

Rare earth Ce^{3+} , Dy^{3+} activated Li_2BPO_5 phosphors for lyoluminescence dosimetry

S P Puppalwar, S J Dhoble*¹ & Animesh Kumar²

Kamla Nehru College, Sakkardara Square, Nagpur 440 009, India

¹Department of Physics, RT M Nagpur University, Nagpur 440 033, India

²National Environmental Engineering Research Institute, Nagpur 440 020, India

*E-mail: sjdhoble@rediffmail.com

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Rare earth Ce and Dy doped polycrystalline Li_2BPO_5 phosphors were prepared by high temperature solid state reaction. Photoluminescence emission spectra of the phosphor suggest the presence of Ce^{3+} ions in $Li_2BPO_5:Ce$ and Dy^{3+} ions in $Li_2BPO_5:Dy$ lattice sites. The prepared phosphors were characterized by the X-ray powder diffraction and photoluminescence techniques. The PL emission spectrum of Dy^{3+} ion under 348 nm excitation was observed at 481 nm (blue) due to ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transitions and 576 nm (yellow) emission due to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transitions in prepared borophosphate phosphor. The PL emission spectra of Ce^{3+} ion was observed at 346 nm in ultraviolet region by 235 nm excitation. In this paper, PL and lyoluminescence (LL) characteristics of $Li_2BPO_5:Ce$, Dy borophosphate phosphors have been reported. The LL results show the LL emission of $Li_2BPO_5:Ce^{3+}$, Dy^{3+} phosphor in blue-yellow region of the spectrum and linear response curve of LL with gamma rays exposure up to 3.5 kGy. These LL characteristics of $Li_2BPO_5:Ce^{3+}$, Dy^{3+} phosphor may be useful for high radiation dose using LL technique.

Keywords: Li_2BPO_5 , Phosphors, XRD, Photoluminescence, Lyoluminescence

1 Introduction

The effects of ionizing radiation in qualitative and quantitative terms have become very important in the present day context due to the influence of nuclear technology in various areas that include radiation medicine, radiotherapy, food processing, radiation based polymerization and non-destructive testing techniques using radiography. Dependable radiation dosimetric procedures need to be developed over wide range of dose levels.

Lyoluminescence (LL) is the phenomenon of light emission when certain substances irradiated with ionizing radiation, are dissolved in a suitable solvent and has been investigated by number of researchers for use in dosimetry application^{1,2}. Several organic and inorganic materials possess the LL property and the most widely studied LL material has been alkali halide³, sacrides⁴ and aminoacid⁵. With inorganic materials such as alkali halide, the reaction of trapped electrons from F centers is responsible for the light emission. In the case of some organic materials, trapped free radicals are involved in the process of LL.

Alkaline earth sulphates activated with rare earth ions are known as phosphors for use in

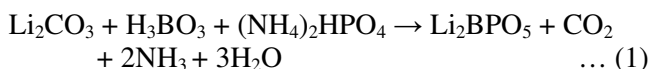
thermoluminescence dosimetry, imagine plates and thin film electroluminescence display^{6,7}. Alkaline earth sulphate activated with Eu^{3+} and Sm^{3+} ions is promising candidate for optical information storage. Gong *et al.*⁸ have reported the effect of gamma ray irradiation on the crystal structure and photoluminescence (PL) of alkaline earth sulphates nanocrystalline activated with Eu^{3+} and Sm^{3+} ions. They stated that PL quenching in alkaline earth sulphates nanocrystalline materials is due to dipole-quadrupole interaction. Sulphate based phosphors are known to be good thermoluminescence (TL) materials. $CaSO_4:Dy$ (Ref. 9) is one of the phosphors, which is being increasingly utilized in radiation dosimetry for low dose measurements because of its favourable properties. In recent years, several sulphate-based phosphors¹⁰⁻¹³, that possess properties useful for thermoluminescence dosimetry (TLD) of ionizing radiations, have been reported. Recently, phosphate based phosphors show potential application as a lamp phosphors and TLD materials¹⁴⁻²¹. Many TL materials also show LL property²². In order to investigate new materials for LL dosimetry of ionizing radiation, we have chosen phosphate-based lamp phosphors and TL phosphors for LL studies. In

the present paper, LL results in $\text{Li}_2\text{BPO}_5\text{:Dy}$; $\text{Li}_2\text{BPO}_5\text{:Ce}$ and $\text{Li}_2\text{BPO}_5\text{:Ce}$, Dy phosphors have been studied.

Here we concentrate on the preparation of borophosphate-based Dy and Ce activated Li_2BPO_5 and Dy co-doped $\text{Li}_2\text{BPO}_5\text{:Ce}$ phosphors by the modified solid state method. The synthesis, PL and LL characterization of Dy and Ce activated Li_2BPO_5 phosphors have been reported in this paper.

2 Experimental Details

The phosphors $\text{Li}_2\text{BPO}_5\text{:Dy}$; $\text{Li}_2\text{BPO}_5\text{:Ce}$ and Li_2BPO_5 , Dy were first time prepared modified solid state reaction at high temperature using high purity Li_2CO_3 , $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$, H_3BO_3 , $(\text{NH}_4)_2\text{HPO}_4$ and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ as initial raw materials. Each initial raw material was weighed using the high precision (0.0001 g) digital monopan balance. By taking together the raw materials in stoichiometric ratio, they were crushed to mix well and preheated to 500°C in the furnace (air) for 2 h followed by cooling to room temperature to obtain the porous floppy white crystalline powder product and crushed again. It was then heated at 1100°C in weak reducing atmosphere for 2 h and slowly cooled down to the room temperature. The samples were obtained by washing repeatedly with double deionized water and drying at 120°C . Then dried samples were slowly cooled at room temperature. The resultant polycrystalline powder was crushed to fine particles in a crucible. This powder was used as a phosphor in further study. A similar procedure was used for the preparation of $\text{Li}_2\text{BPO}_5\text{:Ce}$ and $\text{Li}_2\text{BPO}_5\text{:Ce}$, Dy phosphors. The synthesis reaction could be described as follows:



Formation of the compound was confirmed by taking X-ray diffraction (XRD) pattern which was recorded on Philips PAnalytical XPERT-PRO diffractometer. The photoluminescence (PL) emission spectra of the samples were recorded by using a RF-5301PC SHIMADZU Spectrofluorophotometer (RF5301PC). The same amount of sample was used in each case. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. Samples were exposed to gamma rays using ^{60}Co source having the exposure rate of 0.93 kGy h^{-1} . Lyoluminescence was studied with the usual set-up consisting of a lyoluminescence cell, photomultiplier tube (Hamamatsu 981B), amplifier and recorder.

Dilute H_2SO_4 is used as a solvent. In all the measurement, 2 mg of sample and 1ml of solvent was used. LL emission spectra of the samples were recorded by inserting filters between the tube containing sample and photomultiplier tube.

3 Results and Discussion

Figure 1 shows the first time X-ray diffraction pattern of Li_2BPO_5 phosphor. In standard JCPDS data, there is no XRD pattern of Li_2BPO_5 phosphor for comparison. The XRD pattern did not indicate the presence of the constituents carbonates and traces of ammonia gas, which is indirect evidence of the formation of the desired compound. These results indicate that the final product was formed in homogeneous form.

3.1 PL in $\text{Li}_2\text{BPO}_5\text{:Dy}^{3+}$

The photoluminescence emission spectrum of Dy^{3+} doped Li_2BPO_5 phosphor, obtained under the excitation wavelengths between 300 nm to 400 nm is shown in Fig. 2. The optical spectra taken for the Dy^{3+} ion at 348 nm excitation, showed emission at 481 nm (blue) and 576 nm (yellow). The blue emission band is typical emission of Dy^{3+} ion corresponding to

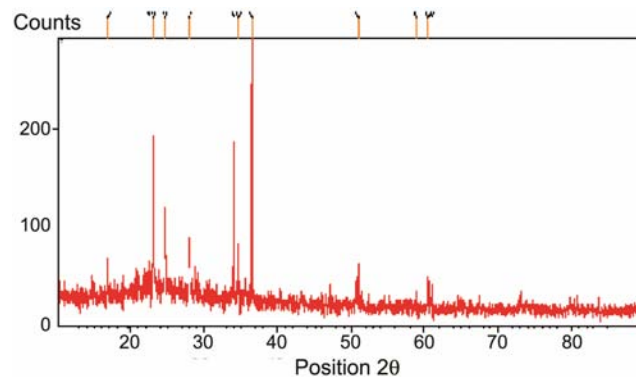


Fig. 1 — X-ray diffraction (XRD) pattern of Li_2BPO_5 phosphor

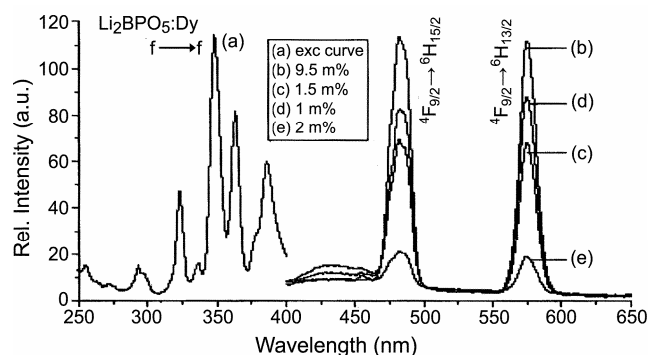


Fig. 2 — PL emission spectra of $\text{Li}_2\text{BPO}_5\text{:Dy}$, emission peak at 576 nm was monitored at 348 nm excitation

${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ transition and yellow emission is corresponding to ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition²³ as shown in Fig. 2.

The optical properties of the material are often influenced by the structure of the matrix and synthesis technique. It is known that Dy³⁺ shows intense peaks at 481 nm due to fluorescent transitions of ${}^4F_{9/2} \rightarrow {}^6H_{15/2}$ due to magnetic dipole and at 576 nm due to fluorescent transitions of ${}^4F_{9/2} \rightarrow {}^6H_{13/2}$ due to electric dipole moment of Dy³⁺ ion, respectively, when Dy³⁺ ions are located at low-symmetry sites with no inversion centers²⁴. Thus, the yellow and blue ratio known as the asymmetry ratio of Dy³⁺ ion varies while locating in different host lattices. With increasing the calcining temperature, the yellow and blue ratio increases due to the change of the local site symmetry around Dy³⁺ ion. The maximum intensity of Dy³⁺ is observed at 0.5 m% in the host lattice. Variation in PL intensity with different concentration of Dy ion is shown in Fig. 2.

The entire characteristics indicate that Li₂BPO₅:Dy phosphor is a good candidate for LL dosimetry applications and in addition to that Li₂BPO₅:Dy shows the switching characteristics by modified solid state synthesis route.

The variation of PL emission intensity with concentration is shown in Table 1 and corresponding graph is shown in Fig. 3.

3.2 PL in Li₂BPO₅:Ce³⁺

The PL emission spectra of Ce³⁺ ions in Li₂BPO₅:Ce phosphor with different concentrations

Table 1 — Variation in PL intensity with conc of Dy in Li₂BPO₅:Dy

Phosphors	PL emission at 348 nm ext.	Intensity (arb.unit)
Li ₂ BPO ₅ :Dy, 0.5% _m	481, 576	112, 112
Li ₂ BPO ₅ :Dy, 1 % _m	481, 576	81, 86
Li ₂ BPO ₅ :Dy, 1.5% _m	481, 576	63, 66
Li ₂ BPO ₅ :Dy, 2 % _m	481, 576	18, 20

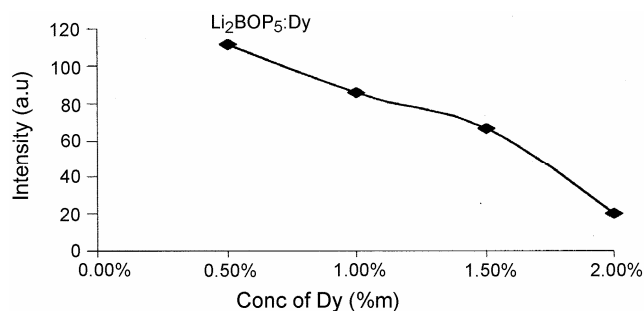


Fig. 3 — Variation in PL intensity with conc of Dy in Li₂BPO₅:Dy

under the excitation 235 nm wavelength of light is shown in Fig. 4. Peaks are observed at 346 nm, which are assigned to the 5d-4f transition of Ce³⁺ ion. The concentration of Ce³⁺ ion increases the corresponding intensity of peaks at higher concentration and for higher concentrations more than 5m%, PL intensity goes on decreasing. This indicates a change of the surrounding of the Ce³⁺ ions at higher concentration in the Li₂BPO₅:Ce lattice.

The observed variations of PL emission intensities may be cross relaxation between Ce³⁺ ions in the case of heavy concentration of Ce³⁺. The PL intensity increases with an increase in Ce³⁺ concentration up to 5 mol%, beyond which, the PL intensity tends to quench. It is also noticed that the peak positions of the emission bands have not changed. This phosphor is emitting in the UV region. The variation of PL emission intensity with concentration is presented in Table 2 and is shown in Fig. 5.

3.3 Energy transfer in Li₂BPO₅ (Ce³⁺ → Dy³⁺)

A method that can be used to demonstrate the occurrence of energy transfer is to measure the excitation spectrum of the emission from the activator. If the excitation spectrum of the activator emission shows the excitation bands of the sensitizer in addition to those of the activator, it indicates energy transfer from the sensitizer to the activator since the excitation energy is absorbed by the

Table 2 — Variation of intensity with conc of Ce in Li₂BPO₅:Ce

Phosphors	PL emission at 235 nm ext.	Intensity (arb.unit)
Li ₂ BPO ₅ :Ce, 1% _m	346	245
Li ₂ BPO ₅ :Ce, 2 % _m	346	544
Li ₂ BPO ₅ :Ce, 5% _m	346	698
Li ₂ BPO ₅ :Ce, 10% _m	346	385

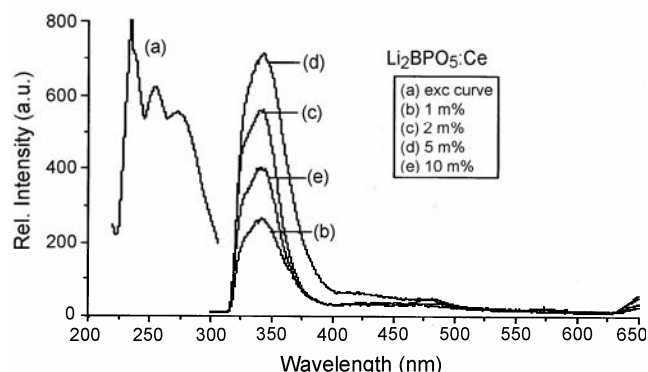


Fig. 4 — PL emission spectrum of Li₂BPO₅:Ce phosphor, emission peak at 346 nm was monitored at 235 nm excitation

sensitizer and emitted by the activator. Much work has been done on the energy transfer from Ce^{3+} to different activator ions in different host lattice²⁵⁻²⁷. The transfer of energy from Ce^{3+} to Dy^{3+} ions in $Li_2BPO_5:Ce, Dy$ lattice brings Ce^{3+} to the ground state and Dy^{3+} to the excited state. The emission in Dy^{3+} comes via a non-radiative transition to the $^4F_{9/2}$ level followed by radiative transitions to $^6H_{15/2}$ and $^6H_{13/2}$ level, which is shown in Fig. 6.

Figure 7 shows PL emission of $Li_2BPO_5:Dy, Li_2BPO_5:Ce$ and $Li_2BPO_5:Ce, Dy$ phosphors. In the PL emission spectra of $Li_2BPO_5:Ce, Dy$ for 301 nm excitation, three peaks are obtained one at around 345 nm and other two at around 484 nm and 576 nm. The first peak is characteristics emission arising from 5d-4f transition of the Ce^{3+} . Characteristic Dy^{3+} emission in the form of bands around 484 nm and 576 nm corresponding to the transitions to $^4F_{9/2} \rightarrow ^6H_{15/2}$ and $^4F_{9/2} \rightarrow ^6H_{13/2}$, respectively are seen in all cases. Fig. 7 shows that when $Li_2BPO_5:Ce$ 5 mole%, Dy phosphor is excited at 301 nm, the maximum PL emission intensity of $Li_2BPO_5:Ce$ 5 mole% was

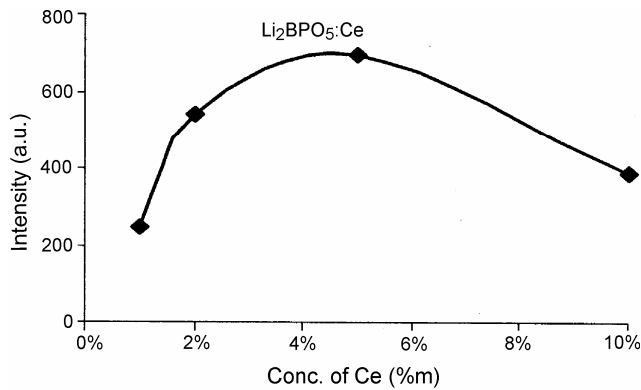


Fig. 5 — Variation of intensity with conc. of Ce in $Li_2BPO_5:Ce$

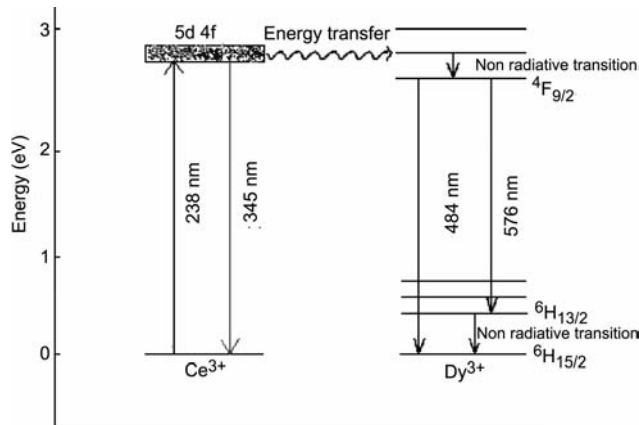


Fig. 6 — Schematic energy level diagram showing energy transfer in $Li_2BPO_5:Ce, Dy$

observed for 0.5 mole % concentration of Dy^{3+} ions at 345 nm in UV range, 484 nm in blue range and 576 nm in yellow range. This indicates that the lattice $Li_2BPO_5:Ce$ 5 mole %, Dy is more suitable for the concentration of 0.5 m % of Dy^{3+} ions which shows the energy transfer of Ce^{3+} ions to Dy^{3+} ions.

It is seen that the PL intensity has increased considerably. Origin of this increase can be understood by studying the excitation spectra as shown in Fig. 8. Excitation of Dy^{3+} in $Li_2BPO_5:Dy$ is shown in the form of narrow bands between 320 nm to 400 nm corresponding to transitions within the 4f shell. In $Li_2BPO_5:Ce, Dy$, there are additional bands around 238 nm and 301 nm. These are characteristics of Ce^{3+} excitation. The Ce^{3+} emission is around 345 nm which overlaps rather well with the Dy^{3+} excitation. Ce^{3+} thus sensitizes the Dy^{3+} emission in Li_2BPO_5 . The Ce^{3+} ions are used as sensitizers and Dy^{3+} ions as activators, depending on the splitting of 5d excited levels by the crystal field symmetry.

Curve(a) of Fig. 8 shows the excitation spectra of $Li_2BPO_5:Dy$ phosphor monitor at 576 nm of Dy^{3+} ion.

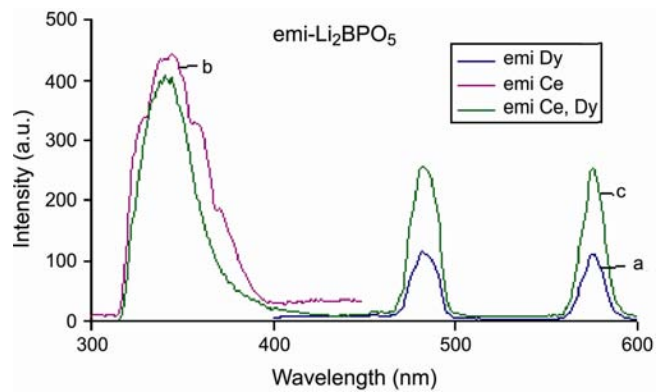


Fig. 7 — PL emission spectra for various Li_2BPO_5 phosphors. (a) $Li_2BPO_5:Dy, \lambda_{ext} = 348$ nm, (b) $Li_2BPO_5:Ce, \lambda_{ext} = 238$ nm and (c) $Li_2BPO_5:Ce, Dy, \lambda_{ext} = 301$ nm

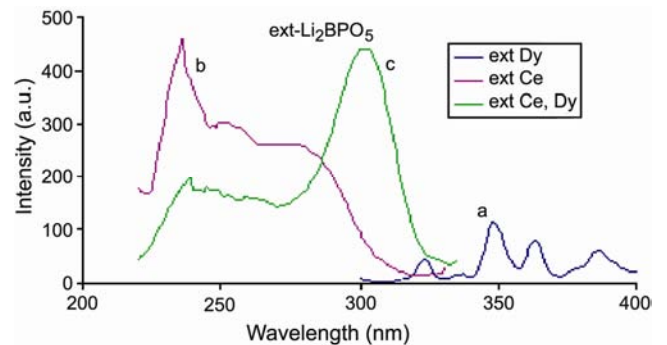


Fig. 8 — PL excitation spectra for various Li_2BPO_5 phosphors. (a) $Li_2BPO_5:Dy, \lambda_{emi} = 576$ nm, (b) $Li_2BPO_5:Ce, \lambda_{emi} = 345$ nm and (c) $Li_2BPO_5:Ce, Dy, \lambda_{emi} = 484$ nm

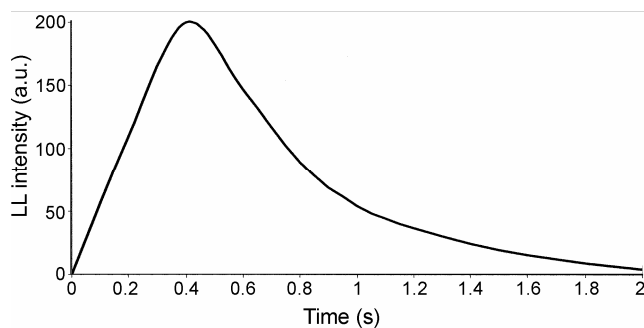
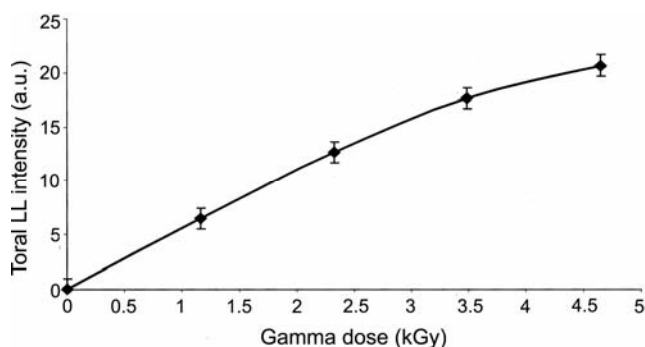
Table 3 — Variation of PL emission intensities of different phosphors

Phosphors	PL emission (nm)	Intensity (arb.unit)
Li ₂ BPO ₅ :Dy, 0.5 mole %	484, 576, ext = 348 nm	110, 105
Li ₂ BPO ₅ :Ce, 5 mole %	346, ext = 238 nm	437
Li ₂ BPO ₅ :Ce, Dy, 5 mole %, 0.5mole %	345, 484, 576, ext = 301 nm	393, 249, 249

This spectrum shows the Dy³⁺ excitation peak at 346 nm, due to 576 nm. Curve (b) shows the Ce³⁺ excitation of Li₂BPO₅:Ce³⁺ phosphor, the emission peak of Ce³⁺ ion is observed at 238 nm. Curve (c) shows the excitation of Li₂BPO₅:Ce, Dy phosphor at monitor at 464 nm of Dy³⁺ ion. In this case, the excitation peak is well matched with the emission peak of Ce³⁺ ion. Hence, energy transfer possibility from Ce³⁺ ion to Dy³⁺ ion is more possible in the Li₂BPO₅ host. The transfer of excitation energy from Ce³⁺ to Dy³⁺ ions brings Ce³⁺ to the ground state and Dy³⁺ to the excited state. In case of PL, UV light (238 nm) cannot be absorbed by Dy³⁺, even the absorption between 320 nm and 400 nm is weak as it is due to parity-forbidden within the 4f shell. Absorption of UV light is much more efficient for Ce³⁺ ions. The energy is then transferred to Dy³⁺ ions and hence sensitization of PL occurs. The variation of PL emission intensity of Li₂BPO₅:Dy, Li₂BPO₅:Ce and Li₂BPO₅:Ce, Dy is shown in Table 3 at different excitations.

3.4 Lyoluminescence characterization of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor

Figure 9 shows typical LL glow curve of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor. The shape of LL glow curve is broad due to prepared phosphor's dissolution rate in dilute H₂SO₄ solvent is less; therefore, during dissolution LL intensity after LL peak slowly decreases with increasing time. This glow curve indicates that only single peak is observed, due to one kind of defect centre developed during gamma rays irradiation and they are released during dissolution in dilute H₂SO₄ solvent. Figure 10 shows the response curve of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor for LL peak intensity versus gamma rays dose. When the concentration of Dy is increased in the sample, initially the number of luminescent centers increases, thereby increasing the LL intensities. However, the intensity cannot be expected to increase indefinitely with the concentration, since the rate of formation of active luminescent centers by capturing the holes during irradiation might be fading rapidly and

Fig. 9 — Typical LL glow curve of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphorFig. 10 — Response curve of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor for LL peak intensity versus gamma rays dose

concentration quenching occurs. The LL glow peak intensity linearly increasing with gamma rays exposures up to 3.5 kGy and above this exposure saturation is observed due to aggregation of defect centre. The increase in LL intensities with increasing gamma rays dose may be due to increase in the density of defect centers during gamma rays irradiation.

Figure 7 shows the PL emission spectra of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor. Dy³⁺ emission peaks are observed at 486 nm and 546 nm which shows the well known emission of Dy³⁺ ion corresponding to blue emission of ⁴F_{9/2} → ⁶H_{15/2} transition and yellow emission is corresponding to ⁴F_{9/2} → ⁶H_{13/2} transition. This emission from Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor in the blue-yellow region of the spectrum, which is sensitive for common PMT generally used in LL detector. LL emission of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor in blue-yellow region of the spectrum and linear response curve of LL with gamma rays up to 3.5 kGy, these are LL characteristics of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor, it may be useful for high radiation dose measurement using LL technique.

Phosphates under gamma irradiation are known to produce various defect centers such as PO₄⁻, O₃⁻, O₂⁻ etc., only with trapped electron centers. On dissolving

such phosphates in dilute H₂SO₄ solvent, the LL observed due to release of trapped energy during dissolution as per the mechanism suggested by Arinkar *et al.*²⁸,



where X = PO₄⁻, O₃⁻, O₂⁻ etc.

It is possible that steps in Eqs (2) and (3) occur together without the intermediate state X^{*}_{aq}. A similar mechanism was also suggested by Ahnstrom²⁹.

4 Conclusions

Rare earth doped polycrystalline Li₂BPO₅:Dy and Li₂BPO₅:Ce phosphors were prepared by high temperature modified solid state reaction. The blue emission band is typical emission of Dy³⁺ ion corresponding to ⁴F_{9/2} → ⁶H_{15/2} transition and yellow emission is corresponding to ⁴F_{9/2} → ⁶H_{13/2} transition. The entire characteristics indicate that Li₂BPO₅:Dy phosphor is a good candidate for LL dosimetry applications. The Ce³⁺ emission is around 345 nm which overlaps rather well with the Dy³⁺ excitation. Ce³⁺ thus sensitizes the Dy³⁺ emission in Li₂BPO₅ host. Increased PL due to Ce addition is explained as sensitization and it may be useful for LL dosimetry application. LL emission of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor in blue-yellow region of the spectrum and linear response curve of LL with gamma rays up to 3.5 kGy, these LL characteristics of Li₂BPO₅:Ce³⁺, Dy³⁺ phosphor may be useful for high radiation dose measurement using LL technique.

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