Elementary results on the dosimetric properties of SrSO$_4$:Eu$^{2+}$ phosphor

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Abstract

A polycrystalline sample of SrSO$_4$:Eu$^{2+}$ phosphor has been successfully synthesized using the co-precipitation method and studied for its luminescence properties. The phosphor showed rather high optical stimulated luminescence (OSL) sensitivity which was about 75% of that for the commercially available $\alpha$-Al$_2$O$_3$:C phosphor (TLD-500). The continuous wave (CW)-OSL curve exhibited three components having photoionization cross-sections of $1.78\times10^{-17}$, $7.70\times10^{-17}$ and $17.69\times10^{-17}$ cm$^2$, respectively. The thermal luminescence (TL) sensitivity was about 100 times higher than that for TLD-500. The kinetic parameters for TL curve such as activation energy and frequency factor were calculated using peak shape treatment. OSL components were determined from CW and linear modulated (LM)-OSL data. The minimum detectable dose was found to be 11.6 mGy with 3σ of background. Also reusability studies showed that it was possible to reuse the phosphor for 10 cycles without change in the OSL output. In the TL mode the dose-response was nearly linear in the range of measurement (20–400 mGy), and fading was 40% in 72 h. Photoluminescence spectra of SrSO$_4$:Eu$^{2+}$ exhibited emission in the near-UV region at 254, 315, and 323 nm when excited with an UV source.

Keywords: Co-precipitation; TLD-500; CW-OSL; Photoionization cross-section.

1. Introduction

Solid-state luminescent dosimetry is based on radiation energy storage in dosimetric materials in the form of lattice defects and captured charge carriers. The stored energy can be released through the light from luminescence centers. Energy release is stimulated either by heating (thermally stimulated luminescence (TSL/TL)) or by irradiating with light quanta of proper energy (optically stimulated luminescence (OSL)). TL-based dosimeters are widely used in radiation dose monitoring but in comparison to TL dosimetry technique OSL has been becoming popular in radiation dosimetry applications [1–4]. OSL has been first used in archaeological dating and later proposed for personnel monitoring and environmental monitoring of radiation with the development of Al$_2$O$_3$:C [5].

Different stimulation techniques have been followed by OSL measurements that offer different signal-to-noise ratio. A few of them are CW-OSL, P-OSL, LM-OSL, TA-OSL and NL-OSL, amongst which CW-OSL is the most preferred and popular

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choice of stimulation mode, because in CW-OSL, the luminescence is recorded very fast and looks like a decay curve, the background count rate or net background is nearly constant and signal-to-noise ratio is high [6].

Over the last several decades sulfate hosts doped with rare earth materials have been widely used in radiation dosimetry, and also these materials show good luminescent properties. Many researchers have reported on these materials with different synthesis methods and studies for different luminescence properties [7–9].

In this paper we are reporting TL and OSL properties (under beta irradiation) of Eu-doped SrSO₄ phosphor synthesized by using co-precipitation.

2. Experimental details

SrSO₄ phosphor activated with Eu was prepared by the co-precipitation method described in our earlier works [10]. The stoichiometry of the reaction was maintained by the formula Sr₁₋ₓSO₄ : xEu²⁺. The nitrate precursor of strontium was dissolved in 100 ml of double-distilled water with drop-wise addition of the stock solution prepared for Eu₂O₃. The solution was prepared in a glass beaker under stirring to form a homogeneous aqueous solution, and it was confirmed that the precursor was dissolved in distilled water. 10 ml of the H₂SO₄ solution were added drop by drop into the mixed aqueous solution of Sr₁₋ₓ(NO₃)₂ : xEu under rigorous stirring at room temperature and white precipitation formed. After that, the SrSO₄ precipitate was centrifuged and rinsed several times by distilled water to remove the excess residual salts. The precipitate was dried at 60 °C for 2 h by optical heating. The dried sample was annealed at 900 °C for 1 h to get a white crystalline powder of SrSO₄:Eu²⁺. The complete process involved in the reaction is presented as a flow chart in Fig. 1.

3. Results and discussion

The structure of the as-prepared samples were analyzed by a Rikagu Miniflex X-ray diffractometer, using monochromatic CuKα₁ (λ = 1.5405 Å) radiation in the 2θ range of 10–60°. Photoluminescence was studied by means of a Hitachi F-7000 fluorescence spectrophotometer. Emission and excitation spectra were recorded using a spectral slit of 2.5 nm for each window. For studying the TL and the OSL response, all the samples were irradiated using a ⁹⁰Sr/⁶⁰Y beta source with the dose rate of 20 mGy per minute. All OSL measurements were carried out using an automatic Risø TL/OSL-DA-15 reader system which capable of accommodating up to 48 disks. Blue-light diodes emitting at 470 nm (LEDs with FWHM = 20 nm) were arranged in four clusters, each containing seven individual LEDs. The total power from 28 LEDs at the sample position was 80 mW/cm². A green long pass filter (GG-420) was incorporated in front of each blue LED cluster to minimize the amount of directly scattered blue light from reaching the detector system. The standard photomultiplier used in the Risø TL/OSL luminescence reader was a bialkali EMI 9235QA, which has an extended UV response with maximum detection efficiency between 300 and 400 nm. To prevent scattered stimulation light from reaching the photomultiplier, the Risø reader was equipped with a 7.5 mm Hoya U-340 detection filter, which has a peak transmission around 340 nm (FWHM ~ 80 nm).

3.1. X-ray diffraction pattern

The structure of SrSO₄:Eu²⁺ phosphor was orthorhombic, with the space group Pbnm (62), and with
the lattice parameters of \( a = 6.86 \), \( b = 8.35 \), \( c = 5.34 \) Å and \( \alpha = \beta = \gamma = 90^\circ \). In order to determine the phase purity, chemical nature of the phosphor, X-ray diffraction (XRD) analysis was carried out. Fig. 2a shows the XRD pattern of SrSO\(_4\):Eu\(^{2+}\) phosphor along with the standard XRD pattern (International Centre for Diffraction Data (ICDD) Card no. 01-075-6773). The XRD pattern showed the formation of pure SrSO\(_4\) phase. The addition of the dopant (Eu) did not seem to have any effect on the XRD pattern which suggested that the dopant was incorporated in the lattice.

### 3.2. Thermally stimulated luminescence

The SrSO\(_4\):Eu\(^{2+}\) phosphor was studied for its TL/OSL defects. Fig. 3 shows the typical TL glow curve of SrSO\(_4\):Eu\(^{2+}\) and its comparison with the commercial \( \alpha\)-Al\(_2\)O\(_3\):C (TLD-500) irradiated to the same dose. The SrSO\(_4\):Eu\(^{2+}\) phosphor was found to be 100 times more sensitive than that of the commercially available \( \alpha\)-Al\(_2\)O\(_3\):C (both materials were in powdered form). By using a convenient peak-shape method, kinetic parameters such as activation energy and frequency factor of glow curve were calculated [11–15]. Fig. 4 presents the TL glow curve of the SrSO\(_4\):Eu\(^{2+}\) phosphor deconvoluted using Origin software. The glow peak does not contain any satellites in the temperature range from 150 to 320°C. The geometrical factor, \( \mu_g \), calculated for the given peak, confirms the second-order kinetic nature of the curve. Thus, by second-order approximations, the activation energy was found to be 1.496 eV while the frequency factor was found to be \( 8.41 \times 10^{13} \) s\(^{-1}\) for the glow peak at 246°C. Fig. 5a shows the dose-response of the phosphor in the range from 20 to 400 mGy, which has been found in linear nature. The linear correlation coefficient of linear fitting was found to be 0.998. Fig. 5b shows the fading response up to 5 days. It is clear from the graph that about 40% fading occurs at the end of 72 h while after this period the intensity remains constant.
3.3. Optically stimulated luminescence (OSL)

The sample was studied for its OSL response using blue LED stimulation (470 nm). Fig. 6 shows the continuous wave-optically stimulated luminescence (CW-OSL) curves of SrSO₄:Eu²⁺ for 20 mGy beta-dose. The third-order exponential decay curves of SrSO₄:Eu²⁺ phosphor can be seen. The goodness of the fit was determined by calculating the figure of merit (FOM), and the obtained value of FOM was 0.415% which also confirmed a very good agreement between theoretical and experimental fitting. The OSL components from the CW-OSL decay curve were evaluated using a third-order equation for the CW-OSL intensity given by the authors of Ref. [16]. The third-order exponential fit to the decay curve showed the presence of three components with photoionization cross-sections of $1.78 \times 10^{-17}$, $7.70 \times 10^{-17}$ and $17.69 \times 10^{-17}$ cm$^2$, respectively. The OSL sensitivities were compared using two different methods. By the first method, the OSL counts during the first second were compared, whereas the second method was used to take the total area under the OSL curve [17]. Fig. 7 shows the OSL sensitivity of the SrSO₄:Eu²⁺ phosphor compared with that of the commercially available $\alpha$-Al$_2$O$_3$:C. The OSL sensitivity of the SrSO₄:Eu²⁺ phosphor was found to be 75% of that of the Al$_2$O$_3$:C phosphor by the first method (OSL counts during the first second).

3.4. Linear modulated optically stimulated luminescence (LM-OSL)

The CW-OSL results only exhibit the multiple components but they do not reveal the contribution of traps responsible for the total OSL signal. On the other hand, the application of LM-OSL is expected to separate the different peaks having a distinct spread in the values of photoionization cross section [7].
Fig. 7. CW-OSL response of SrSO₄:Eu²⁺ phosphor (b) as compared with that of the commercial α-Al₂O₃:C one (a) for 20 mGy beta dose.

Fig. 8. Deconvolution of the LM-OSL curve for SrSO₄:Eu²⁺: the first component (a), the second (b) and the third (c) ones.

Fig. 8 presents the LM-OSL response of the SrSO₄:Eu²⁺ phosphor under beta irradiation. The LM-OSL curve is shown to consist of three OSL components similar to those for CW-OSL. The geometrical factor, μₓ, calculated for the given components, confirmed the first-order kinetic nature of the curve components [1]. The calculated results related to the LM-OSL curve are given in Table 1.

### Table 1

<table>
<thead>
<tr>
<th>Component</th>
<th>μₓ</th>
<th>τ = Tₘ – T₁</th>
<th>β = T₂ – T₁</th>
<th>ω = T₂ – T₁</th>
</tr>
</thead>
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<tr>
<td>First</td>
<td>0.498</td>
<td>11.30</td>
<td>11.20</td>
<td>22.50</td>
</tr>
<tr>
<td>Second</td>
<td>0.502</td>
<td>16.10</td>
<td>16.20</td>
<td>32.30</td>
</tr>
<tr>
<td>Third</td>
<td>0.501</td>
<td>26.80</td>
<td>26.90</td>
<td>53.71</td>
</tr>
</tbody>
</table>

3.5. Reusability

This is one of the most important properties that any dosimetric material should possess. A SrSO₄:Eu²⁺ phosphor disk was exposed to beta radiation of 20 mGy, and the OSL response was measured. Ten such cycles were carried out. The studies showed that it was possible to reuse the phosphor for 10 cycles with no change in the OSL output (Fig. 9).
Fig. 10. The combined excitation (a) and emission (the rest) spectra of the SrSO₄:Eu²⁺ phosphor. The emission wavelengths (nm): 254 (b), 315 (c) and 323 (d).

3.6. Minimum detectable dose (MDD)

This parameter of the phosphor depends on the standard deviation of the background signal which affects the signal-to-noise ratio. MDD is a function of phosphor sensitivity and instrumentation. The minimum detectable dose was found to be 11.6 mGy corresponding to 3σ of the background.

3.7. Photoluminescence

The combined excitation and emission spectra of the SrSO₄:Eu²⁺ phosphor was shown in Fig. 10. The excitation spectra consist of a broad peak around 220–360 nm and relatively weak peaks at 254, 315 and 323 nm arising from the transition from ⁸S₇/₂ state of ⁴F⁰ configuration to the states belonging to the ⁴F⁶5d⁰ one. However, emission was observed at 254, 315 and 323 nm. A narrow peak around 377 nm in the emission spectra was observed for all the excitations. This wavelength corresponds to the transition from the lowest band of the ⁴F⁶5d⁰ configuration to the ⁸S₇/₂ state of the ⁴F⁰ configuration of the Eu²⁺ ion [18].

4. Conclusions

The co-precipitation method was successfully employed for the preparation of potential TLD and OSLD SrSO₄:Eu²⁺ phosphor. The XRD profile of SrSO₄:Eu²⁺ was in good agreement with the ICDD file. The comparison of TL and OSL sensitivities showed that the former for SrSO₄:Eu²⁺ was 100 times higher than that for TLD-500 and the latter for SrSO₄:Eu²⁺ was 75% of the sensitivity for the commercially available α-Al₂O₃:C phosphor (TLD-500). The CW-OSL decay curve was found to consist of three OSL components having photoionization cross-sections of 1.78×10⁻¹⁷, 7.70×10⁻¹⁷ and 17.69×10⁻¹⁷ cm², respectively. OSL components were determined from the CW and the LM-OSL data. The minimum detectable dose (MDD) was found to be 11.6 mGy with 3σ of background. Also the reusability studies showed that the phosphor could be reused for 10 cycles without any change in the OSL output. In the TL mode phosphor showed the linear dose response. The fading turned out to be up to 40% at the end of 72 h, and after that the TL intensity became constant.

Although SrSO₄:Eu is not a material equivalent to TLD-500 but, due to its high TL and OSL sensitivities and linear dose response, this phosphor can be proposed as a suitable candidate for radiation dosimetry, of course, after further progress in the studies.

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References


