Synthesis, Photoluminescence and Thermoluminescence Characterization of K_2SrSiO_4: Eu phosphor

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Abstract— **K_2SrSiO_4: Eu was prepared by high temperature solid state diffusion method. The sample was characterized by X-ray diffraction, scanning electron microscope, photoluminescence (PL) and thermoluminescence (TL). PL emission spectra consists prominent peaks at around 590 and 614 nm when excited by 394nm wavelength. TL glow curve of K_2SrSiO_4: Eu phosphor shows single peak at 2800c indicating that only one set of trap is activated within the particular temperature range. The TL intensity is found to increase with increasing γ-ray dose. The kinetic parameters such as activation energy, frequency factor and order of kinetics were estimated using glow peak shape method.**

Keywords— **K_2SrSiO_4: Eu; solid state reaction method; XRD; Photoluminescence; Thermoluminescence.**

I. INTRODUCTION

Alkaline earth orthosilicate phosphors have a great attention due to their potential properties as phosphors in w-LED. M_2SiO_4:Ce^{3+}, Eu^{2+} (M=Ca, Sr, Ba) phosphors show new properties of tuning emission [1-3]. The alkaline orthosilicates doped with Eu^{2+} have excellent property to convert UV light of InGaN diode into white light [4, 5]. Yellow phosphor γ-Ca_2SiO_4: Ce^{3+} is the key component of w-LED based on blue (Ga, In) N LED [6]. Eu^{2+} activated Ca_2SiO_4 and Ba_2SiO_4 show green, orange emission band [7]. The long lasting phosphor Ba_2SiO_4: Eu^{2+} shows a great application for X-ray technique and cathode ray tube [8]. Silicate based hosts are generally preferred as compared to sulfide, oxide and aluminate based hosts [9, 10], because of their stability towards visible light transparency, relative easy preparation [11, 12] and their ability to show various emissions depending on the host lattice. The selection of host materials is an important issue for new phosphor materials, because the ligand field of hosts can modify the colours of emission of the activator. Therefore, studies of the luminescence behaviour of activators in different hosts can create new opportunities for researchers and for the applications of luminescence materials.

Thermoluminescence is widely used for dosimeter applications to measure different kinds of radiation doses [13–17]. On the basis of study of all these past work the aim of present research work is to develop orthosilicate phosphors by solid state diffusion method. It is non-hazardous and cost effective technique applicable to photoluminescence and thermoluminescence properties of the materials. To the best of our knowledge, there are no reports available on the photoluminescence and thermoluminescence study of Eu^{3+} doped K_2SrSiO_4 phosphors. Here we have reported PL and TL properties K_2SrSiO_4: Eu^{3+} phosphor along with crystallinity and morphology study.

II. MATERIALS AND METHOD

The phosphors were prepared by solid state reaction. Stoichiometric amounts of starting materials, K_2CO_3, $SrCO_3$, SiO_2 (all A.R. grade) and Eu_2O_3 (99.99 purity) were ground well and preheated at 500 0C for 5h. After the preheat treatment, the obtained product was ground well and placed in an silica crucible inside the furnace at 900 0C for 5h under a reducing atmosphere of carbon and then cooled to room temperature. The resultant powder was crushed to fine particles using an agate pestle and mortar. The concentrations of Eu was taken x = 0.2, 0.5, 1, 1.5 and 2 mol %. To confirm the nature of crystal, X-ray diffraction (XRD) characterization is done using Panalytical diffractometer with Copper Kα radiation (λ=1.5405 AU) operating at 40Kv, 30mA. The XRD data were collected in a 2θ range from 10 to 70°, with the continuous scan mode. The morphology was characterized by scanning electron microscope (SEM) using JEOL, JSM-6360LV SEM. The PL excitation and emission spectra were recorded using RF-5301PC Spectrofluorophotometer fitted with a sensitive photomultiplier tube with 150W 'xenon flash lamp' as an excitation source. The thermoluminescence (TL) data were collected using a TLD Reader Nucleonix TL 1009I. All the measurements were carried out at room temperature.

III. RESULTS AND DISCUSSION

A. Phase identification and morphology

The X-ray diffraction pattern of KSS: Eu^{3+} phosphor is shown in Fig.1. All XRD patterns show well-defined peaks, which indicate the crystallinity and phase configuration of prepared sample. There is no any standard JCPDS file observed for XRD pattern of KSS phosphor for comparison. The surface morphology of KSS phosphor is shown in Fig.2 at various magnifications. Figure shows that the particles are not uniform and forms agglomerization.

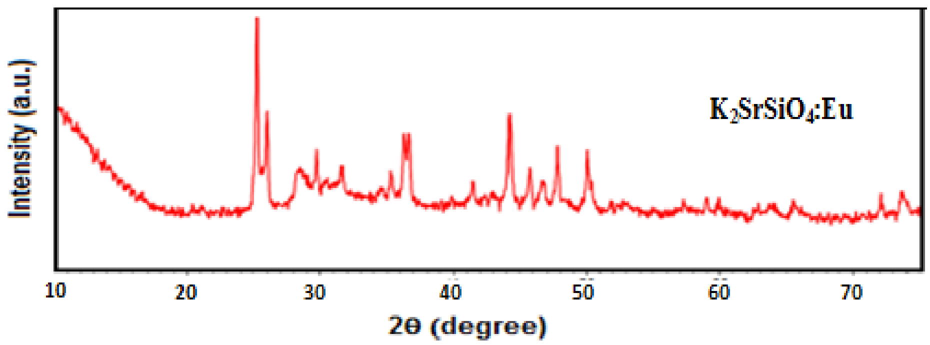

Fig.1 Powder XRD pattern of K_2SrSiO_4: Eu^{3+} (1.5 mol %).

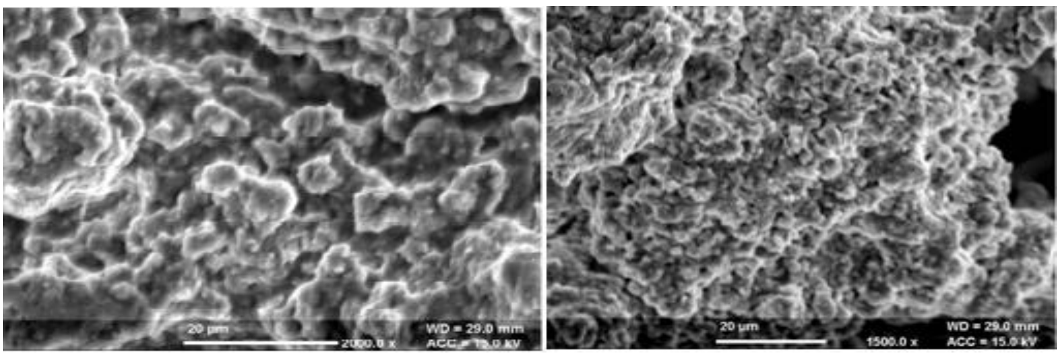

Fig.2 SEM images of KSS phosphor.

B. Photoluminescence studies

Fig. 3(a) shows the PLE spectrum of KSS: Eu^{3+} phosphor. The excitation spectrum exhibits four peaks in the range from 300-420 nm located at 317, 361, 381 and 392 nm. An intense excitation peak centred at 392 nm is observed due to $^7F_0 \rightarrow {}^5L_6$ transition. A positive side is that KSS: Eu^{3+} phosphor intensely absorb

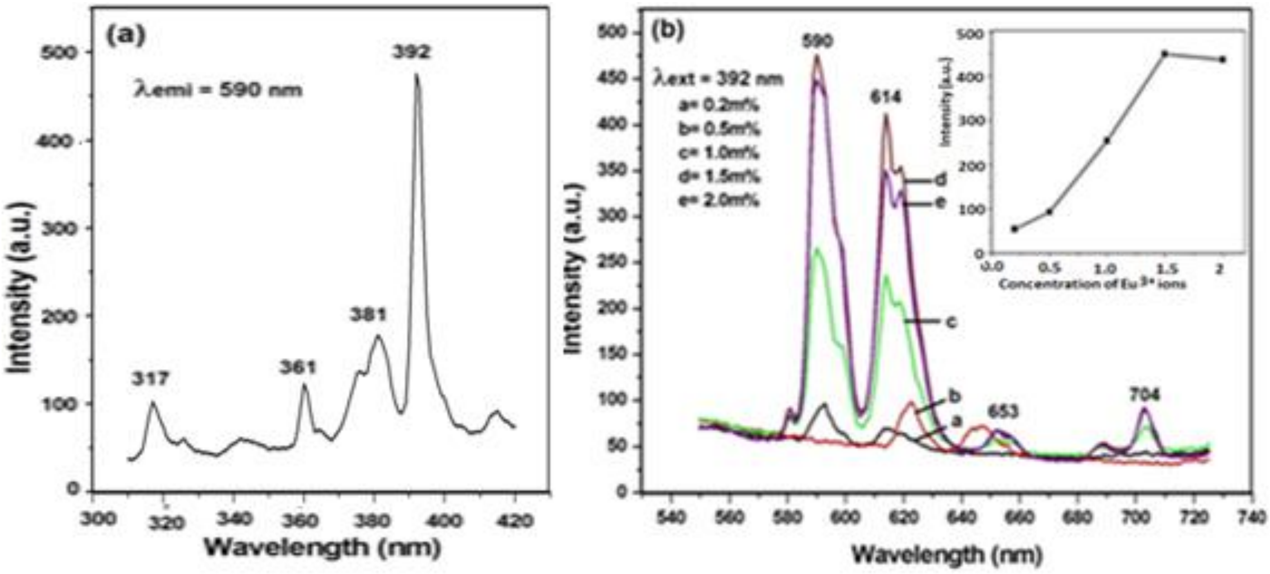

Fig. 3 (a) PLE spectrum of KSS: Eu^{3+} phosphor monitored at λemi = 590 nm (b) PL spectra monitored at λext = 392 nm with different concentrations. Inset shows the variation of intensity with concentrations.

UV light and well matched with emission of n-UV LED chips. The PL emission spectra of KSS: Eu^{3+} phosphors are shown in Fig. 3(b). Four bands are observed at 590, 614, 653 and 704 nm which are originate due to $^5D_0 \rightarrow {}^7F_j$ (j= 1, 2, 3 and 4) transitions of Eu^{3+} [18]. The orange emission ($^5D_0 \rightarrow {}^7F_1$) is stronger than the red emission ($^5D_0 \rightarrow {}^7F_2$) which indicates that Eu^{3+} is located in symmetry site in KSS. Inset of Fig. 3(b) shows emission intensity depends on the content of Eu^{3+} in KSS: Eu^{3+} phosphor. PL emission intensity increases with the increasing Eu^{3+} concentration and reaches maximum at 1.5 mol%, after which intensity decreases, due to concentration quenching effect occurs.

C. Thermoluminescence studies

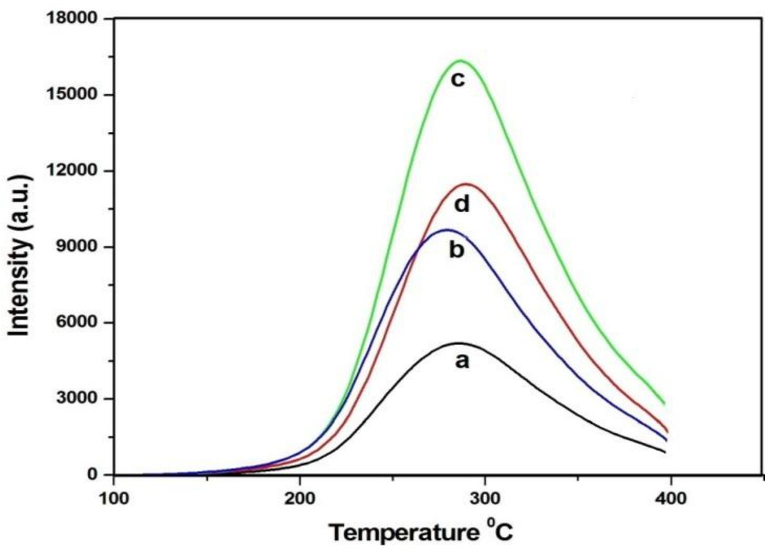

Fig.4 TL glow curve of KSS:Eu phosphor at concentration of Eu at 2.0m% for different Doses, (a) 1min, (b) 2 min, (c) 3 min and (d) 5 min.

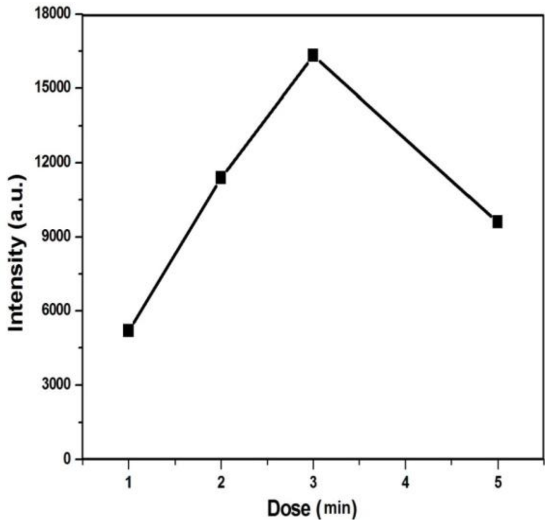

Fig. 5 TL response of KSS:Eu (2.0 mol %) exposed to γ-rays in the dose range 1-5 min.

The TL glow curves of KSS: Eu phosphor for different doses like 1, 2, 3 and 5 min with corresponding doses ranging from 16 to 80 Gy. The samples have been irradiated by ^{60}Co γ-rays with the dose rate being 16 Gy/min, are shown in the Fig.4. TL glow curves are recorded in the temperature range of 50–400 °C. TL responses of the KSS: Eu (2.0 mol %) phosphor samples were recorded at a heating rate of 5 °C/s and under pre-excitations with γ-radiations. The glow curve possesses single sharp and well-defined dosimetric peak at 280 °C in Eu^{3+} doped KSS phosphor, corresponding to a single set of traps formed due to the replacement of Eu^{3+} ions at the vacancies created by Sr^{2+} ions. This glow peak is observed at much higher temperature than that of the commercially available thermoluminesent dosimeters (TLDs) such as LiF: Mg, Cu; $CaSO_4$: Dy; $CaSO_4$: Tm etc., whose main dosimetric peaks lie between 200 and 250 °C [19]. Usually high temperature dosimetry applications need dosimeters with intense emission in the temperature region above 250 °C. Dose dependence of TL emission of the phosphor KSS: Eu (2.0 mol %) was observed for different doses of γ-radiation from 1min to 5 min at room temperature. The shape of the glow peak curve remains almost the same for different doses. The variation of TL intensity with γ-dose was studied and shown in Fig. 5. TL intensity increases with increasing γ-ray dose, and gets maximum value when γ-ray exposure is 3 min, after which concentration quenching occurs results in the decrease of TL intensity. Kinetic parameters were calculated by peak shape method (Chen's method) [20] from glow curve of KSS: Eu (Fig.4) for 280 0C glow peak. The average value of the activation energy (trap depth) was found to be 1.14 eV for 280 °C peaks, indicating that less energy is required for electron to release from the trap. The frequency factor was found to be 4.94 $x10^9$ s^{-1}. The phosphor KSS: Eu is found to have second-order kinetics in TL studies.

IV. CONCLUSIONS

K_2SrSiO_4 phosphors doped with varying concentration of Eu^{3+} ions were synthesized by solid state reaction technique. XRD analysis confirmed that the synthesized samples showed crystalline structure. PL emission spectra showed different peaks at 590, 614, 653 and 704 nm arising due to transitions from the different energy levels of Eu^{3+} ions. Concentration quenching occurs at 1.5 mol% of Eu^{3+}. Phosphor is excited by UV wavelength and gives emission in orange-red region; hence it may be applicable as an efficient orange-red phosphor and can be used in lamp industry. Its thermoluminescence properties are also studied and found that it may be a TLD material applicable in radiation dosimetry.

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