Thermally stimulated luminescence and photoluminescence investigations of Eu^{3+} and Eu^{2+} doped SrBPO_5

MITHLESH KUMAR, T K SESHAGIRI* and S V GODBOLE

Radiochemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

MS received 13 January 2012; revised 31 July 2012

Abstract. Thermally stimulated luminescence (TSL) investigations of $\text{SrBPO}_5:\text{Eu}^{3+}$ and $\text{SrBPO}_5:\text{Eu}^{2+}$ phosphors were carried out in the temperature range of 300–650 K. In order to characterize the phosphors, X-ray diffraction and photoluminescence (PL) techniques were used. The emission spectrum of air heated $\text{SrBPO}_5:\text{Eu}^{3+}$ phosphor exhibited emission bands at 590, 614, 651 and 702 nm under 248 nm excitation, assigned to transitions of Eu^{3+} ion. In phosphor prepared in reducing ($\text{Ar} + 8\% \text{H}_2$) atmosphere, a broad emission band due to Eu^{2+} ranging from 350 to 400 nm was observed with 340 nm excitation. EPR studies have confirmed the presence of Eu^{2+} ions in the samples prepared in reducing atmosphere. TSL glow curve of $\text{SrBPO}_5:\text{Eu}^{3+}$ had shown intense peaks around 397, 510, 547 K and a weak peak around 440 K whereas in case of $\text{SrBPO}_5:\text{Eu}^{2+}$ system, glow peaks at 414, 478 and weak peak at 516 nm were observed. The shift in TSL glow pattern can be attributed to stabilization of different oxidation states of the dopant ion in the host lattice. Apart from this, TSL trap parameters such as trap depth and frequency factor were determined. Spectral characteristics of TSL emission have shown that $\text{Eu}^{3+}/\text{Eu}^{2+}$ ion acts as the luminescent centre in the respective phosphors.

Keywords. Thermally stimulated luminescence; photoluminescence; Eu^{3+} and Eu^{2+} doped SrBPO_5 .

1. Introduction

Alkaline earth borophosphates doped with rare-earth elements are new phosphors in the field of compact fluorescent lamps on UV excitation and in medical diagnosis exhibiting luminescence on X-ray irradiation (Liang *et al* 2004). The development work of SrBPO_5 doped with Eu^{2+} phosphor is reported as it can be used for its possible application in radiography (Sonoda *et al* 1983). The spectral features of this system, viz. blue-violet emission with high sensitivity for photo-detectors and fast luminescence decay time facilitating fast read-out, are highly favourable for radiographic imaging applications. The rare earth ions doped phosphors have been used in varied fields based on their electronic and optical characters arising from their $4f$ electrons. Among the rare earth elements, europium is a special element as dopant, because it exhibits the property of valence fluctuation, i.e. the valence state is divalent or trivalent. The stabilization of a particular oxidation state is influenced by synthesis conditions and host matrix. It shows different characteristics luminescence due to different valences. It has been reported that Eu^{2+} ions or Eu^{3+} ions exhibit favourable luminescence behaviour in many matrices. The rare-earth ions Eu^{3+} , Tb^{3+}

and Dy^{3+} form red, green and yellow phosphors, respectively, when they are doped in suitable matrices. The red light emission of Eu^{3+} is centred at near 614 nm, which is owing to intra- $4f$ transition. While the emission of Eu^{2+} from the dipole allowed $5d-4f$ transition varies in a wide range from red to ultraviolet, which depends on the crystal structure of host materials. SrBPO_5 belongs to the stillwellite type compound with hexagonal system. Sr^{2+} ions are 10-fold coordinated by O^{2-} ions in the form of C_2 symmetry. Crystal structure of SrBPO_5 compound is similar to that of mineral, stillwellite $\text{CeBO}(\text{SiO}_4)$. Stillwellites are rare-earth(s) borosilicates built up of $(\text{BO}_4)^{3-}$ and $(\text{SiO}_4)^{4-}$ tetrahedral. The main constituents of stillwellite are $(\text{SiO}_4)^{4-}$ tetrahedra set on edges in the form of vertical column(s) parallel to c -axis. Each $(\text{BO}_4)^{3-}$ tetrahedron is connected by its free vertices with two $(\text{SiO}_4)^{4-}$ tetrahedra and has two common edges with Ce^{3+} (or lanthanide) polyhedra of adjacent columns (Zeng *et al* 2003).

We have undertaken systemic studies of Ce, Sm, Eu, Tb and Dy, etc doped SrBPO_5 matrix to understand its stabilization in the host and its effect on spectroscopic properties. Karthikeyani and Jagannathan (2000) reported that Eu^{2+} doped SrBPO_5 is a new luminescent system which shows intense photostimulated luminescence for UV and X-ray radiations. The suitability of this system is compared with various features of $\text{BaFBr}:\text{Eu}^{2+}$ for radiography application. Sakasai *et al* (2002) reported about characteristics of the $\text{SrBPO}_5:\text{Eu}^{2+}$ material, such as spectral characteristics, fading characteristics and two-dimensional imaging for

*Author for correspondence (giritks@gmail.com)

actual application in storage phosphor for neutron imaging. Lan *et al* (2010) presented photoluminescence (PL) studies of Eu^{2+} - and Mn^{2+} -doped SrBPO_5 . The experimental results show that the sample is a promising single host phosphor to use in white light emitting diode. Some of the researchers have reported (Liang *et al* 2004) existence of Eu^{3+} and Eu^{2+} oxidation states in BaBPO_5 matrix. However, TSL investigations of $\text{SrBPO}_5\text{:Eu}^{3+}$ and $\text{SrBPO}_5\text{:Eu}^{2+}$ phosphors were not fully reported. In view of the utility of rare earth ions doped strontium borophosphates phosphor for various applications, in the present work, Eu^{3+} and Eu^{2+} doped SrBPO_5 phosphors were synthesized, characterized and investigated using PL and thermally stimulated luminescence (TSL) techniques. The work on Ce, Sm and Tb doped SrBPO_5 was already reported from our laboratory (Mithlesh *et al* 2011). PL studies give information about oxidation state of dopant ions and their life time parameters. On the other hand, TSL is a technique that gives information on $e-h$ recombination process on thermal stimulation. TSL experiments yield values of activation energy (E) and frequency factor (s). Further, spectral characteristics of TSL emission have shown Eu^{3+} to act as emission centre in $\text{SrBPO}_5\text{:Eu}^{3+}$ sample, while in Eu^{2+} doped SrBPO_5 sample, Eu^{2+} ion acts as the luminescent centre.

2. Experimental

Strontium borophosphate doped with Eu^{3+} and Eu^{2+} (1 mol%) was prepared by conventional solid state reaction method. Stoichiometric amounts of SrCO_3 , H_3BO_3 (with 5 mol% in excess), $(\text{NH}_4)_2\text{HPO}_4$ and nitrate form of dopant were thoroughly ground and heated in air atmosphere at 873 K for 4 h. Further, it was ground and heated at 1173 K for 4 h. The sample heating at 1173 K was repeated twice. This process obtained the final product of Eu^{3+} doped SrBPO_5 sample. A part of this sample was heated in ($\text{Ar} + 8\% \text{H}_2$) atmosphere at 1173 K for 6 h. Further, it was ground thoroughly and again heated in ($\text{Ar} + 8\% \text{H}_2$) at 1173 K for 6 h to get final product of Eu^{2+} doped SrBPO_5 sample. The chemical equation can be expressed as follows:

Un-doped SrBPO_5 phosphor was prepared in a similar manner. The obtained products were characterized by powder X-ray diffraction (XRD). Absence of trace metallic constituents at 10 ppm or above in un-doped and Eu-doped samples have been ascertained by inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis of the dissolved samples of SrBPO_5 . PL emission and excitation spectra were recorded on an Edinburgh F-900 fluorescence spectrometer in 200–800 nm region with Xe lamp as an excitation source, M-300 monochromators and Peltier cooled photo-multiplier tube as detector (Jain *et al* 2008). The acquisition and analysis of the data were carried

out by F-900 software supplied by Edinburgh Analytical Instruments, UK. Thermally stimulated luminescence (TSL) glow curves were recorded using home-built unit between 300 and 650 K (Rajore *et al* 2000). The phosphors were γ -irradiated using ^{60}Co source having a dose rate of 2 kGy/h for TSL studies. Electron paramagnetic resonance (EPR) studies were carried out at X-band frequency on a Bruker ESP-300 spectrometer with 100 kHz modulation frequency.

3. Results and discussion

3.1 XRD studies

The synthesized products were characterized by powder XRD using $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) employing a Philips X-ray diffractometer (model PW 1710, The Netherlands) fitted with a Ni filter and graphite crystal monochromator. X-ray diffraction pattern of Eu^{3+} -doped SrBPO_5 phosphor along with the standard pattern reported for SrBPO_5 (ICDD file no. 18-1270) is shown in figure 1. XRD pattern was found to be similar to the earlier reported one confirming the formation of single phase. All the peaks could be indexed on the trigonal system with cell parameters $a = 6.8850(3)$; $c = 6.8700(2)$ which are in close agreement with the reported values. XRD pattern of Eu^{2+} doped SrBPO_5 was similar to Eu^{3+} doped system. Table 1 gives the observed and calculated values of d along with their intensity and (h, k, l) reflections. The agreement between the observed and calculated d values clearly indicates that no impurity phases are present in the sample. It is reported in the literature (Kniep *et al* 1994; Shi *et al* 1998; Pan *et al* 2003) that MBPO_5 ($M = \text{Ca, Sr, Ba}$) belongs to stillwellite type compound, which crystallized in the trigonal system with space group $P3_221$ and three formula units per cell.

Figure 1. (a) Powder X-ray diffraction pattern of $\text{SrBPO}_5\text{:Eu}^{3+}$ phosphor and (b) ICDD stick pattern for card no. 18-1270.

Table 1. X-ray diffraction values of $\text{SrBPO}_5\text{:Eu}^{3+}$ indexed on trigonal system with cell parameters.

d_{obs} (Å)	d_{cal} (Å)	hkl	I
4.480	4.476	102	20
3.439	3.426	110	80
3.060	3.061	112	6
2.966	2.967	200	100
2.957	2.956	104	100
2.718	2.720	202	5
2.416	2.416	114	10
2.272	2.273	006	10
2.242	2.243	210	40
2.239	2.238	204	40
2.129	2.129	106	50
1.977	1.978	300	6
1.900	1.899	302	6
1.894	1.894	116	10
1.873	1.874	214	60
1.804	1.804	206	2
1.713	1.713	220	10
1.711	1.711	304	10
1.662	1.661	222	2
1.645	1.646	310	6
1.639	1.638	108	6
1.600	1.600	312	6
1.596	1.596	216	6
1.531	1.531	224	10
1.526	1.526	118	10

Figure 2. Excitation spectrum obtained on Eu^{3+} doped SrBPO_5 with $\lambda_{\text{em}} = 614$ nm.

3.2 Photoluminescence studies

The excitation spectrum using $\lambda_{\text{em}} = 614$ nm of Eu^{3+} -doped SrBPO_5 phosphor (heated in air) is shown in figure 2. An intense band is observed between 220 and 250 nm which is attributed to the charge transfer transition originating from $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$. According to García-Hipólito *et al* (2003), the charge transfer state is usually the most intense excitation mechanism, generally occurring between 250 and 300 nm due to charge transfer transitions from O^{2-} to Eu^{3+} ions. The other less intense excitation peaks observed at 320, 365, 380 and 395 nm are assigned to the $f-f$ transitions from the 7F_0

Figure 3. (a) Emission spectrum obtained on Eu^{3+} doped SrBPO_5 with $\lambda_{\text{ex}} = 248$ nm and (b) emission spectrum recorded on SrBPO_5 blank.

ground state to 5H_3 , 5L_9 , 5G_3 and 5L_6 levels, respectively (Dieke 1968).

Figure 3 shows PL emission spectrum obtained on Eu^{3+} -doped SrBPO_5 phosphor heated in air using $\lambda_{\text{ex}} = 248$ nm. The emission spectrum of the phosphor exhibits bands at 590, 614, 651 and 702 nm with red emission centred at 614 nm being the most prominent. These bands 590, 614, 651 and 702 nm are assigned to the ${}^5D_0 \rightarrow {}^7F_J$ ($J = 1, 2, 3, 4$) transitions, respectively of Eu^{3+} on the basis of earlier reports (Werts *et al* 2002). The band appearing at around 614 nm is an electric dipole transition of the $4f$ shell and is hypersensitive to structural changes and environmental effects in the vicinity of Eu^{3+} ($4f^6$ configuration) ion. The luminescence spectrum of this ion is slightly influenced by surrounding ligands of the host material, because electronic transitions of Eu^{3+} involve only a redistribution of electrons within the inner $4f$ sub-shell. The peak, which is centred at 590 nm, corresponds to the ${}^5D_0 \rightarrow {}^7F_1$ transition and occurs by means of the magnetic dipole, indicating that the ion Eu^{3+} is in a low symmetry environment. Generally, it does not change with the crystal field strength around the Eu^{3+} ion. Other peaks, which are observed at 651 and 702 nm, correspond to transitions from the 5D_0 to the 7F_3 and 7F_4 levels, respectively. Apart from this, two additional weak emission peaks at 502 and 522 nm are observed (shown in inset of figure 3(a) which are most likely due to the luminescence of defects on the basis of oxygen vacancies. Similar emission peaks were observed in SrBPO_5 blank sample, which are shown in the inset of figure 3(b). It is well known that $4f-4f$ transition and charge transfer band (CTB) are two types for excitation of the trivalent lanthanide ions in crystals. The $4f$ orbital is shielded from the surroundings by the filled $5s^2$ and $5p^6$ orbital. Therefore, influence of the host lattice on the optical transition within the $4f^n$ configuration is small and $4f-4f$ transitions are sharp lines. CTB shows a broad band character and is intense than that of $4f-4f$

Figure 4. PL (a) excitation and (b) emission spectra recorded on Eu^{2+} doped SrBPO_5 .

transitions. In the present case of $\text{SrBPO}_5:\text{Eu}^{3+}$, PL emission spectrum indicated the absence of $^5D_0 \rightarrow ^7F_0$ transition. The intensity ratio of the two $^5D_0 \rightarrow ^7F_2$ (614 nm) and $^5D_0 \rightarrow ^7F_1$ (590 nm) transitions was evaluated to be 2.03. The fluorescence intensity ratio of ($= I_{614}/I_{590}$) $^5D_0 \rightarrow ^7F_2$ to $^5D_0 \rightarrow ^7F_1$ transitions, generally called asymmetry ratio, gives a measure of the degree of distortion from the inversion symmetry of the local environment of the Eu^{3+} ion in the matrix. Therefore, a large asymmetry ratio value indicates strong electric fields of low symmetry at the Eu^{3+} ions.

Figure 4 shows PL excitation and emission spectrum obtained on Eu^{2+} doped SrBPO_5 phosphor heated in ($\text{Ar} + 8\% \text{H}_2$) atmosphere. A broad excitation band ranging from 200 to 400 nm is seen to well match with the reported ones in the literature (Kostova *et al* 2010). The strong excitation at 340 nm is consistent with the observed energy level scheme for Eu^{2+} ions and it can be attributed to the transitions from the $4f^7(^8S_{7/2})$ ground state to the $4f^65d^1$ excited state of the Eu^{2+} ions. The $4f^65f^1$ electron state is not shielded from the surroundings and has a strong interaction with neighbouring anion ligands in the compounds, which results in a broad absorption band. The emission spectrum displays intense broad emission band in the range of 350–450 nm with a maximum around 395 nm corresponding to $4f^65d^1 \rightarrow 4f^7$ electric dipole transition of Eu^{2+} ions and the electron–phonon broadening (Chung *et al* 2009).

3.3 Electron paramagnetic resonance studies

Figure 5 shows EPR spectrum of Eu doped SrBPO_5 phosphor (heated in $\text{Ar} + 8\% \text{H}_2$) at room temperature. The spectrum appears to be complex having several EPR lines of parallel and perpendicular components between 0 and 10 KG. Eu^{3+} ions with configuration $4f^6$ has 7F_0 as its electronic ground state and hence is diamagnetic. Eu^{2+} with $4f^7$ configuration has $^8S_{7/2}$ as its electronic ground state. Divalent europium, in lower symmetries (Vijay Singh *et al* 2007), has a complex EPR spectrum consisting of several lines, which arises from

Figure 5. EPR at 300 K of un-irradiated Eu^{2+} doped SrBPO_5 .

the seven allowed fine structure transitions for electronic spin $S = 7/2$. The seven lines can further split into six hyperfine lines corresponding to the two stable isotopes, ^{151}Eu [(47.8% abundance, $I = 5/2$) and ^{153}Eu (52.2% abundance, $I = 5/2$)]. However, in cubic symmetry, only a single line around $g = 2$ will be observed as the lines overlap/coincide. The observation of fine structure in the cubic symmetry with fine structure depends on the zero field splitting (Kawano *et al* 1983; Edgar *et al* 2010; Vrielinck *et al* 2012). Unlike most of the other rare earth ions, EPR of Eu^{2+} could easily be observable even at room temperature in view of its long spin lattice relaxation times. In the present studies, Eu^{2+} doped SrBPO_5 phosphor have shown several EPR lines between 0–10 KG due to large zero field splitting of Eu^{2+} ground state with g around (1.9999 ± 0.0002) with orthorhombic distortion. The observed EPR spectra are similar to those reported earlier (Vijay Singh *et al* 2007; Karthikeyani and Jagannathan 2000). This confirms the lower symmetry around Eu^{2+} ions in SrBPO_5 matrix. No hyperfine structure due to Eu^{2+} were observed in the present studies, probably due to high concentration of Eu (1 mol%). Large zero field splitting of Eu^{2+} ground state has also been reported by other authors (Karthikeyani and Jagannathan 2000; Nakamura *et al* 2003; Natarajan *et al* 2004; Vijay Singh *et al* 2007, 2009). It should be borne in mind that the information obtained from the powder or polycrystalline EPR spectrum is rather limited. The recorded spectrum is an orientational average and most of the detailed structure is often smoothed out. Hence, due to strong anisotropic nature of the fine structure (fs) transition(s), other than the central fine structure transition, it is possible to observe only the central fine structure ($+1/2 \rightarrow -1/2$) transition. No significant changes were observed in the EPR of Eu^{2+} , on gamma irradiation of Eu^{2+} doped SrBPO_5 . Further, EPR investigations were also carried out on air heated Eu-doped SrBPO_5 phosphor at room temperature both before and after gamma irradiation. No EPR signal due to Eu^{2+} was observed in air-heated sample in either of the cases. However, PL studies had shown the existence of only Eu^{2+} ions in ($\text{Ar} + 8\% \text{H}_2$) heated samples, while, existence of Eu^{3+} ions only was observed in air-heated samples as discussed earlier.

Figure 6. TSL glow curves on gamma irradiated (a) Eu^{3+} and (b) Eu^{2+} doped SrBPO_5 ; β = heating rate.

Figure 7. γ -dose dependence plots of 510 K peak in SrBPO_5 : Eu^{3+} and 414 K peak in SrBPO_5 : Eu^{2+} .

3.4 Thermally stimulated luminescence studies

The trapping centres or defects in a material play a major role in the luminescence process and modulate quite significantly. To gain a complete insight into the trapping mechanism, TSL analysis is widely used as an effective tool. The determination of trapping parameters is of immense importance to find the material's suitability for various applications. Prior to γ -irradiation no glow peaks were observed in un-doped SrBPO_5 and SrBPO_5 doped with $\text{Eu}^{3+}/\text{Eu}^{2+}$ phosphors. Figure 6 shows TSL emission glow curves recorded on γ -irradiated (dose 2 kGy) Eu^{3+} and Eu^{2+} doped SrBPO_5 phosphors at a heating rate of (β) = 2.0 K/s. The glow curve of SrBPO_5 : Eu^{3+} sample has shown intense peaks around 397, 510, 547 K and a weak peak around 440 K whereas in case of SrBPO_5 : Eu^{2+} sample glow peaks at 414, 478 and weak peak at 516 K were observed. Figure 7 shows TSL intensity vs gamma dose plots of Eu^{3+} (510 K) and Eu^{2+} (414 K) of glow peaks. The glow peaks had given maximum TSL yield for a dose of 2 kGy. Gamma dose dependence behaviour of other prominent TSL glow peaks in both Eu^{3+} and Eu^{2+}

Table 2. Trap parameters.

Sl. No.	Peak temperature (T_m in °K)	Activation energy, E (eV)	Frequency factor, s (s^{-1})
SrBPO_5:Eu^{3+}			
1	397	0.79	1.5×10^9
2	440 (W)*	0.88	—
3	510	1.02	1.3×10^9
4	547	1.09	1.1×10^9
SrBPO_5:Eu^{2+}			
5	414	0.83	1.8×10^9
6	478	0.95	1.2×10^9
7	516 (W)*	1.03	—

*Empirical formula, $E = T_m/500$.

doped samples were also found to be similar. To determine the trap parameters, viz. trap depth (E) and frequency factor (s), the glow curves were recorded at different heating rates (0.5, 1, 2.0 and 2.5 K/s). Thermal bleaching of the lower temperature peaks were done to get reliable trap depth values for high temperature TSL glow peaks. A plot of $\ln T_m^2/\beta$ vs $1/T_m$ (where β represents the heating rate and T_m represents the glow peak temperature) was obtained and a least square fit program was employed to obtain the best fit for E and s factors (Nambi 1977). The trap parameters calculated are shown in table 2. For order of kinetics calculation, T_1 , T_2 and T_m were evaluated from TSL glow shape for well-resolved peaks. The symmetry of the glow peak is measured in terms of T_1 , T_2 and T_m as

$$\mu_g = \frac{\delta}{\omega} = \frac{\tau_2 - \tau_m}{\tau_2 - \tau_m}.$$

It is known that,

$$\mu_g < \frac{1 - \Delta}{\varepsilon} \text{ for first order kinetics,}$$

and

$$\mu_g \geq \frac{1 - \Delta}{\varepsilon} \text{ for second order kinetics,}$$

where

$$\Delta = 2kT_m/E.$$

Order of kinetics of 397 K (SrBPO_5 : Eu^{3+}) and 414 K (SrBPO_5 : Eu^{2+}) TSL peaks were determined using the above glow curve shape method. Both TSL peaks belong to first order kinetics. Further, TSL emission spectra were obtained on γ -irradiated SrBPO_5 : Eu^{3+} and SrBPO_5 : Eu^{2+} phosphors using transmittance and narrow band interference filters. Spectral characteristics of the TSL glows have shown emission around 600 nm in Eu^{3+} -doped sample while emission around 400 nm was prominent in samples prepared in reducing ($\text{Ar} + 8\% \text{H}_2$) atmosphere indicating thereby that Eu^{3+} and Eu^{2+} ions act as luminescent centres in the respective phosphors.

PL and TSL investigations of SrBPO₅:Eu phosphor suggested that (i) stabilization of Eu²⁺ and Eu³⁺ depend on synthesis conditions and host matrix, (ii) shift in TSL glow pattern can be attributed to stabilization of different oxidation states of the dopant ion in the host lattice, (iii) *e-h* recombination process involved various trap levels at different temperatures and (iv) Eu²⁺ as well as Eu³⁺ ions act as luminescent centres.

4. Conclusions

PL studies of Eu³⁺-doped SrBPO₅ sample heated in air have revealed groups at 590, 614, 651 and 702 nm assigned to the ⁵D₀ → ⁷F_J (*J* = 1, 2, 3, 4) transitions due to Eu³⁺. PL emission spectrum obtained on (Ar + 8% H₂) heated Eu²⁺ doped SrBPO₅ has shown broad emission band in the range of 350–450 nm with maximum around 395 nm corresponding to 4*f*⁶5*d*¹–4*f*⁷ electric dipole transition of Eu²⁺. The existence of Eu²⁺ in SrBPO₅ matrix was also confirmed by EPR experiments. TSL glow curves of SrBPO₅:Eu³⁺ and SrBPO₅:Eu²⁺ phosphors were obtained between 300 and 650 K regions. The shift in TSL glow pattern can be attributed to stabilization of different oxidation states of the dopant ions. TSL trap parameters such as trap depth and frequency factor were determined.

Acknowledgements

The authors are grateful to Dr A Goswami, Radiochemistry Division, BARC, for his keen interest and encouragement during the course of this work. The authors are also thankful to Dr R M Kadam, Radiochemistry Division, for his help in conducting the EPR experiments.

References

Chung Jong Won, Yang Hyun Kyoung, Moon Byung Kee, Choi Byung Chun and Jeong Jung Hyun 2009 *J. Korean Phys. Soc.* **55** 1965
 Dieke G H 1968 In *Spectra and energy levels of rare earth ions in crystals* (eds) H M Crosswhite and H Crosswhite (New York: Interscience Publishers)

Edgar A, Zimmermann J, von Seggern H and Varoy C R 2010 *J. Appl. Phys.* **107** 083516
 García-Hipólito M, Hernández-Pérez C D, Alvarez-Fregoso O, Martínez E, Guzmán-Mendoza J and Falcony C 2003 *Opt. Mater.* **22** 345
 Jain A, Mohapatra M, Godbole S V and Tomar B S 2008 *Spectrochim. Acta: Part A* **71** 1007
 Karthikeyani A and Jagannathan R 2000 *J. Lumin.* **86** 79
 Kawano K, Shimizu M, Nakata R and Sumita M 1983 *Radiat. Eff.* **73** 167
 Kniep R, Godel G, Eisenmann B, Rohr C, Asbrand M and Kizilyalli M 1994 *Angew. Chem. Int. Ed. Engl.* **33** 749
 Kostova M H, Batentschuk M, Goetz-Neunhoffer F, Gruber S, Winnacker A, Greil P and Zollfrank C 2010 *Mater. Chem. Phys.* **123** 166
 Lan Yuwei, Yi Linghong, Zhou Liya, Tong Zhangfa, Gong Fuzhong and Wang Rongfang 2010 *Physica* **B405** 3489
 Liang Hongbin, Tao Ye, Chen Wenxuan, Ju Xin, Wang Shubin and Su Qiang 2004 *J. Phys. Chem. Solids* **65** 1071
 Mithlesh Kumar, Seshagiri T K, Kadam R M and Godbole S V 2011 *Mater. Res. Bull.* **46** 1359
 Nakamura T, Takeyama T, Takahashi N, Jagannathan R, Karthikeyani A, Smith G M and Reidt P C 2003 *J. Lumin.* **102&103** 369
 Nambi K S V 1977 *Thermoluminescence: Its understanding and applications* (Em Marco: Aprovado para publicacao) p. 26
 Natarajan V, Bhide M K, Dhobale A R, Godbole S V, Seshagiri T K, Page A G and Lu C H 2004 *Mater. Res. Bull.* **39** 2065
 Pan Shilie, Wu Yicheng, Fu Peizhen, Zhang Guochun, Li Zhihua, Du Chenxia and Chen Chuangtian 2003 *Chem. Mater.* **15** 2218
 Rajore S B, Seshagiri T K, Mhatre J B, Venkiteswaran S V and Sastry M D 2000 *International symposium on thermoluminescence and its applications* Baroda, India
 Sakasai K, Katagiri M, Toh K, Takahashi H, Nakazawa M and Kondo Y 2002 *Appl. Phys. (Suppl.)* **A74** S1589
 Shi Y, Liang J, Zhan H, Liu Q, Chen X, Yang J, Zhuang W and Rao G 1998 *J. Solid State Chem.* **135** 43
 Sonoda M, Takano M, Miyahara J and Kato H 1983 *Radiology* **148** 833
 Vijay Singh, Jun-Jie Zhu, Bhide M K and Natarajan V 2007 *Opt. Mater.* **30** 446
 Vijay Singh, Jun-Jie Zhu, Manoj Tiwari, Manish Soni, Mahendra Aynayas, Seok-Hee Hyun, Narayanan R, Manoj Mohapatra and Natarajan V 2009 *J. Non-Cryst. Solids* **355** 2491
 Vrielinck H, Zverev D G, Leblans P, Tahon J P, Matthys P and Callens F 2012 *Phys. Rev.* **B85** 144119
 Werts M H V, Jukes R T F and Verhoeven J W 2002 *Phys. Chem. Chem. Phys.* **4** 1542
 Zeng Qinghua, Kilah Nathan and Riley Mark 2003 *J. Lumin.* **101** 167