 2 °C s⁻¹ and irradiated for 50 Gy, 100 Gy, 200 Gy, and 300 Gy. Figure 9 outlines the thermoluminescence glow curve of 0.8ZnO-0.2SrO-Al2O3: Eu³⁺ (0.4 mol%) at various gamma-ray dosages.

Two different peaks identified in the TL glow curve, one at temperature 132 °C and other at 348 °C. The latter one is more notable except for gamma-ray dosages at 300 Gy. The general structure and peak position of the curve has not undergone major variations for change in gamma-ray dose levels. At 300 Gy gamma dose, the shoulder peak got subdued and almost vanished. Thus the peak formed at around 348 °C is a stable one and can be termed as a dosimetry peak.

3.5.1. Determination of kinetic parameters

3.5.1.1. Order of kinetics

The kinetic order of the acquired glow peak was determined from the shaping factor \( \mu_g \).

\[
\mu_g = \frac{\delta}{\omega} = \frac{T_2 - T_m}{T_2 - T_1}
\]  

(3)

Where \( \omega = (T_2 - T_1) \) represents the total half-width intensity, and \( \delta \) represents the trailing side half-width of the curve (T2-Tm). The symmetry factor of the glow curve having peak at 348 °C was calculated to be 0.54, which reveals that the peak achieves second-order kinetics [28].

3.5.1.2. Activation energy

From Chen’s equation, the activation energy is given by

\[
E = c \gamma [KT_m^2 / \gamma] - b \gamma [2KT_m]
\]  

(4)

Where \( T_m \) represents glow peak temperature, \( c \), and \( b \), are constants for second-order kinetics, which carries values 1.71 and 0.0 respectively [29]. \( \delta \) is the high-temperature half-width, and K represents the Boltzmann’s constant. The activation energy for the glow peak of the prepared sample at 348 °C was found to be 0.8193 eV using the equation (4).

3.5.1.3. Frequency factor

Frequency factor gives the inputs for identifying the probability of electron ejection from their traps on exposure to ionizing radiation. It is a significant factor in the TL characterization for various applications. The phosphor’s ability to retain the past events of exposure information for a certain period directly depends on the frequency factor, which is also temperature-dependent [30, 31]. The frequency factor was computed using the equation.
\[
S = \frac{\beta E}{K T_m^2 (1 + 2K T_m/E)} \exp(\frac{E}{K T_m})
\]  

(5)

Where \( \beta \) denotes the heating rate. The frequency factor of the sample phosphor at 348 °C glow peak was found to be \(2.8 \times 10^7\) s\(^{-1}\).

### 3.6. Mechanoluminescence studies of 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.4 mol%)

The capability to detect mechanical stress in objects makes mechanoluminescence property suitable for application in various crack monitoring and stress sensing applications. Figure 10 depicts the ML responses for various impact velocities of the phosphor. The impact velocities were estimated by dropping a load of 100 gm over the sample at different heights viz., 5, 10, 15, 20 cm. Impact velocity is the velocity with which the load hits the sample. The impact velocity is estimated using the equation \(\sqrt{2gh}\), where \(g\) (acceleration of gravity) and \(h\) stands for the height from which the load is dropping. The ML intensity displays an apparent increase when impact velocity increases. The ML should depend on the impact velocity or strain rate. Strain rate is the ratio of impact velocity to mass of the moving piston. As given in the figure, characteristic of impact velocity versus ML intensity corresponding to the sample 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.4 mol%) has a single peak, and the peak intensity shows an abrupt increase when the velocity rises from 100 cm s\(^{-1}\) to 200 cm s\(^{-1}\). It is noted that prepared phosphor is capable of producing intense ML without any pre-irradiation. Various models were put forward by researchers about the emergence of ML activity in crystals. Some of the prominent models describing the origin of ML activity are hole de-trapping model, the formation of the local piezoelectric field due to the presence of impurities and defects, charged dislocation movements, diffusion of defects in crystals, etc [32–34]. As the height increases, more fractures are created in the sample, resulting in more surface area. When the piston smashes the 0.8ZnO-0.2SrO-Al\(_2\)O\(_3\):Eu\(^{3+}\) (0.4 mol%) phosphor, generates a piezoelectric field due to their non-centrosymmetric property [35]. In certain defect centres, the material exhibits a high piezoelectric field due to the variation in local structure. The piezoelectric field results in reducing the trap depth of the electrons. This eventually causes movement of electrons from the traps to the conduction band. Subsequently, the moving charge carriers in the CB (conduction band) moves to the excited state located beneath the CB, and thus the...
excited ions are produced. Thus the electron- hole recombination causes photon emissions \[36-38\]. Researches reveal the fact that, when the ML materials are coated over any objects, the stress distribution of the object underneath the layers gets reflected from the ML intensity thus produced. Thus ML phosphors can act as sensors for the stress detection in an object \[39\]. The figure 11 illustrates the reliance on ML intensity on gamma dosage (1Kgy) exposed to the sample. The two peaks are spotted as a result of the increase in density of trap centres on rising in gamma dosage, owing to the trapping of more charge carriers in the traps.

3.7. OSL studies of 0.8ZnO-0.2SrO-Al2O3: Eu3+ (0.4 mol%)

Figure 12 outlines the Continuous-wave OSL (CWOSL) of gamma-irradiated 0.8 ZnO-0.2SrO-Al2O3; Eu3+ (0.4 mol%). The wavelength of stimulating light source was at 470 nm. The band pass filter U-340 was used to deter the stimulation radiation attaining the PMT. The OSL curve constitutes one quick component followed by a slow component.

4. Conclusion

Eu3+ doped xZnO-(1-x)SrO-Al2O3 (x = 0, 0.2, 0.4, 0.5, 0.6, 0.8, 1) phosphors are successfully synthesized using the SSR method in the air atmosphere. The XRD of the prepared phosphor shows two phases of ZnAl2O4 and SrAl2O4. Among all the phosphor compositions, 0.8ZnO-0.2SrO-Al2O3; Eu3+ (0.4 mol%) is having maximum PL. The 0.8ZnO- 0.2SrO- Al2O3; Eu3+ (0.4 mol%) exhibits orange-red emission when excited by 393 nm. It is
substantiated by the CIE diagram that the prepared phosphor is capable of yielding efficient orange-red emission. This makes the phosphor find applications in near UV LEDs. The luminescence quantum yield of $0.8\text{ZnO-0.2SrO-Al}_2\text{O}_3: \text{Eu}^{3+}$ (0.4 mol%) was around 11.83% at room temperature. It is remarkable that the $0.8\text{ZnO-0.2SrO-Al}_2\text{O}_3: \text{Eu}^{3+}$ (0.4 mol%) phosphor yields a quantum efficiency better than the commercially available red phosphors. Mechanoluminescence intensity increases directly with impact velocities, which makes ML materials suitable for stress sensing application. The results of gamma-irradiated TL studies of the phosphor reveals that TL intensity depends on the gamma dosage exposed to the sample. So the present study divulges the feasibility of its potential applications in TL dosimetry. The phosphor also exhibits OSL when stimulated with a 470 nm photon.

Acknowledgments

The authors are extremely thankful to Sophisticated Analytical Instruments Facility (SAIF), STIC, Cochin for providing XRD. SICC University of Kerala for providing XPS Facility, Sophisticated Analytical Instruments Facility (SAIF), MG University Kottayam for providing PL measurements and IGCAR, Chennai for TL and OSL measurements.

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