Photoluminescence, thermally stimulated luminescence and electron paramagnetic resonance of europium-ion doped strontium pyrophosphate

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Abstract

Europium-ion doped strontium pyrophosphate was prepared via a chemical precipitation method to investigate the fluorescence of europium ions, the phosphate radical ions formed upon gamma-ray irradiation and their role in the thermally stimulated luminescence (TSL) of this compound. Fluorescence spectra revealed that europium ions were present in divalent as well as trivalent oxidation states. The measurements of fluorescence life time indicated that Eu\textsuperscript{3+} ions existed in two different types of environments in the lattice. Gamma irradiated europium-ion doped Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7} showed the presence of two thermo-luminescence glow peaks at 465 and 565 K; however, no glow was observed in the undoped sample. Electron paramagnetic resonance (EPR) studies of europium-ion doped samples showed signals from Mn\textsuperscript{2+} ions (present as impurity) prior to and after gamma irradiation. Upon gamma irradiation, signals originating from PO\textsubscript{2}\textsuperscript{2−}, PO\textsubscript{3}\textsuperscript{2−} and O\textsubscript{2−} radical ions were observed in the undoped and doped samples. In the gamma irradiated europium-ion doped samples, additional low-field EPR signals, attributed to Eu\textsuperscript{2+} ions, were observed. By correlating the TSL and EPR results on europium-ion doped Sr\textsubscript{2}P\textsubscript{2}O\textsubscript{7}, the mechanism for the glow peak at 565 K was identified.

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1. Introduction

Rare earth activated inorganic phosphors are widely used in a variety of applications, such as lamp industry, color display, radiation dosimetry and X-ray imaging. In particular, the luminescent properties of europium-ion activated phosphors have been studied extensively for their applications in these areas [1]. The emission of Eu$^{2+}$ ions varies from blue to red depending on the host lattice due to crystal-field effects [2]. In view of the general interest in the green and yellow emitting Eu$^{2+}$ activated compositions in recent years, calcium and strontium silicates and phosphates have been investigated in detail [3,4]. Further investigations on the luminescent characteristics of Eu$^{2+}$ activated alkaline earth aluminates have been reported in view of their potential application in luminous paints [5]. Strontium halophosphate doped with Eu$^{2+}$ ions has been reported to be useful for thermo-luminescence dosimetry [6], while Eu$^{2+}$ activated strontium borate (SrB$_4$O$_7$) and strontium pyrophosphate (Sr$_2$P$_2$O$_7$) phosphors have been reported to be applicable in photo-therapy [7].

Eu$^{2+}$ activated strontium pyrophosphate is considered to be a potential candidate for use in lamps for photo-therapy of hyper bilirubinemia (infant jaundice), since its emission is at 420 nm with negligible contribution from ultra-violet radiation; and hence, will be safe for treating infants. In fact, Eu$^{2+}$ and Mn$^{2+}$ co-doped Sr$_2$P$_2$O$_7$ has been suggested as one of the potential phosphors, to be used in the phosphor mixture for obtaining white light emission from UV LED devices [8]. Although, fluorescence studies on Sr$_2$P$_2$O$_7$:Eu$^{2+}$ has been reported long ago by Blasse et al. [9], there are no reported investigations on the thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) of this system, as far as we know. There is indeed one report on the TSL and EPR of Tm$^{3+}$ activated Ca$_2$P$_2$O$_7$ [10]. In view of these, Sr$_2$P$_2$O$_7$ doped with Eu ions (0.5 at.%) was prepared in our study via a chemical precipitation method, followed by heating the sample in nitrogen atmosphere and was investigated using fluorescence, TSL and EPR techniques in order to understand the role of europium ions in fluorescence and TSL properties. In this paper, the evidence for the co-existence of Eu$^{2+}$ and Eu$^{3+}$ in the samples is presented. In addition, the gamma radiation induced defect centers formed in this lattice were identified and their role in the TSL glow peaks was examined.

2. Experimental

Strontium hydrogen phosphate was precipitated from strontium nitrate solution containing Eu$^{3+}$ (0.5 at.%) by adding diammonium hydrogen phosphate. The pH of the solution was adjusted to be around 7–8. Analytical grade strontium nitrate, diammonium hydrogen phosphate and very pure Eu$_2$O$_3$ (99.999%) were used for the preparation. The precipitate was filtered and dried with alcohol. Later, it was ground thoroughly and heated at 1173 K for 3–4 h in nitrogen atmosphere. X-ray diffraction analysis of the sample confirmed that the compound formed was α-Sr$_2$P$_2$O$_7$ [11]. Undoped Sr$_2$P$_2$O$_7$ sample was also prepared in a similar way. About 20 mg of the samples was used for TSL measurements carried out on a home-built unit between 300 and 700 K. The samples were irradiated with Co$^{60}$ rays inside a gamma chamber. Photoluminescence spectra were recorded using a Hitachi 2000 fluorescence spectrometer equipped with a 150 W Xe arc lamp. Fluorescence lifetime measurements were carried out using an Edinburgh Fluorescence lifetime spectrometer equipped with a hydrogen flash lamp having a pulse width of 1–2 ns. EPR spectra were recorded using a Bruker ESP-300 spectrometer at x-band frequencies both at room temperature and 77 K. Spectra were also recorded at different temperatures.
ranging from 100–400 K using a Bruker low temperature accessory. Further, spectra of the gamma irradiated samples were recorded after annealing in the temperature range of 450–575 K.

3. Results and discussion

3.1. Luminescence of europium-ion doped Sr₂P₂O₇

Europium ions can be stabilized in Sr₂P₂O₇ lattice in either divalent or trivalent oxidation state. The incorporation and stabilization of Eu ions in the sample were confirmed by the luminescence investigations. The fluorescence spectra of the samples are shown in Figs. 1 and 2. The emission spectra corresponding to excitation of Eu³⁺ at 256 and 270 nm are depicted in Fig. 1 with two peaks at 594 and 615 nm. The excitation spectra corresponding to these peaks are also shown in the figure. The characteristic excitation and emission spectra of Eu²⁺ ions are illustrated in Fig. 2.

It is obvious from Fig. 1 that emission peaks characteristic of Eu³⁺ ions are present in the samples. The emission peaks at 594 and 615 nm corresponding to ⁵D₀ → ⁷F₁ and ⁵D₀ → ⁷F₂ transitions, respectively, are observed on excitation with both 256 and 270 nm. The emission peak intensity ratio (R) of ⁵D₀ → ⁷F₂ to that of ⁵D₀ → ⁷F₁ transition is known to provide structural information [12]. As seen from the data illustrated in Fig. 1, the intensity ratio (R) of the sample varies with excitation wavelength (256 and 270 nm). The changes in the intensity ratio suggest the existence of Eu³⁺ ions at two different sites in Sr₂P₂O₇ lattice corresponding to two charge transfer excitation peaks. The crystallographic data of Sr₂P₂O₇ are reported to contain two types of sites for Sr²⁺ ions in the unit cell [13]. The differences in the spectra thus reveal that Eu³⁺ ions are situated at the two types of sites corresponding to Sr²⁺ ions. On excitation with 256 nm, ⁵D₀ → ⁷F₁ emission at 594 nm is the predominant one, while ⁵D₀ → ⁷F₂ emission

![Fig. 1. Excitation spectra of Eu³⁺ in europium doped Sr₂P₂O₇ corresponding to (a) emission peak at 594 nm and (b) emission peak at 615 nm. Emission spectra of Eu³⁺ ion corresponding to (c) excitation spectra at 256 nm and (d) excitation at 272 nm.](image-url)
at 615 nm is relatively weak. The peak at 615 nm is due to $^5\text{D}_0 \rightarrow ^7\text{F}_2$ transition, which is parity forbidden and observed only when the lattice environment is distorted and contains non-inversion symmetry. Being a forced electric-dipole transition, this transition is hypersensitive to the environment. Therefore, it is inferred that the 256-nm excited emission peaks at 594 and 615 nm correspond to Eu$^{3+}$ ions occupying a site with a smaller deviation from inversion symmetry. On the other hand, 270 nm excitation leads to the observation of 594 and 615 nm emission with nearly same intensity. This indicates that the emission originates from Eu$^{3+}$ ions occupying sites lacking inversion symmetry.

The luminescence spectra illustrated in Fig. 2 reveal that Eu$^{2+}$ ions with characteristic emission at 422 nm, are also formed during synthesis. This observation suggests that synthesis conditions help in the partial reduction of Eu$^{3+}$ ions to Eu$^{2+}$ ions and inert atmosphere facilitates the partial reduction of Eu$^{3+}$ to Eu$^{2+}$. The excitation spectra monitored for 422 nm contain broad and strong peaks at 300 and 330 nm. As compared to the emission from Eu$^{3+}$ ions, the emission spectra of Eu$^{2+}$ ions were recorded at lower PM tube voltage as the signals were very intense, if recorded at identical PM tube voltage. The strong emission due to Eu$^{2+}$ ions is associated with the allowed transitions of $5d \rightarrow 4f$. The fluorescence lifetime for emission from Eu$^{3+}$ ions were determined to be 110 and 522 $\mu$s by monitoring the 594 nm peak. For Eu$^{2+}$ ions, the life time was determined to be 1.6 $\mu$s by monitoring at 422 nm. These values are consistent with the forbidden and allowed nature of transition involving these ions.

### 3.2. TSL of europium-ion doped Sr$_2$P$_2$O$_7$

TSL glow curves of the Eu-ion doped Sr$_2$P$_2$O$_7$ samples exposed to 100 and 200 Gy doses of Co$^{60}$ gamma-rays were recorded. Two glow peaks were observed around 465 and 565 K (heating rate = 5 K/s) and the latter one is more intense than the former one (Fig. 3). The glow is not strong enough for recording the emission spectra. However, a red glow could be seen visually on heating the irradiated samples at 465 and 565 K, indicating that Eu$^{3+}$ acts as the luminescent center for the glow peaks. On the other hand, the undoped Sr$_2$P$_2$O$_7$ sample did not show any TSL peak.
3.3. EPR of europium-ion doped and undoped Sr$_2$P$_2$O$_7$

To clearly distinguish the signals of Sr$_2$P$_2$O$_7$ from those of Eu-ion doped Sr$_2$P$_2$O$_7$ and also to identify the radical ions formed on gamma irradiation, EPR spectra of Eu-ion doped and undoped Sr$_2$P$_2$O$_7$ samples were recorded before and after gamma irradiation with a dose of 2–4 kGy. It should be borne in mind that TSL is at least three to four orders more sensitive than EPR in the detection of small concentration of defects. Hence, for interpreting TSL mechanisms, EPR measurements were carried out on samples subjected to higher irradiation doses as compared to TSL experiments in order to produce significant quantities of the paramagnetic centers.

EPR spectra of the unirradiated and gamma irradiated Sr$_2$P$_2$O$_7$ samples were recorded at room temperature and 77 K. At room temperature, EPR spectrum of unirradiated Sr$_2$P$_2$O$_7$ did not show any signal, while that of the gamma irradiated (dose = 4 kGy) sample consisted of a composite signal of eight lines centered around 3.4 kG ($g = 2.0$) along with a doublet signal with a large separation ($A = 740$ G) with $g = 2.0303$. The composite signal has a set of five intense lines in addition to a triplet with moderate intensity (Fig. 4). The microwave power dependence of this signal in the range of 2–24 mW indicated different saturation behavior of the doublet ($A = 740$ G) signal centered at $g = 2.0303$ (P$_1$ center) as compared to that of the composite signal at $g = 2.0$. In order to identify the origins of radicals contributing to the composite signal, EPR spectrum of a sample irradiated with low gamma dose (1 kGy) was investigated. EPR spectrum of the low dose sample was recorded at room temperature, which showed dose dependent saturation of the most intense signal at $g = 2.00472$ (P$_2$ center). Thus, a quartet of intense lines with $A_\perp = 57.8$ G and $A_\parallel = 121.84$ G, $A_{iso} = 79.1$ G and $g_\perp = 2.0041$ and $g_\parallel = 2.0042$ have different

![Fig. 3. TSL glow curves of 200 Gy gamma-ray irradiated europium-ion doped Sr$_2$P$_2$O$_7$ sample recorded at the heating rates of 5 K/s and 10 K/s.](image)
Furthermore, the EPR spectrum of the 4 kGy irradiated sample was recorded in second harmonic mode in order to resolve the triplet (P_4 center) overlapping with signal of P_3 centers (Fig. 5). Signal of P_4 center has \( g = 2.0052 \) and \( A = 30 \) G. The temperature dependence of the EPR spectrum of the sample was carried out in the temperature range of 300–575 K. On heating above room temperature, the intensity of the composite signal decreases at 525 K (Fig. 6). However, on heating at 575 K, this composite signal disappears. Interestingly, on cooling the sample to 77 K, it did not appear again indicating that the center associated with this signal got destroyed.

SrOPO_4 subjected to gamma-ray irradiation might yield different \(^{31}\)P (natural abundance = 100\% and nuclear spin, \( I = 1/2 \)) centered radicals, viz. PO_2\(^-\), P_2O_7\(^3-\), PO_2\(^2-\), PO_3\(^2-\) and PO_4\(^2-\) as reported in literature [14–16]. P_1 center obtained in the present study is attributed to PO_3\(^2-\) radical with its large hyperfine coupling coming from electron in the 3s orbital. P_3 center has smaller hyperfine splitting, but not as small as reported [14] for PO_4\(^2-\) and P_2O_7\(^3-\) ions. However, it is close to the one reported for PO_2\(^2-\) center in KCl [15]. Hence, the intense quartet signal is attributed to axially distorted PO_2\(^2-\) centers and the close resemblance of its \( g \) values (\( g_{\perp} = 2.0041 \) and \( g_{\parallel} = 2.0042 \)) suggests isotropic nature of the radical. The signal of P_2 centers, with \( g_{\perp} = 2.0047 \) and \( g_{\parallel} = 2.0030 \), overlapping with low-field parallel component of P_3 center is assigned to O_2\(^-\) radical ion on the basis of its \( g \) values reported in apatites [16]. P_4 center could not be identified.
EPR spectra of the unirradiated and gamma irradiated Eu-ion doped Sr$_2$P$_2$O$_7$ sample were recorded at room temperature and 77 K. The spectra of both unirradiated and irradiated samples showed signals in the 320–370 mT region. (Fig. 7). The signals consisted of two sets of sextet hyperfine lines with $A = 92$ G (a) and $A = 94$ G (b), respectively, and slightly different $g$ values ($g = 2.0032$ and 2.0024). These lines are characteristic of Mn$^{2+}$ ions as reported in the literature [17,18], indicating that Mn$^{2+}$ has entered the lattice (at two different Sr$^{2+}$ sites) as an impurity from the analytical grade reagents used for the preparation, namely strontium nitrate or diammonium hydrogen phosphate. Similarly, weak Mn$^{2+}$ lines are observed in the undoped Sr$_2$P$_2$O$_7$ samples.

The hyperfine lines from Eu$^{2+}$ (Eu$^{151,153}$) expected in the 340–360 mT (3.4–3.6 kG) region (with $A \sim 30$ G for Eu$^{151}$ and $\sim 15$ G for Eu$^{153}$ [19], respectively, and $g$ around 2.000) seem to be hidden under strong Mn$^{2+}$ lines. The spectra also show signals from PO$_2^{2-}$ (P$_3$) and O$_2^{-}$ (P$_2$) radical ions around $g = 2.0042$, similar to those observed in undoped irradiated Sr$_2$P$_2$O$_7$. EPR spectra of gamma-ray irradiated
Fig. 6. EPR spectra of gamma-ray irradiated Sr$_2$P$_2$O$_7$ recorded at various temperatures.

Fig. 7. EPR spectrum of unirradiated Eu-ion doped Sr$_2$P$_2$O$_7$ at room temperature. The two sets of hyperfine lines from Mn$^{3+}$ ion (Mn$^{55}$) at two different sites are marked ‘a’ and ‘b’ in the figure.
Eu-ion doped Sr$_2$P$_2$O$_7$ samples were recorded in the 100–500 K range. On heating above the room temperature, the intensity of the signals from PO$_2^{2-}$ and O$_2^-$ radicals decreases, while further heating at 575 K, signals of both the radicals disappear together (Fig. 8). This behavior of these two radical ions is similar to that observed in undoped samples. The destruction of these radical ions around 575 K strongly suggests their role in the TSL peak in Eu-ion doped Sr$_2$P$_2$O$_7$ at this temperature. In view of these results, the mechanism for the 565 K glow peak is confirmed to be due to the recombination of PO$_2^{2-}$ and O$_2^-$ ions and the associated energy transfer to nearby Eu$^{3+}$ ions.

The spectra of gamma irradiated europium-ion doped Sr$_2$P$_2$O$_7$ recorded at 175 K consist of several broad signals over a wide range of magnetic-field (0–200 mT); but these signals are quite weak as compared to those observed around 340 mT (Fig. 9). It is noted that these features are absent in the unirradiated samples. Such a spectrum is reported to be typical of Eu$^{2+}$ ion with large zero-field splitting and might be a pointer to the presence of Eu$^{2+}$ at a low symmetry site as in the case of SrBPO$_5$:Eu$^{2+}$ [20]. This signal is probably associated with Eu$^{2+}$ ions formed on gamma-ray irradiation due to electrons captured by Eu$^{3+}$ ions.

Fig. 8. EPR spectra recorded at 100 K: (a) gamma-ray irradiated sample; (b) gamma irradiation followed by annealing at 575 K; and (c) difference between spectrum a and spectrum b.
4. Conclusion

The present investigation on Eu-ion doped strontium pyrophosphate sample prepared via a chemical precipitation method followed by heating in nitrogen indicates that europium ions were present both in divalent as well as trivalent oxidation states in the sample. Fluorescence life time measurements revealed that Eu\(^{3+}\) ion existed at two different environments in the lattice. Two glow peaks were observed in gamma irradiated europium ion doped samples at 465 and 565 K. Eu\(^{3+}\) ion was identified as the luminescent center for the glow peaks. In gamma irradiated samples, PO\(_2\)^{2-}, PO\(_3\)^{2-} and O\(_2^-\) radical ions were observed. By correlating the TSL and EPR results on europium-ion doped Sr\(_2\)P\(_2\)O\(_7\), the mechanism for the glow peak at 565 K was identified.

Fig. 9. EPR spectrum of gamma-ray irradiated Eu-ion doped Sr\(_2\)P\(_2\)O\(_7\) recorded at 175 K in the 0–4500 mT range.
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