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

V. Natarajan[a], M.K. Bhide[b], A.R. Dhobale[a], S.V. Godbole[b], T.K. Seshagiri[b], A.G. Page[b], Chung-Hsin Lu[a,*]

[a]*Department of Chemical Engineering, No. 1, Sec. 4, Roosevelt Road, National Taiwan University, Taipei 106, Taiwan*
[b]*Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai*

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^{3+} ions existed in two different types of environments in the lattice. Gamma irradiated europium-ion doped $Sr_2P_2O_7$ 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^{2+} ions (present as impurity) prior to and after gamma irradiation. Upon gamma irradiation, signals originating from PO_2^{2-}, PO_3^{2-} and O_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^{2+} ions, were observed. By correlating the TSL and EPR results on europium-ion doped $Sr_2P_2O_7$, the mechanism for the glow peak at 565 K was identified.
© 2004 Elsevier Ltd. All rights reserved.

* Corresponding author. Tel.: + 886 2 2365 1428; fax: +886 2 2362 3040.
 E-mail address: chlu@ccms.ntu.edu.tw (C.-H. Lu).

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_4O_7) and strontium pyrophosphate ($Sr_2P_2O_7$) 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 $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$: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 $Ca_2P_2O_7$ [10]. In view of these, $Sr_2P_2O_7$ 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_2O_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-$Sr_2P_2O_7$ [11]. Undoped $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$

Europium ions can be stabilized in $Sr_2P_2O_7$ 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 Eu^{3+} 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 Eu^{2+} ions are illustrated in Fig. 2.

It is obvious from Fig. 1 that emission peaks characteristic of Eu^{3+} ions are present in the samples. The emission peaks at 594 and 615 nm corresponding to $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions, respectively, are observed on excitation with both 256 and 270 nm. The emission peak intensity ratio (R) of $^5D_0 \rightarrow {}^7F_2$ to that of $^5D_0 \rightarrow {}^7F_1$ 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 Eu^{3+} ions at two different sites in $Sr_2P_2O_7$ lattice corresponding to two charge transfer excitation peaks. The crystallographic data of $Sr_2P_2O_7$ are reported to contain two types of sites for Sr^{2+} ions in the unit cell [13]. The differences in the spectra thus reveal that Eu^{3+} ions are situated at the two types of sites corresponding to Sr^{2+} ions. On excitation with 256 nm, $^5D_0 \rightarrow {}^7F_1$ emission at 594 nm is the predominant one, while $^5D_0 \rightarrow {}^7F_2$ emission
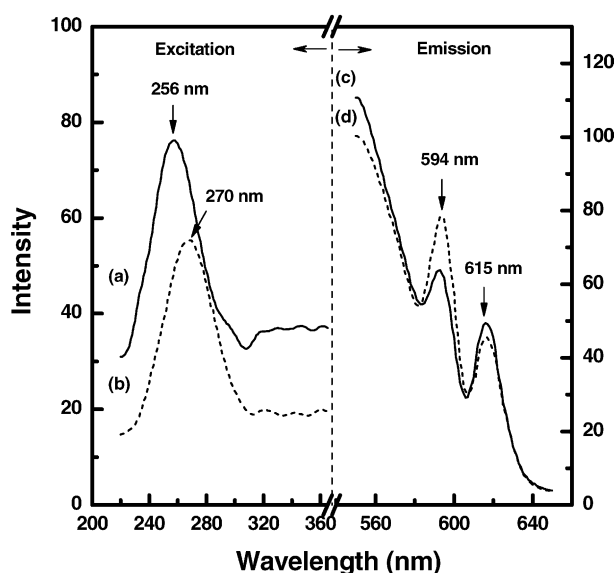

Fig. 1. Excitation spectra of Eu^{3+} in europium doped $Sr_2P_2O_7$ corresponding to (a) emission peak at 594 nm and (b) emission peak at 615 nm. Emission spectra of Eu^{3+} ion corresponding to (c) excitation spectra at 256 nm and (d) excitation at 272 nm.
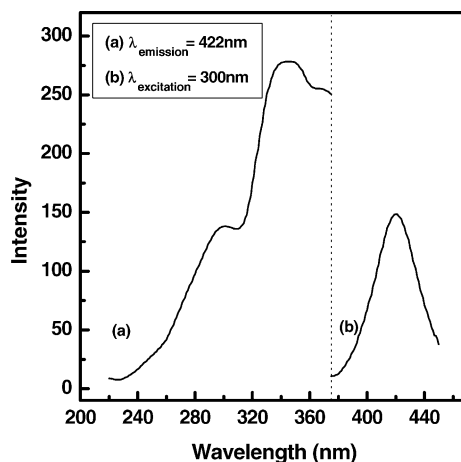
Fig. 2. (a) Excitation and (b) emission spectra of Eu^{2+} ion in europium doped $Sr_2P_2O_7$.

at 615 nm is relatively weak. The peak at 615 nm is due to $^5D_0 \rightarrow {}^7F_2$ 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 μs by monitoring the 594 nm peak. For Eu^{2+} ions, the life time was determined to be 1.6 μs 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 $Sr_2P_2O_7$

TSL glow curves of the Eu-ion doped $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$ sample did not show any TSL peak.
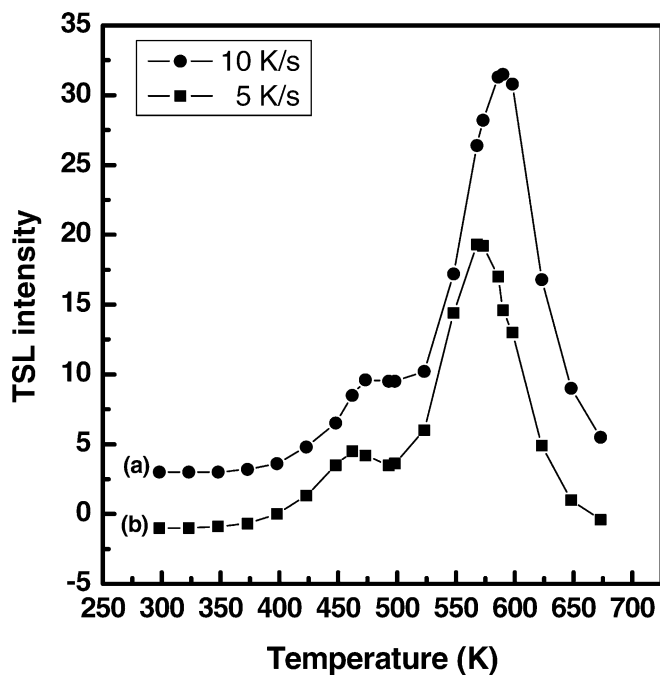
Fig. 3. TSL glow curves of 200 Gy gamma-ray irradiated europium-ion doped $Sr_2P_2O_7$ sample recorded at the heating rates of 5 K/s and 10 K/s.

3.3. EPR of europium-ion doped and undoped $Sr_2P_2O_7$

To clearly distinguish the signals of $Sr_2P_2O_7$ from those of Eu-ion doped $Sr_2P_2O_7$ and also to identify the radical ions formed on gamma irradiation, EPR spectra of Eu-ion doped and undoped $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$ samples were recorded at room temperature and 77 K. At room temperature, EPR spectrum of unirradiated $Sr_2P_2O_7$ 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

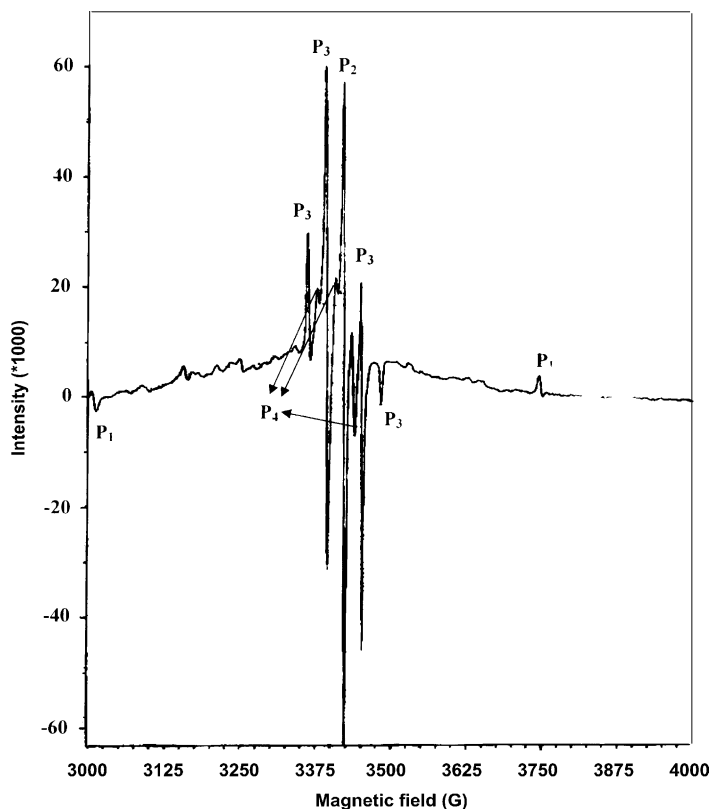Fig. 4. EPR spectrum of gamma-ray irradiated-undoped $Sr_2P_2O_7$ (dose = 4 kGy) at room temperature. Signals marked as P_1 (doublet), P_2, P_3 (quartet) and P_4 (triplet) are discussed in the text.

origin (P_3 center). 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.

Strontium pyrophosphate 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.
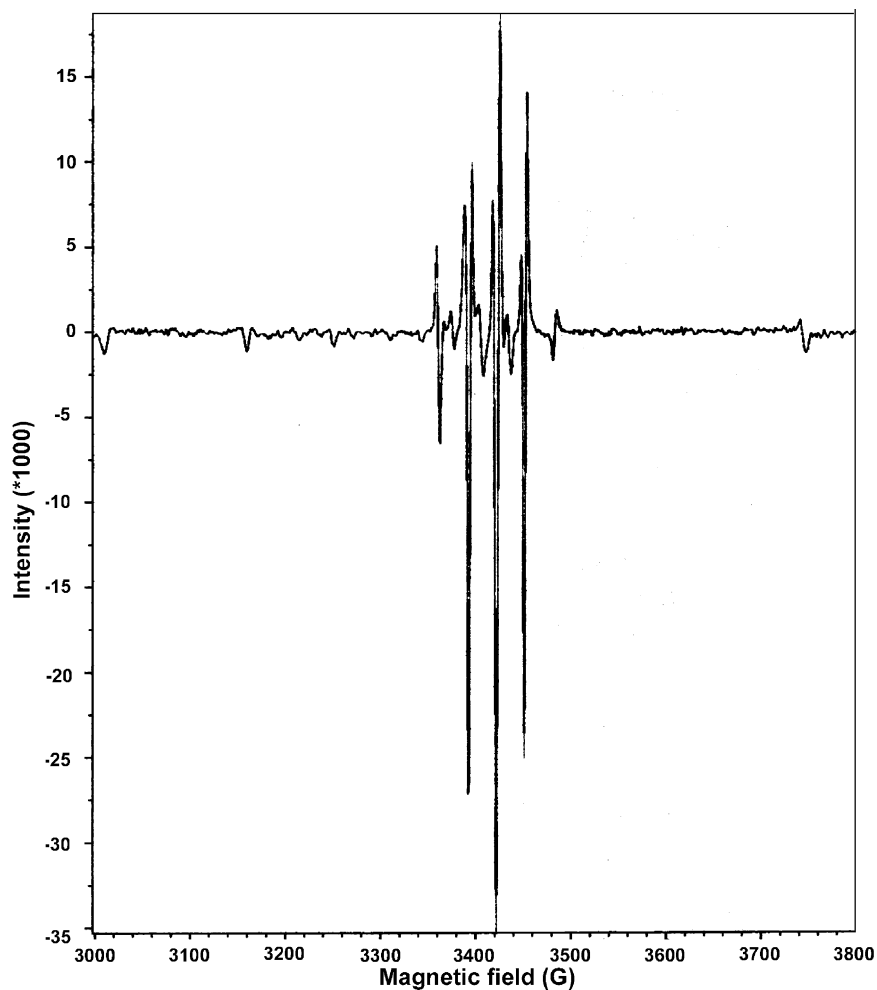
Fig. 5. Second harmonic EPR spectrum of gamma-ray irradiated $Sr_2P_2O_7$ at room temperature.

EPR spectra of the unirradiated and gamma irradiated Eu-ion doped $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$ 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 ~ 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 $Sr_2P_2O_7$. EPR spectra of gamma-ray irradiated
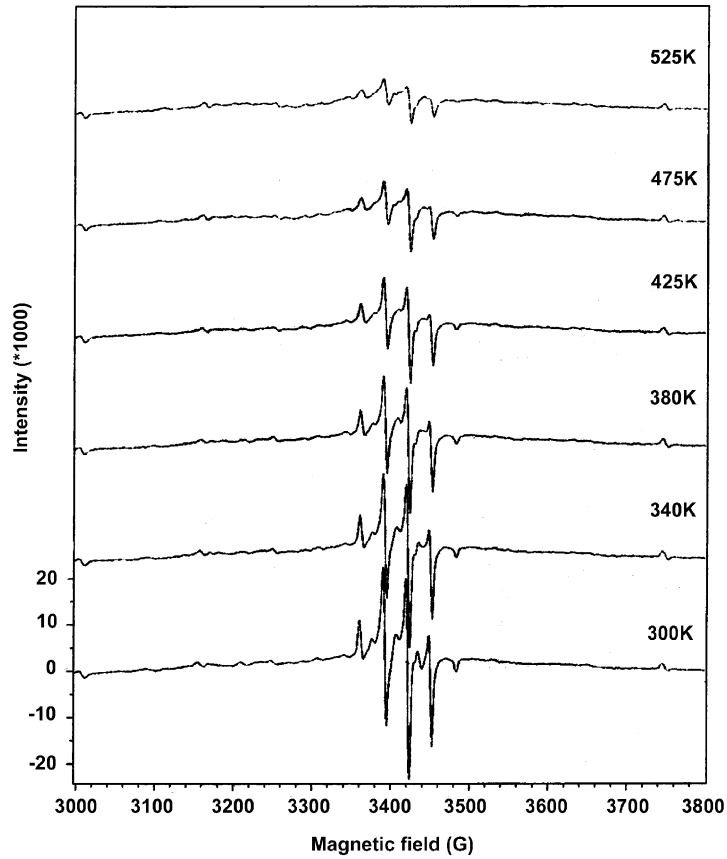
Fig. 6. EPR spectra of gamma-ray irradiated $Sr_2P_2O_7$ recorded at various temperatures.

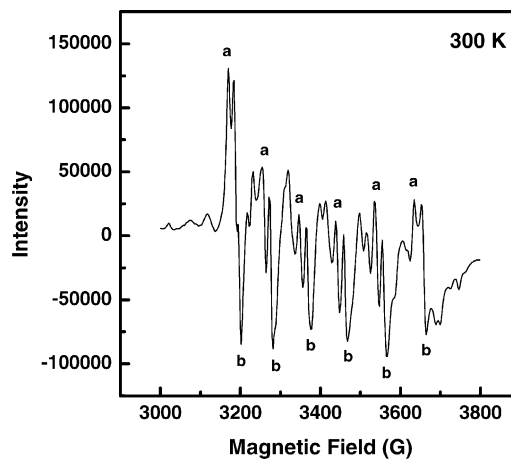Fig. 7. EPR spectrum of unirradiated Eu-ion doped $Sr_2P_2O_7$ at room temperature. The two sets of hyperfine lines from Mn^{2+} ion (Mn^{55}) at two different sites are marked 'a' and 'b' in the figure.
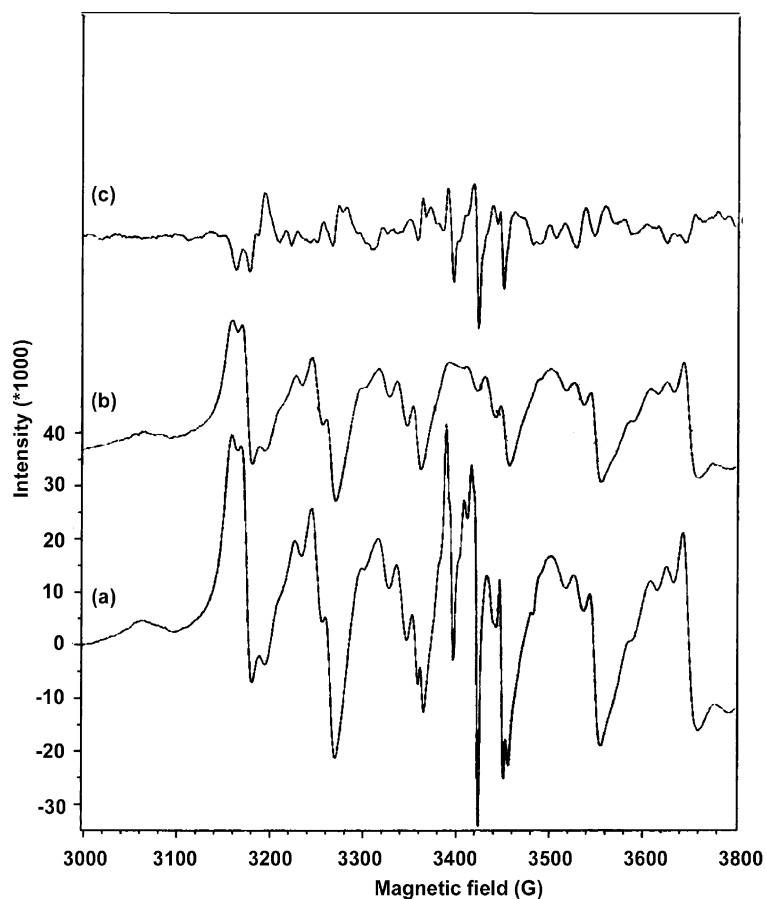
Fig. 8. EPR spectra recorded at 100 K: (a) gamma-ray irradiated sample; (b) gamma irradiation followed by annealing at 575 K; and (c) difference between spectrum a and spectrum b.

Eu-ion doped $Sr_2P_2O_7$ 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 $Sr_2P_2O_7$ 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^- and O_2^- ions and the associated energy transfer to nearby Eu^{3+} ions.

The spectra of gamma irradiated europium-ion doped $Sr_2P_2O_7$ 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.
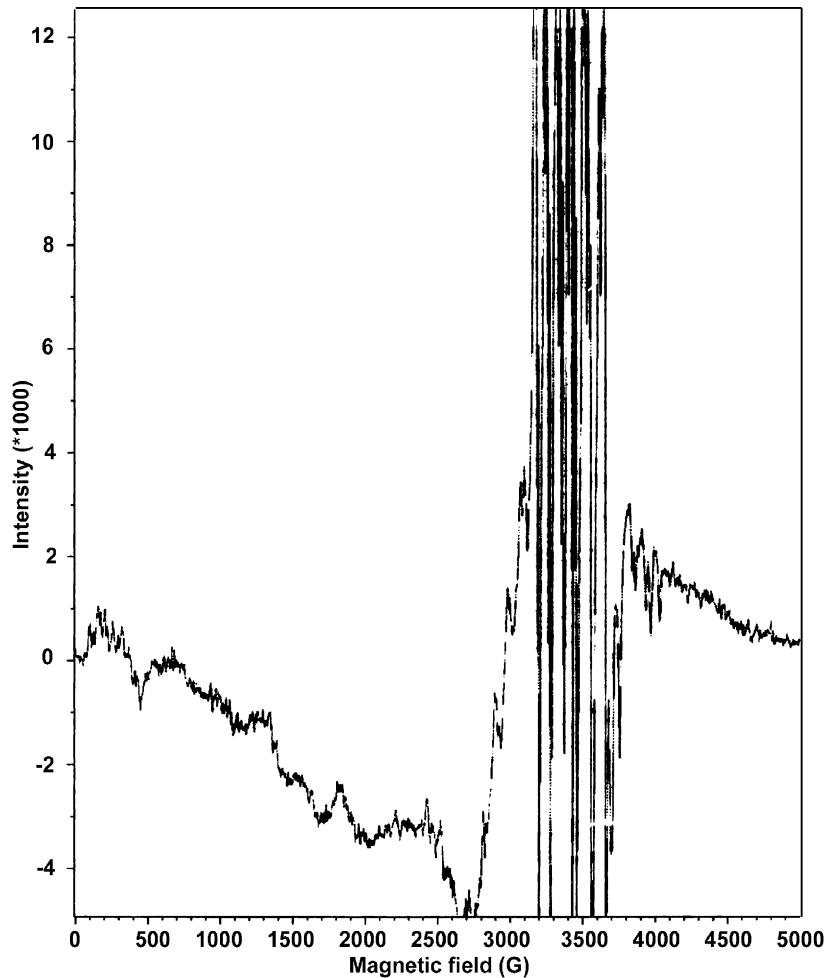
Fig. 9. EPR spectrum of gamma-ray irradiated Eu-ion doped $Sr_2P_2O_7$ recorded at 175 K in the 0–4500 mT range.

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 $Sr_2P_2O_7$, the mechanism for the glow peak at 565 K was identified.

References

[1] S. Shionoya, W.M. Yen, Phosphor Hand Book, CRC Press, Washington DC, 1999, pp. 391–432.

[2] S.H.M. Poort, W.P. Blokpoel, G. Blasse, Chem. Mater. 7 (1997) 1547–1551.

[3] S.H.M. Poort, W. Janssen, G. Blasse, J. Alloys Compd. 260 (1997) 93–97.

[4] J.K. Park, M.A. Lim, C.H. Kim, H.D. Park, Appl. Phys. Lett. 82 (2003) 683–685.

[5] Y. Murayama, N. Takeuchi, Y. Aaoki, T. Matsuzawa, US patent 5424006 (1995).

[6] S.J. Dhoble, S.V. Moharil, J. Phys. D. Appl. Phys. 33 (2000) 158–161.

[7] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer Verlag, Berlin Heidelberg, 1994, p. 127.

[8] A.M. Srivastava, US patent Application 0030067008 (2003).

[9] G. Blasse, W.L. Wanmaker, J.W. Ter Vrught, J. Electrochem. Soc. 115 (1968) 673.

[10] H. Miyoshi, T. Yoshino, Radiat. Phys. Chem. 48 (1996) 315–318.

[11] Powder Diffraction File, Card no. 24-1011, Joint Committee on Powder Diffraction Standards, Swathmore, PA.

[12] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer Verlag, Berlin Heidelberg, 1994, pp. 41–43.

[13] J.C. Grenier, R. Masse, Bulletin de la Societe Francaise de Minerologie et de Cristallographie 90 (1967) 285–292.

[14] S. Subramanian, M.C.R. Symons, H.W. Wardale, J. Chem. Soc. A (1970) 1239–1241.

[15] F. Callens, F. Maes, P. Moens, P. Matthys, E. Boesman, J. Phys. Condens. Matter 4 (1992) 6593–6602.

[16] A.S. Marfunin, Spectroscopy Luminescence and Radiation Centers in Minerals, Springer, New York, 1979, pp. 258–261.

[17] R.S. de Biasi, M.L.J. Grillo, J. Phys. Chem. Solids 64 (2003) 1365–1369.

[18] R.S. de Biasi, J. Am. Ceram. Soc. 86 (2003) 195–196.

[19] N. Yamashita, J. Lumin. 59 (1994) 195–199.

[20] T. Nakamura, T. Takeyama, N. Takahashi, R. Jagannathan, A. Kartikeyani, G.M. Smith, P.C. Reidi, J. Lumin. 102–103 (2003) 369–372.