Luminescence properties of terbium-doped Li_3PO_4 phosphor for radiation dosimetry

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Abstract. A polycrystalline sample of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor was successfully synthesized using solid-state diffusion method. This synthesis method is of low cost, low temperature and does not require any other atmospheres for the synthesis. The powder X-ray diffraction (PXRD), photoluminescence (PL) emission and excitation spectra, thermoluminescence (TL) and optically stimulated luminescence (OSL) were measured. The particle size was calculated using the Debye Scherrer formula and found to be 79.42 nm. PL emission spectra of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor show the strong prominent peak at 544 nm corresponding to $^5\text{D}_4$ to $^7\text{F}_5$ transitions of Tb^{3+} . The OSL sensitivity of prepared $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor was 50% of that of $\alpha\text{-Al}_2\text{O}_3:\text{C}$. Its decay curve consists of three components with photoionization cross-sections 0.44×10^{-17} , 3.09×10^{-17} and $23 \times 10^{-17} \text{ cm}^2$. The TL glow curve of the prepared sample consists of two characteristic peaks, which were deconvoluted using the peak fit software, and kinetic parameters were determined using the peak shape method. TL intensity was compared with that of the commercially available TLD-500 phosphor. OSL dose response was linear in the measured range and the minimum detectable dose (MDD) was found to be 67.42 μGy , while fading of the OSL signal was found to be about 27% in 4200 min after which the OSL signal stabilizes.

Keywords. $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$; OSL; radiation dosimetry; TLD-500.

1. Introduction

Radiation dosimetry using luminescence techniques has made tremendous progress during the last two decades. Several techniques (TL, OSL and passive solid-state detectors) have now found routine use and have received due recognition. Among them, optically stimulated luminescence dosimetry (OSLD) is one of the techniques used in radiation dosimetry. OSL has virtually replaced thermoluminescence (TL) dosimetry in personnel monitoring. The OSL technique is now well developed and extensively used in radiation dosimetry applications [1]. Antonov-Romanovskii *et al* [2] firstly suggested applications of OSL for personal dosimetry. This technique got momentum for personnel dosimetry after the development of $\alpha\text{-Al}_2\text{O}_3:\text{C}$. OSL properties of $\alpha\text{-Al}_2\text{O}_3:\text{C}$ have been investigated for personnel dosimetry, environmental dosimetry, medical dosimetry and space dosimetry. The OSL technique is more popular in radiation dosimetry because of faster and multiple readout, very high sensitivity, absence of thermal quenching and possible use of phosphor in plastic binders [3–15].

Recently rare-earth-doped orthophosphates, including LiMgPO_4 , LiBaPO_4 , LiCaPO_4 and Li_3PO_4 phosphors, have found increasing interest for their potential applications in the field of PL, TL and OSL [16–20]. The effective atomic

numbers (Z_{eff}) of the above phosphate phosphors are high as compared with that of our prepared Li_3PO_4 ($Z_{\text{eff}} = 10.6$) phosphor, which exhibits useful TL/OSL properties in personal dosimetry of ionizing radiations. Sahu *et al* [20] reported lyoluminescence and mechanoluminescence of $\text{Li}_3\text{PO}_4:\text{Ce-Eu}$ phosphors using a two-step solid-state reaction. The total time required for this reaction was more than 24 h [21]. Barve *et al* [22] reported TL/OSL properties of $\text{Li}_3\text{PO}_4:\text{Cu}$ phosphor using the co-precipitation method.

Apart from the solid-state and co-precipitation method, we have developed Li_3PO_4 phosphors using a modified solid-state reaction. This synthesis technique was developed to reduce the time required for the synthesis, which was about 12 h, without any special outer atmospheres for synthesis.

In the present work we report luminescence properties of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor using a modified solid-state method for the applications in radiation dosimetry.

2. Experimental

Li_3PO_4 phosphors doped with rare-earths ions of different concentrations were synthesized using a modified solid-state method. High purity starting materials lithium nitrates ($\text{LiNO}_3 \cdot 3\text{H}_2\text{O}$), ammonium dihydrogen orthophosphate ($\text{NH}_4\text{H}_2\text{PO}_4$) and terbium nitrates ($\text{Tb}_4\text{O}_7 + \text{HNO}_3$) were used in the synthesis. Details of molar ratio of constituents used for phosphor synthesis are given in table 1.

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Table 1. Molar ratio of ingredients used for material preparation and corresponding chemical reaction.

Compound	Molar ratio
$\text{Li}_{(3-x)}\text{PO}_4:x\text{Tb}^{3+}$	$\text{Li}(\text{NO}_3):\text{NH}_4\text{H}_2\text{PO}_4:x(\text{Tb}_4\text{O}_7+\text{HNO}_3)$ (3-x) : 1 : x (x = 0.001, 0.002, 0.005 and 0.01)
$(3-x)\text{Li}(\text{NO}_3) + \text{NH}_4\text{H}_2\text{PO}_4 + x(\text{Tb}_4\text{O}_7+\text{HNO}_3) \rightarrow \text{Li}_{(3-x)}\text{PO}_4:x\text{Tb}^{3+} + (\text{gaseous product like NO}_3, \text{H}_2\text{O})$	

The starting materials were taken in a proper stoichiometric ratio, mixed in a china basin and by adding small amounts of acetone a clear solution was obtained. This mixture was heated on a hot plate at 100°C for 30 min and then the sample was placed in a muffle furnace with the instalment of 200°C for 2 h, 400°C for 2 h, 800°C for 3 h and 950°C for 1 h, between two intermediate grindings and the sample was suddenly quenched to room temperature. The same process was repeated for the different concentrations of dopant.

The phase purity of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ sample was checked by powder X-ray diffraction (PXRD) using a Rigaku miniflex II diffractometer with Cu K α ($\lambda = 1.5405 \text{ \AA}$) operated at 5 kV. The data were collected in a 2θ range of 10 to 90 degrees. Irradiation of all the samples was performed at room temperature using a calibrated $^{90}\text{Sr}/^{90}\text{Y}$ beta source housed in a RISO TL/OSL Reader (DA-20 Model). The activity of the source was 40 mCi and the dose rate was 20 mGy s $^{-1}$. All TL/OSL measurements were carried out using an automatic Risø TL/OSL-DA-20 reader system, which can accommodate up to 48 discs. Blue LEDs emitting at 470 nm (FWHM = 20 nm) are arranged in four clusters each containing seven individual LEDs. PL and PL excitation (PLE) spectra were measured on a (Hitachi F-7000) fluorescence spectrophotometer with a 450 W xenon lamp, in the range 200–700 nm, with spectral slit width of 1 nm and PMT voltage of 700 V at room temperature.

3. Results and discussions

3.1 XRD pattern

The XRD pattern of the as-synthesized $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor is presented in figure 1. The XRD pattern was fully matched with the International Center for Diffraction data (ICDD) file with card no. 01-083-0339. Structure of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ was orthorhombic system with space group Pmnb (62) and lattice parameters $a = 6.111 \text{ \AA}$, $b = 10.4612 \text{ \AA}$, $c = 4.920 \text{ \AA}$ and $\alpha = \beta = \gamma = 90^\circ$. The average crystallite size of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor determined from the Debye–Scherrer formula [23] was found to be 79.42 nm.

3.2 Photoluminescence (PL)

The combined excitation and emission spectra of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor with varied Tb^{3+} concentrations ($x = 0.001$,

Figure 1. XRD pattern of the $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ sample along with the ICDD standard pattern no. 01-083-0339. **Figure 2.** Excitation and emission spectra of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor synthesized by solid-state reaction.

0.002, 0.005 and 0.01) are shown in figure 2. The excitation spectra were monitored at 544 nm and emission spectra were monitored at 225 nm. The excitation spectra consist of a broad peak from 200 to 250 nm and higher intensity peaks appear at 225 nm corresponding to the $4f^8-4f^75d$ transitions of Tb^{3+} . The emission spectrum consists of relatively weak peaks at 353, 370 and 377 nm corresponding to the $^5\text{D}_3$ to $^7\text{F}_j$ ($J = 5, 4, 3$) transitions while strong peaks were observed at 488, 544, 584, and 621 nm corresponding to the $^5\text{D}_4$ to $^7\text{F}_j$ ($J = 6, 5, 4, 3$) transitions with the $4f^8$ configurations of Tb^{3+} [24]. Among the emission lines from the $^5\text{D}_4$

state the dominant emission was observed at 544 nm, corresponding to the $^5\text{D}_4$ to $^7\text{F}_5$ transition observed at 225 nm excitation. From the figure it was observed that 0.002 mol was the optimum concentration for the prepared phosphor. The luminescence intensity was observed to be decreased when the concentration of Tb^{3+} ions was increased beyond this optimum value, due to the well-known phenomenon of concentration quenching [25].

3.3 Optically stimulated luminescence

The sample was studied for its optically stimulated luminescence (OSL) response using blue LED stimulation ($\lambda = 470$ nm). Initially a powder disc (~ 3 mg) of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor was irradiated using the β -source. Figure 3 shows the typical CW-OSL response of $\text{Li}_{(3-x)}\text{PO}_4:x\text{Tb}^{3+}$ ($x = 0.001, 0.002, 0.005$ and 0.01 mol) for 100 mGy of β -dose. As concentration of Tb^{3+} ions increased beyond 0.002 mol the OSL intensity was found to have decreased. From the figure, OSL intensity is optimum at 0.002 mol of Tb^{3+} ions. Hence this phosphor is used for remaining studies. A 3rd order exponential fit on the decay curve shows the presence of three OSL components with and photoionization cross-sections of 0.44×10^{-17} , 3.09×10^{-17} and $23 \times 10^{-17} \text{ cm}^2$. Figure 4 presents comparison of prepared phosphor with commercially available phosphors. Sensitivity of the prepared phosphor was found to be 50% of that of commercially available $\alpha\text{-Al}_2\text{O}_3:\text{C}$ phosphor. Figure 5 presents dose response of the prepared phosphor for variation of doses (0.04 to 12 Gy). The nature of dose response was found to be linear. The response is described by linear correlation co-efficient of linear fitting and was found to be 0.99.

3.3a Batch homogeneity: To study the batch homogeneity 10 discs were prepared from the same batch of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor exposed to 20 mGy of $^{90}\text{Sr}/^{90}\text{Y}$ β -source. The deviation of maximum OSL signal from that of the minimum

Figure 4. $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor compared with $\alpha\text{-Al}_2\text{O}_3:\text{C}$ phosphor under 20 mGy of β -ray.

Figure 5. Dose response of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ under β -irradiation.

Figure 3. CW-OSL response of $\text{Li}_3\text{PO}_4:x\text{Tb}^{3+}$ ($x = 0.001, 0.002, 0.005$ and 0.01 mol) under β -irradiation.

Figure 6. Reusability studies of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor.

signal was about 20%. Hence the studied discs satisfy the IEC requirement [1].

3.3b Minimum detectable dose (MDD): To determine MDD, 10 powder discs (same weight) of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor were used for background variation measurement. The OSL reader was calibrated using 10 discs, which were irradiated with 100 mGy. The MDD was found to be 67.42 μGy (dose corresponding to 3σ of the background).

3.3c Reusability: Figure 6 presents the reusability characteristics of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor. This study was carried out by exposing the disc (powder form) of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$

phosphor to 20 mGy dose of $^{90}\text{Sr}/^{90}\text{Y}$ β -rays and then recording OSL for 60 s after the discs recorded OSL for 100 s so that the discs were bleached completely. Ten such cycles were carried out. The study shows that the phosphor can be reused for 10 cycles with less than 0.5% changes in the OSL output signal.

3.3d Fading: The long-term stability (low fading) of the radiations induced OSL signal is advantageous in the dosimetry field. Fading of the OSL signal from $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphors at room temperature was tested for 4200 min following 100 mGy of $^{90}\text{Sr}/^{90}\text{Y}$ β -irradiations, which is presented in figure 7. Here the prepared sample shows about 27% loss of signal after 4200 min.

Figure 7. Room temperature fading of OSL signal with time.

3.4 Thermoluminescence (TL)

Figure 8a presents TL glow curves of Li_3PO_4 phosphors. The peak was deconvoluted using the peak fit software and figure of merit (FOM) was found to be 0.047. The glow curve exhibits two prominent well separated TL peaks and these peaks appear at 143°C (peak 1 (P_1)) and at 260°C (peak 2 (P_2)). The TL counts at 50°C were due to the plate emission of sample holder. For the calculation of kinetic parameter such as activation energy and frequency factor of the glow peak, the easiest and most popular peak shape method was utilized [26–28]. Geometrical factor μ_g calculated for peaks P_1 and P_2 confirms second order of kinetic nature of the curve. The activation energies for peaks P_1 and P_2 were found to be 0.751 and 1.126 eV, while frequency factors were found to be 2.48×10^8 and $7.98 \times 10^9 \text{ s}^{-1}$. The TL glow curve of $\text{Li}_{2.998}\text{PO}_4:0.002\text{Tb}^{3+}$ was compared to the glow curve obtained from commercial TLD-500 for the

Figure 8. (a) TSL glow curve of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor along with the deconvoluted glow curves of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor. (b) Comparison of TL glows with that of TLD-500.

same dose of exposure. The comparative glow curves are presented in figure 8b. It was clearly observed that the sensitivity of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ was nearly 1.2 times that of commercially available TLD-500.

4. Conclusions

In the present work a polycrystalline sample of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor was successfully synthesized using a modified solid-state diffusion method. PL emission spectra of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ phosphor showed the strong prominent peak at 544 nm corresponding to $^5\text{D}_4$ to $^7\text{F}_5$ transition of Tb^{3+} ion. OSL sensitivity of $\text{Li}_3\text{PO}_4:\text{Tb}^{3+}$ was 0.5 times that of $\alpha\text{-Al}_2\text{O}_3:\text{C}$ and OSL decay curve consists of three components with photoionization cross-sections were 0.44×10^{-17} , 3.09×10^{-17} and $23 \times 10^{-17} \text{ cm}^2$. TL glow curve peaks appeared at 143 and 260°C and TL sensitivity was about 1.2 times that of TLD-500. In OSL mode the dose response was linear (0.4–12 Gy) and fading was 27% in 4200 min, after which the OSL signal stabilized. MDD was found to be 67.42 μGy . Effective atomic number Z_{eff} (~ 10.6) of prepared phosphors is equivalent to that of human tissue ($Z_{\text{eff}} = 7.4$) and the phosphor shows excellent dosimetric properties such as sensitivity, dose linearity, reusability and fading. Hence this phosphor is used for dose measurement in radiation dosimetry.

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