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Investigation of thermoluminescence and kinetic parameters of gamma ray exposed LiF: Sm^{3+}, Eu^{3+} nanophosphors for dosimetric applications

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ABSTRACT

Thermoluminescence (TL) properties of LiF: Sm^{3+} (0.05 mol%) co-doped with Eu^{3+} (0.02, 0.04, 0.06, 0.08 mol %) nanophosphor for the applications of TL dosimetry have been studied. The nanophosphors have been synthesized by chemical co-precipitation method at 8 pH value. The phase purity of the prepared samples has been confirmed by using X-ray diffraction (XRD) data. The XRD peaks broadening revealed the formation of the nanostructure, complemented by the TEM image. For TL studies, the samples have been irradiated with gamma rays using ^{60}Co source in the irradiation dose range of 0.1 kGy to 30 kGy. In gamma exposed samples, the TL glow curve consists of single glow peak at 410 K and three shoulder peaks at 475 K, 550 K and 632 K. The dosimetry properties such as the effects of exposure doses, heating rates and fading characteristics have also been studied. The kinetic parameters such as activation energy (E), the frequency factors (s) and order of kinetic (b) of the glow curves have also been calculated by using Chen's peak shape method. The linear behavior of TL intensity with radiation doses and low fading shows that the LiF: Sm^{3+}, Eu^{3+} Nanophosphor is a potential candidate for dosimetry applications.

1. Introduction

Thermoluminescence (TL) in alkali halides is being studied form the last four decades [1,2] as to be the potential candidates of the radiation dosimetry application. TL is the process of emission of light from an insulator or semiconductor, when they are thermally stimulated following the absorption of energy from radiation [3–6]. The existence of the intrinsic and extrinsic defects present in the inorganic phosphors induce energy levels in forbidden gap, which are important for thermoluminescence (TL) phenomenon [7–9]. TL is highly sensitive technique for radiation dose measurement and is used for radiation dosimetry application. As the TL intensity is proportional to the absorbed dose, so the materials to be employed for radiation dosimetry application must have high sensitivity and low fading characteristics. The light emitted during TL process is plotted as intensity versus temperature or time and is known as glow curve, which may have one or more peak corresponding to the energy level of the substance participating in the TL process [10,11]. The shape, position and intensities of the glow peaks are related to the properties of the trapping states responsible for TL phenomenon. The dosimetry properties of thermoluminescent material are mainly dependent on trapping parameters such as activation energy (E), frequency factor(s), order of kinetics (b) and peak temperature (T_m) of the glow curve. Activation energy is an energy required to eject an electron from trap, order of kinetics gives the information about whether the trapped charge carriers will be re-trapped on heating or not and frequency factor is number of times electron tried to eject from trap per second [12–20]. Many experimental techniques such as initial rise (IR) method, curve fitting methods, Chen's half width methods, heating rates methods, etc have been developed to determine these parameters from TL glow curves [21].

The use of thermoluminescence dosimeters (TLD) is increasing day by day in the radiation dosimetry, being important as a protective measure of patients and radiation workers against harmful effects of too much exposure of radiation. Different types of materials are being synthesized for the application as TLD batches to monitor the magnitude of ionizing radiation. There are several TLD phosphors studied so for such as LiF: Mg, Cu, P, LiF: Mg, Cu, Na, Si, LiF: Mg, Ti, LiF: Mg, Dy, LiF: Dy, LiF: Eu, LiF: Cr, CaS: Ce, $K_3Y(PO_4)_2$: Eu^{3+}, $CaSO_4$: Dy, CaF: Dy,

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Al_2O_3: Si, Ti, $Li_2B_4O_7$: Cu [22–29]. Among all, lithium fluoride is one of the potential candidate for thermoluminescence dosimetry as its effective atomic number (Z_{eff} = 8.1) is close to biological tissue (Z_{eff} = 7.4) and having large band gap (E_g ~ 13.6 eV). The existence of a very small amount of impurities in the lattice structure of LiF provides enhanced thermoluminescence response than its purest form [30].

In the present work, we report thermoluminescence behavior of rare earth doped (Sm^{3+} along with Eu^{3+}) LiF nanophosphors with gamma irradiation. There are no reports on the thermoluminescence characteristics of LiF: Sm^{3+}, Eu^{3+} nanophosphors irradiated with gamma rays. The thermoluminescence properties of LiF: Sm^{3+}, Eu^{3+} nanophosphor synthesized by co-precipitation method and irradiated with gamma–rays to different irradiation doses (0.1 kGy, 1 kGy, 5 kGy, 10 kGy, 30 kGy,) have been discussed. TL glow curves have been deconvoluted using the TLAnal computer software version 1.0.3 [31] and the kinetic parameters using Chen's peak shape method have also been reported.

2. Experimental details

Powder samples of nanocrystalline Lithium Fluoride (LiF) co-doped with Sm^{3+} and Eu^{3+} ions has been synthesized by chemical co-precipitation method by maintaining a pH value of 8.00 via the following chemical reaction [32].

$$LiCl + NH_4F + Sm(NO_3)_3 + Eu(NO_3)_3 \rightarrow LiF: Sm^{3+}, Eu^{3+} + NH_4Cl \quad (1)$$

The analytical grade ammonium fluoride (NH_4F), lithium chloride (LiCl), ammonium hydroxide (NH_4OH), samarium nitrate $Sm(NO_3)_3$, europium nitrate $Eu(NO_3)_3$ have been taken as precursors. In this reaction, homogeneous aqueous solutions of LiCl (1 mol), NH_4F (1 mol), $Sm(NO_3)_3$ (0.05 mol%), and $Eu(NO_3)_3$ of concentrations in the range (0.02–0.08 mol%) have been prepared in deionised water. The solutions of $Sm(NO_3)_3$ (0.05 mol%), $Eu(NO_3)_3$ (x mol%) and LiCl have been mixed and stirred for two hours at room temperature by using the magnetic stirrer and the homogeneous solution has been taken in the burette. The homogeneous solution is added drop by drop (1 ml min^{-1}) into 1 mol solution of NH_4F taken in conical flask under vigorous stirring. The pH of the solution is maintained at 8.0 throughout by adding the required amount of NH_4OH solution. The resulting solution is stirred continuously for 3 h. The as-grown precipitates are allowed to settle down at room temperature. The precipitates are repeatedly washed with deionized water in order to remove the undesired impurities (nitrate ions, chloride ions etc.). The precipitates are dried in hot air oven at 343 K for 24 h. The samples have been annealed at a temperature of 773 K for two hours to eliminate any inherent or residual impurities. After two hours of annealing, the samples have been cooled to room temperature naturally and afterwards kept in air tight glass tube for further characterization.

To confirm the phase formation and particle size, X-ray diffraction measurements have been performed using Cu-target (Cu-K_α X-ray with λ = 1.545 Å) and data were collected from 20° to 80° at room temperature. The structure analysis has been carried out using high resolution transmission electron microscope (HRTEM JEOL 2100). For TL studies, the prepared samples are irradiated to ^{60}Co gamma radiation with dose varied from 0.1 kGy to 30 kGy using BRIT Gamma chamber 1200 at the Health Physics Laboratory at Inter University Accelerator Centre, (IUAC) New Delhi. During irradiation, the effective gamma dose rate has been 3.894 kGy/h. The TL glow curves of the exposed phosphors have been recorded on the HARSHAW QS 3500 TLD reader in the temperature range from 323 K to 673 K for 5 mg of sample taken each time by selecting the uniform heating rates of 3 K s^{-1}, 5 K s^{-1} and 7 K s^{-1}.

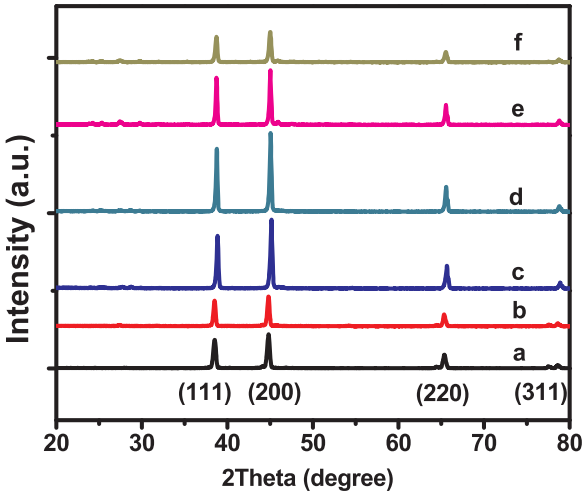

Fig. 1. XRD pattern of pure LiF, LiF: Sm^{3+} (0.05 mol%) and LiF: Sm^{3+} (0.05 mol%) co-doped with Eu^{3+} (0.02, 0.04, 0.06, 0.08 mol%) nanophosphors marked by a, b, c, d, e and f respectively.

3. Results and discussion

3.1. Structural studies

X-ray diffraction pattern of pure LiF(marked as “a”), samarium (Sm^{3+} 0.05 mol%) doped LiF(marked as “b”) and LiF doped samarium (Sm^{3+} 0.05 mol%) and co-doped with different concentration of europium (Eu^{3+}) (0.02, 0.04, 0.06, and 0.08 mol% marked as “ c–f”) powder samples prepared via chemical co-precipitation method annealed at 773 K is shown in Fig. 1.

In the XRD pattern, high intensity peaks have been observed at 2θ = 38.82°, 45.07°, 65.61° and 78.86° which matched well with the available data in the JCPDS card (No. 04-0857). The peaks are identified to originate from (111), (200), (220), and (311) crystal planes of cubic phase of LiF. The absence of any additional peak due to secondary phase, confirmed phase purity of Sm^{3+} and Eu^{3+} co-doped samples. The average crystallite size is computed from the full width half maximum of XRD peaks by using the Scherrer's formula [33].

$$D = 0.89\lambda/\beta \cos\theta \quad (2)$$

where D is crystallite size, λ is the incident wave length of K_α (1.545 Å) radiation, β is the full width at half maxima (in radian) and θ is the Bragg diffraction angle. The average crystallite size is approximately 40 nm.

3.2. EDS

Fig. 2 shows the energy dispersive X-ray spectroscopy (EDS) spectra of LiF: Sm^{3+} (0.05 mol%), Eu^{3+} (0.04 mol%) nanophosphor. The Li is not detectable due to low Z value and low energy of the characteristic radiation. EDS peaks confirms the presence of dopants, Sm and Eu in LiF and there are no peaks due to nitrogen and chlorine elements confirming the absence of unwanted impurities like nitrate ions and chlorides ions, respectively.

3.3. TEM

Fig. 3(a) show the TEM image of LiF: Sm^{3+}(0.05 mol%), Eu^{3+} (0.04 mol%) nanophosphor. TEM image shows that the nanoparticles are cubical in shape with an average size of 32–45 nm. Fig. 3(b) shows the selected area electron diffraction pattern (SAED) pattern of the nanoparticles formed. The closed rings in SAED pattern confirm the cubic symmetry of the sample. So the TEM results are found to be consistent with the XRD results.