

Absorption, photoluminescence and thermoluminescence studies of γ - irradiated pure and Eu doped LiF phosphors

Satinder Kumar^{1,3*}, Arvind K. Gathania², Ankush Vij¹, A. K. Sharma⁴, R. Dogra⁴, S. P. Lochab⁵ and Ravi Kumar^{1,4}

¹Center for Material Science & Engineering, National Institute of Technology, Hamirpur, India

²Department of Physics, National Institute of Technology, Hamirpur, India

³Department of Physics, Government College, Hamirpur, India

⁴Beant College of Engineering & Technology, Gurdaspur Punjab, India

⁵Health Physics Division, Inter University Accelerator Centre, Aruna Asaf Ali Marg, New Delhi, India

*Corresponding author. E-mail. sksharma1564@gmail.com

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ABSTRACT

We synthesized single phase pure and Eu doped LiF having micro-cubical morphology by modified co-precipitation method. The complete solid solubility of Eu in LiF has been observed up to 0.04 mol% and afterwards phase segregation started. The absorption spectra of pure and Eu doped LiF revealed the formation of γ -irradiation induced and dose dependent F, M and F₃ color centers at room temperature. The concentrations of both F and M color centers calculated by using Smakula's formula, increased almost ten times for γ - irradiated Eu doped LiF in comparison to γ -irradiated pure LiF. Non irradiated LiF doesn't show any photoluminescence (PL) signal. However, γ -irradiated LiF showed broad emission peak around 681 nm, which is due to the excitation of F₂ color centers. The Eu doped LiF samples exhibit PL emission peaks at 577, 591, 612, 648 and 690-698 nm correspond to Eu³⁺ ion transitions from ⁵D₀ to ⁷F_J (J=0,1,2,3,4). The γ -irradiated Eu doped LiF show simultaneous PL emission spectrum of Eu³⁺ ions and radiation induced F₂ color centers. Thermoluminescence (TL) glow curves of γ - irradiated LiF and LiF: Eu (0.03 mol %) samples were also investigated and various trapping parameters for were evaluated by using Chen's peak shape method. Copyright © 2015 VBRI Press.

Keywords: Color centers; photoluminescence; thermoluminescence; irradiation

Introduction

Lithium fluoride (LiF), a member of alkali halides, possesses unique physical and optical properties. It is almost non hygroscopic, relatively harder and has effective atomic number ($Z_{\text{eff}}=8.04$), close to its value for biological tissues (7.4) and its response slightly varies with photon energy, hence also known as tissues equivalent material. The formation of stable color centers (CCs) in LiF were investigated because of their peculiar active properties, which find many applications in the fabrication of broad band lasers and amplifiers in optical domain operating at room temperature [1].

In recent years, much interest has been devoted to propose and investigate various synthesis techniques and irradiation methods for the development of miniaturized and efficient light emitting devices based on CCs in LiF [1-4]. The optical properties of LiF can be tuned by doping it with suitable activators such as rare earth ions (RE). The rare earth ions are generally characterized by partially filled

4f shell which is well shielded by 5s² and 5p⁶ orbitals. The rare earth ions activated phosphors show narrow to visible line spectra which subsequently result into both high efficiency and high intensity [5-7]. Among different RE ions, europium ion (Eu³⁺) has attracted wide attention. The emission lines due to Eu³⁺ ions are extending from visible to near infrared region, enable to ascertain the microscopic symmetry around Eu³⁺ sites thus making it an ideal experimental probe to study the crystalline environment [8-11]. The effect of incorporating rare earth impurities into host lattice of LiF involves several considerations which, include whether interstitial or substitution sites are occupied, the clustering of impurities, possible precipitations of the impurities for the formation of new undesired phases and question of charge compensation of impurities ions [12]. Many researchers have studied LiF based bulk phosphors synthesized by solid state method [13, 14]. However, optical properties of pure and singly Eu³⁺ doped LiF micro-cubes are rarely reported to the best of our knowledge. The effect of γ -irradiation on the optical

properties of pure and Eu doped LiF microcubes have also been investigated. Thermoluminescence (TL) is an appropriate and experimental technique used for measuring absorbed dose as well as to investigate the effect of impurities and defects formation in the crystals [15, 16]. TL glow curves are used to determine the trapping parameters and its integral is proportional to the radiation dose absorbed by the irradiated sample. The position, shape and intensities of the glow peaks are related to the properties of traps responsible for the TL, therefore it becomes important to evaluate the trapping parameters by using some suitable method.

In the present work, we have successfully synthesized pure and Eu doped LiF micro-cubes via modified co-precipitation method by increasing reaction time and maintaining constant pH value at 8.00. The optical absorption and photoluminescence spectra of pure and Eu doped LiF microcubes were investigated before and after γ -irradiation from ^{60}Co source. The thermoluminescence (TL) studies of samples at various irradiation doses has also been conducted and analyzed to calculate TL parameters such as symmetry factor μ_g , activation energy, frequency factor and order of kinetics using Chen's peak shape method [17].

Experimental

Lithium fluoride (LiF) micro cubes were synthesized by using modified co-precipitation method by controlling reaction time and constant pH 8.00 [18]. The LiCl , NH_4F , $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ and NH_4OH solution (AR grade) were used as precursor materials in the synthesis. In this method, 1M homogeneous solution of LiCl was prepared in 100 ml deionized water by using magnetic stirrer. It was mixed drop wise at constant rate of 2.5 ml/minute into a beaker containing 1M solution of NH_4F placed on magnetic stirrer. For better homogeneity, the solution was continuously stirred using magnetic stirrer till the completion of reaction. The pH of the solution was maintained at 8.00 throughout by adding required amount of NH_4OH solution. The as-grown precipitates were aged for 6 hours. The undesired impurities in these as-grown precipitates were removed on washing five times with deionized water. The precipitates so formed were dried in air at 50°C for 24 hours. The final product in its powdered form was further annealed at 200°C for 2 hour in a furnace then kept in air tight glass tube for future characterization. In the synthesis of Eu doped LiF samples, homogeneous aqueous solutions of $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ of different molar concentrations from 0.01 to 0.05 mol% were prepared in deionized water and mixed stepwise into 1M solution of LiCl . The mixed solution of LiCl and $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ was poured stepwise into 1M solution of NH_4F and repeated the already stated procedure to obtain Eu doped LiF samples of required concentration.

The structural characterization was performed by X-ray diffraction (XRD) in the θ - 2θ mode using $\text{Cu K}\alpha$ line ($1.54\text{\AA}$) on X'Pert PRO PANalytical Diffractometer operated at 40 kV and 30 mA current. The field emission scanning electron microscope from FEI Quanta FEG-400 was employed to study the surface morphology of samples. Prior to FESEM experiment, a thin layer of gold was coated on samples to prevent their surface charging. The elemental analysis of the powder samples was also

confirmed by energy dispersive spectroscopy (EDS) using Bruker Nano X-flash detector 5030 attached with FESEM. Pure and Eu doped LiF samples were irradiated at various doses of γ -rays from ^{60}Co source by using BRIT Gamma Chamber 1200 having effective dose rate 5.574 kGy/hour . Optical absorption spectra of samples were recorded on Shimadzu UV-VIS 2700 spectrophotometer in the range 200-800 nm at a wavelength resolution of 2 nm. The micro-photoluminescence (PL) emission spectra were recorded on Renishaw Invia Raman Microscope equipped with He-Cd laser (325 nm line) as a source of excitation. TL data of γ -irradiated samples at various doses were acquired at constant heating rate 5 K/sec in temperature range 325 K to 625 K by using PC driven Harshaw 3500 TLD reader. In each TL measurement, 5mg of powder was poured onto the planchet as a layer through a vibrating dispenser by assuming that temperature distribution within sample remained uniform throughout the measurements.

Results and discussion

The synthesized pure and Eu doped LiF microcubes were structurally characterized using x-ray diffraction (XRD) technique. Fig. 1 shows the XRD pattern of pure and Eu doped LiF microcubes. In pure LiF, the XRD peaks appearing at $2\theta = 38.66^\circ$, 45.04° , 65.51° & 78.76° were neatly indexed with standard data available in JCPDS file No. (4-857) which corresponds to (111), (200), (220) and (311) planes respectively. The absence of any additional XRD peak confirmed the single phase cubic structure. Further Eu doped LiF samples were also exhibiting similar single phase cubic structure up to 0.04 mol% concentration of Eu in LiF. However, the secondary phase was observed at 0.05 mol %. Thus we have restricted our studies on single phase samples.

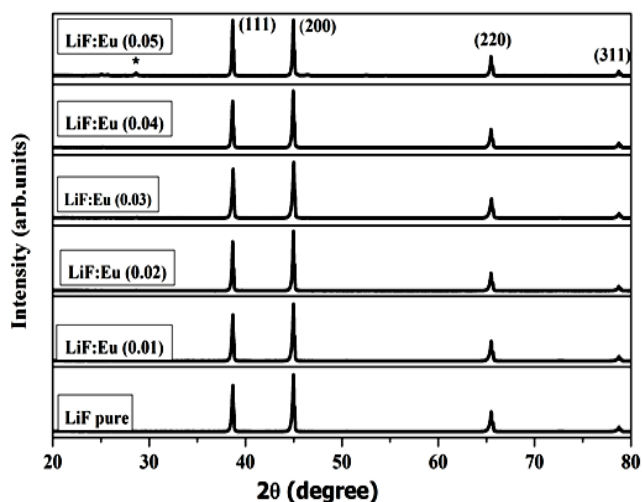


Fig. 1. XRD pattern of pure and Eu (0.01-0.05 mol %) doped LiF at room temperature. (*) indicates the secondary phase).

The calculated lattice parameter for LiF is $4.029\text{\AA}$, while lattice parameters for x mol% ($x = 0.01, 0.02, 0.03$ & 0.04) Eu doped LiF are $4.030\text{\AA}$, $4.031\text{\AA}$, $4.032\text{\AA}$, and $4.041\text{\AA}$ respectively. The increase in lattice parameter revealed lattice expansion on doping LiF with Eu. This lattice expansion may be because of either the dopant atoms occupying the interstitial positions or the atoms of host

lattice being replaced by the dopant of bigger atomic radii. The average crystallite sizes of the samples were calculated using well known Debye Scherrer equation [19].

$$d = \frac{0.89\lambda}{\beta \cos \theta} \quad \dots\dots\dots (1)$$

where d is the average crystallite size, λ is the wavelength of $\text{Cu K}\alpha$ ($1.54\text{\AA}$) radiation, β is the full width at half maximum (FWHM) in radians and θ is the Bragg diffraction angle. The average crystallite sizes were calculated to be in the range 35 - 57 nm.

The surface morphology of pure and Eu doped LiF samples was investigated by using field emission scanning electron microscopy (FESEM) and results are depicted in **Fig. 2(a)**. These results clearly show the cubical morphology of the samples. The electron dispersive x-ray spectra (EDS) of LiF: Eu (0.03 mol %) sample is also shown in **Fig. 2(b)** which confirmed incorporation of Eu in LiF. Since XRD pattern didn't reveal any Eu based phase segregation up to 0.04 mol% concentration, thus it is quite reasonable to interpret that Eu is doped in the host matrix of LiF.

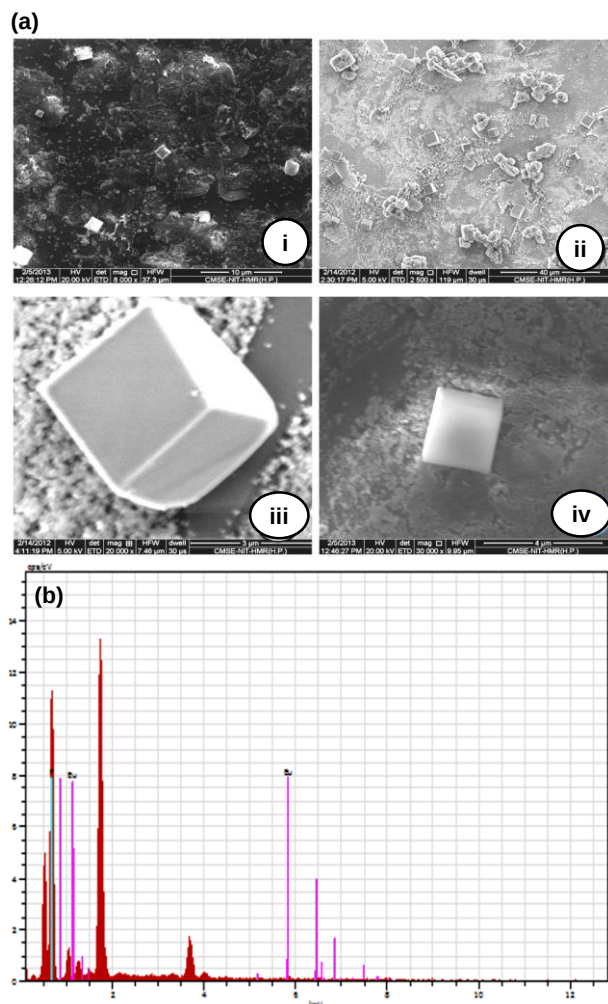


Fig. 2. (a). SEM images of (i) Pure LiF (ii) LiF: Eu (0.01mol %) (iii) LiF: Eu (0.02 mol %) and (iv) LiF: Eu (0.03 mol %), clearly revealing the micro-cubical morphology. (b). EDS of LiF:Eu (0.03 mol %) sample clearly showing peaks correspond to Eu and F. No peak for element Li was observed because of its low atomic number.

UV-Vis studies

Fig. 3 shows the absorption spectrum of pure LiF microcubes which consists of only a single peak at around 224 nm. The 224 nm absorption peak has also been observed upon irradiating LiF by γ - rays in the dose range 100 Gy – 50 kGy. However, another absorption band around 250 nm appeared at 5 kGy, which become pronounced on increasing the γ - irradiation doses. Since LiF is a large band gap (~ 13.6 eV) material [20], so 224 nm absorption peak cannot be assigned to an inter band transition. The discussion about this peak has been presented later. The absorption band around 250 nm in irradiated alkali halides is well known and has been ascribed to F color centre (anionic vacancy occupied by an electron) [21, 22].

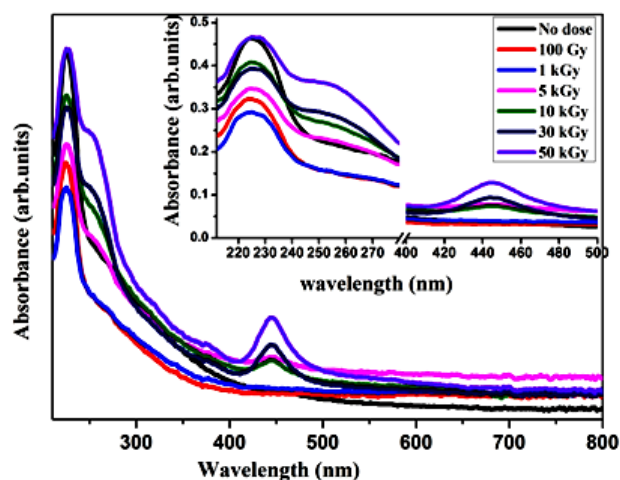


Fig. 3. UV-Vis absorption spectra of γ -irradiated pure LiF at all irradiation doses. The figure also includes absorption spectrum for non irradiated LiF. The M-absorption band at 445 nm started appearing at 10 kGy and continued to improve at higher irradiation.

In addition, an absorption band around 445 nm has been observed at 5 kGy, which become pronounced on increasing the irradiation dose. This band has been assigned to M centre and is formed by overlapping of two kinds of color centers (CCs) namely, F_2 and F_3^+ (two and three anionic vacancies occupied by two electrons respectively) [23]. At high γ -irradiation doses 30 kGy and 50 kGy, a very weak absorption band at 376 nm has also been observed, which is identified as F_3 color center (three anions vacancies occupied by three electrons) [24, 25]. These measurements revealed the formation of γ -rays induced and dose dependent color centers in LiF microcubes at room temperature. It is worth mentioning that Delbecq *et al.* and Klick *et al* have also reported F centre around 250 nm for X-ray exposed LiF crystal, which shifts to 224-220 nm after bleaching F centre with F-light [26-28]. Authors have speculated that if band appearing around 220 nm is not an intrinsic band in LiF, then it may be because electrons released from F-centers were captured by some impurity atoms, or anion vacancies decomposed from F-centers were combined adjacent to the foreign atom sites [29]. The present study in non-irradiated LiF microcubes also exhibit 224 nm band, even without formation of any F centre. It shows that 224 nm band may be intrinsic band in LiF, the origin of which needs further in-depth investigations.

Fig. 4 shows the absorption spectra of single phase Eu (0.01-0.04 mol %) doped LiF microcubes. The prominent absorption peak was observed at 252 nm (F-centre) at all doping concentrations, which shows a slight red-shift in comparison to γ -rays irradiated LiF microcubes while the other absorption peak observed at 222 nm is considerably suppressed and is slightly blue shifted than γ -irradiated LiF. No absorption peak corresponding to M band and F_3 centre has been observed in non-irradiated Eu doped LiF.

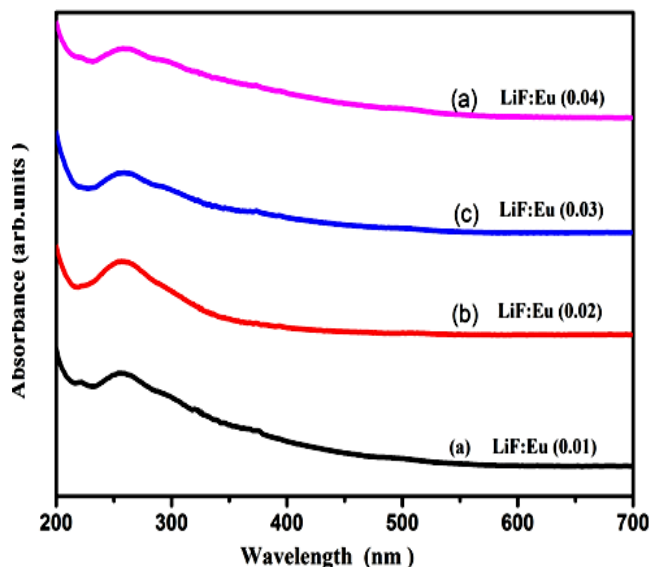


Fig. 4. UV-Vis absorption spectra for non-irradiated x mol % Eu doped LiF, where $x = (0.01, 0.02, 0.03 \text{ and } 0.04)$ marked (a), (b), (c) and (d) respectively which, clearly revealed 252 nm absorption band due to F-color centers.

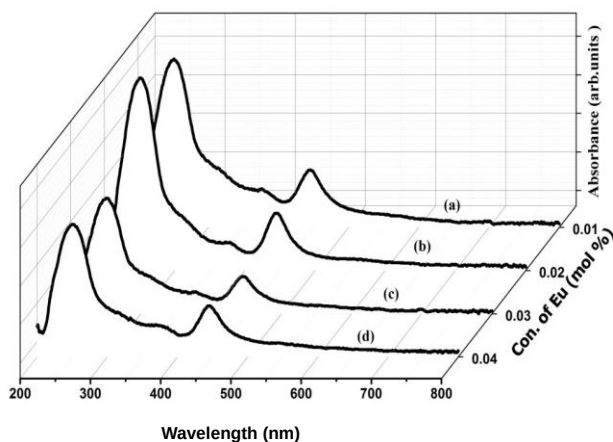


Fig. 5. UV-Vis absorption spectra for x mol % Eu doped LiF, where $x = (0.01, 0.02, 0.03, 0.04)$ marked (a), (b), (c) and (d), respectively, all were irradiated at same 50 kGy dose. For sample LiF: Eu (0.02 mol %), both F (250 nm) and M (445 nm) absorption bands are prominent. A low intensity absorption peak at 376 nm due to F_3 CCs was also observed at all concentrations of Eu in LiF.

The effect of γ -irradiation on single phase Eu doped LiF samples has also been studied. **Fig. 5** shows the UV-VIS absorption spectra of γ -irradiated Eu (0.01-0.04 mol %) doped LiF at 50 kGy irradiation dose. The F- centre at 250 nm and M- centre at 445 nm were observed for all concentrations of Eu in LiF [22]. The γ -irradiated Eu doped LiF samples exhibit both F and M absorption bands at

wavelengths 250 nm and 445 nm respectively, as observed in γ -irradiated LiF micro-cubes.

The intensity of both F and M absorption bands approached their maxima for 0.02 mol% concentration of Eu. Like γ -irradiated pure LiF sample, Eu (0.02 mol %) doped LiF also exhibit dose dependant color centers as shown in **Fig. 6**. The low intensity absorption peak at 376 nm (F_3 CC) also started appearing at dose of 30 kGy, which grew on increasing the irradiation dose.

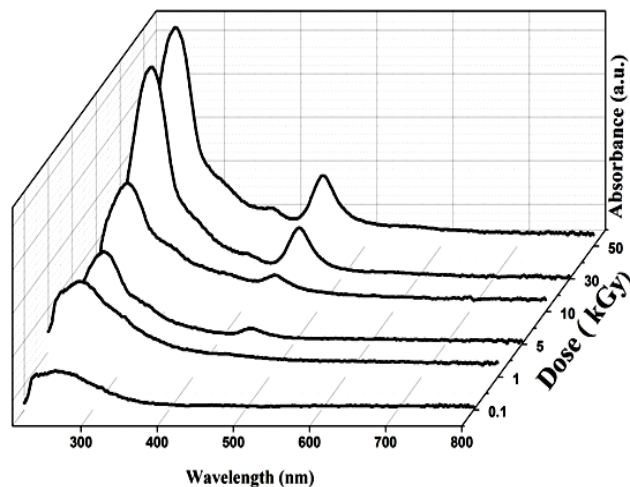


Fig. 6. Absorption spectra of LiF: Eu (0.02 mol %) irradiated at various doses. With the increase in γ -irradiation dose, the intensity of F and M-absorption bands at 250 nm and 445 nm respectively increases.

The absorption spectra of γ -irradiated pure and Eu doped LiF were further analyzed to calculate the concentrations of F and M color centers using Smakula formula modified by Dexter [30].

$$N(\text{cm}^{-3}) = 0.87 \times 10^{17} \frac{n}{(n^2+2)^2} \frac{W(\text{eV})}{f} \alpha_{\text{max}} (\text{cm}^{-1})$$

where W is the full width at half maximum (FWHM) in eV of respective absorption band, n is the refractive index of LiF at wavelength corresponds to absorption peak and f is oscillator strength of optical absorption. Using $f = 0.56$, $n=1.42$ and $f=0.28$, $n=1.396$ [31, 32] for F and M-absorption bands respectively, the concentrations of F and F_2 color centers were calculated. It has been found that, for γ -irradiated samples, concentrations of both F and M color centers increases almost ten times with Eu doping in LiF.

Photoluminescence studies

The photoluminescence (PL) emission spectra of LiF exposed to various irradiation doses were acquired by using 325 nm line of He-Cd laser as an excitation source, which is shown in **Fig. 7**. Pure LiF doesn't show any PL signal as expected, however in γ -irradiated LiF, dose dependant PL signal was observed. At irradiation doses of 100 Gy and 1 KGy, the PL emission intensity is almost negligible and emission spectrum is much similar to that of non-irradiated LiF. It may be attributed for reason that there is no color centre formation at low irradiation doses as described in the earlier section. At higher irradiation doses, a broad emission band at 681 nm was observed which may be attributed to

formation of F_2 (M band) CCs [33]. The PL emission spectrum shows increase in intensity on increasing the irradiation dose. This enhancement in PL intensity may be due to the increase in concentration of F_2 color centers at higher irradiation doses.

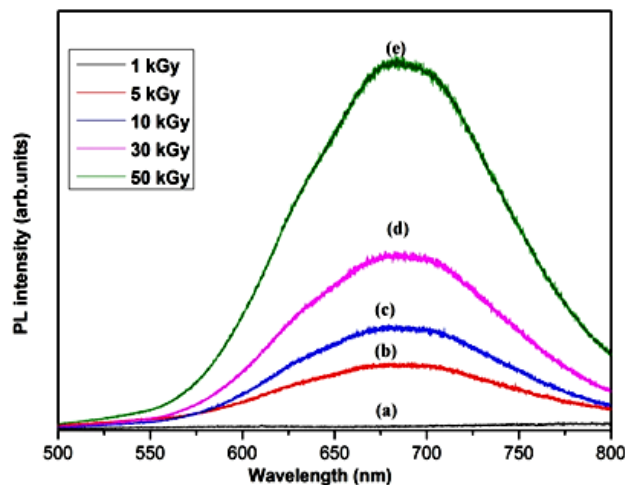


Fig. 7. PL emission spectra of γ – rays irradiated pure LiF at (a) 1 kGy, (b) 5 kGy, (c) 10 kGy, (d) 30 kGy and (e) 50 kGy doses for excitation wavelength of 325 nm. For irradiation dose of 1kGy and lower dose, no PL emission was observed.

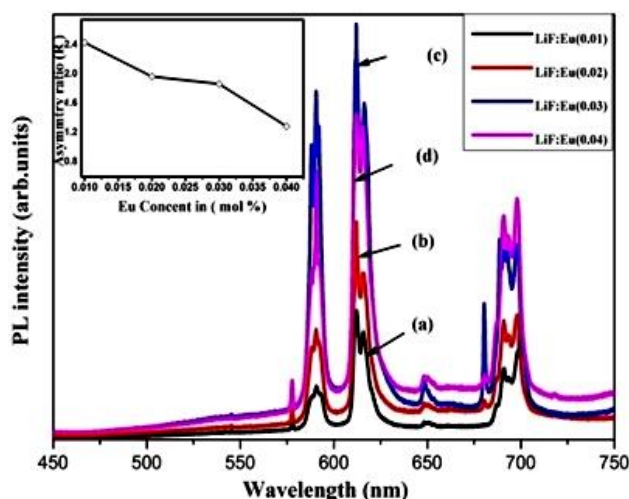


Fig. 8. PL emission spectrum of non- irradiated x mol% Eu doped LiF, where x = (0.01, 0.02, 0.03, 0.04) at 325 nm excitation marked a, b, c and d respectively. The maximum PL emission intensity was observed for LiF: Eu(0.03 mol%) sample. The inset included in figure shows variation of asymmetry ratio vs. Eu^{3+} concentration.

Fig. 8 shows the room temperature PL emission spectra of Eu (0.01-0.04 mol %) doped LiF samples. Several sharp emission peaks at 577, 591, 612, 648 and 690-698 nm were observed [34, 35]. These emission spectra for all doping concentrations are very much similar in terms of positions of observed emission lines due to Eu^{3+} with only difference in their intensities. The maximum PL emission for main transitions at 591 nm and 612 nm was observed for LiF: Eu (0.03mol %). The decrease in intensity for Eu concentration higher than 0.03 mol% in LiF, which may be attributed to concentration quenching phenomenon [36]. It is also known that the valence state of europium Eu^{3+} and Eu^{2+} gives rise to red and bluish luminescence respectively. In case of Eu^{3+}

state, photoluminescence arises within f-f transitions and corresponding emission spectrum comprises sharp emission lines. In solid lattice, it is generally dominated by the $^5D_0 \rightarrow ^7F_J$ transitions. On the other hand, f-d relaxation ($^4f_65d \rightarrow ^4f_7$) is responsible for Eu^{2+} photoluminescence and corresponding emission bands are rather broad [37]. Thus, the observed sharp emission lines appeared in the PL emission spectrum correspond only to Eu^{3+} transitions from $^5D_0$ to ^7F_J level for ($J=0, 1, 2, 3, 4$). This measurement revealed complete absence of Eu^{2+} in LiF crystal lattice. Further, it is well known fact that the orange transition at 591 nm from $^5D_0 \rightarrow ^7F_1$ is a magnetic dipole transition and dominates in the spectrum only if Eu^{3+} ion occupies center of symmetry in the host lattice. The red emission peak at 612 nm from $^5D_0 \rightarrow ^7F_2$ is an electric dipole transition and its PL emission intensity strongly depends on the symmetry of Eu^{3+} environment. This transition will dominate when Eu^{3+} is located in a site without inversion symmetry [38]. The intensity of both emission peaks increases on increasing the Eu^{3+} concentration. The ratio of emission peaks intensity ($^5D_0 \rightarrow ^7F_2$) / ($^5D_0 \rightarrow ^7F_1$), is termed as asymmetry ratio (R) and is a measure of degree of distortion from the inversion symmetry of local surrounding of Eu^{3+} in crystal lattice [39]. In present study, the decrease in asymmetry ratio on increasing the concentration of Eu^{3+} in LiF revealed that Eu^{3+} ions occupy their positions in increasingly symmetric surrounding environment. The variation in the asymmetry ratio as a function of Eu^{3+} concentration has also been presented in the inset of Fig. 8.

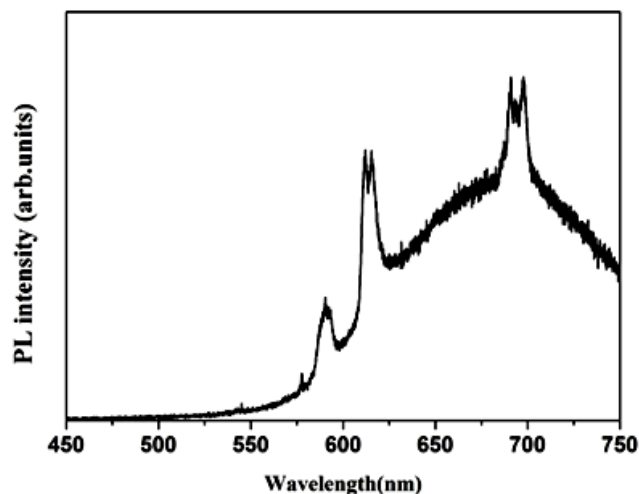


Fig. 9. PL emission spectrum of LiF: Eu (0.03 mol %) irradiated at 30 kGy. In this spectrum, various emission lines of Eu^{3+} are observed embedded in the emission spectrum of pure LiF irradiated at 30 kGy

The PL emission spectrum of γ -irradiated LiF: Eu (0.03 mol %) sample (30 kGy) under similar conditions has also been acquired as shown in Fig. 9. The PL spectrum comprises of several sharp emission lines on a broad curve, which shows that both gamma induced color centres and Eu^{3+} ions are excited together and give their respective emission as discussed earlier. This spectrum may be supposed to form as a result of superimposing two emission spectra i.e. emission spectrum due to Eu^{3+} ions and that of undoped γ - irradiated LiF at 30 kGy doses. The presence of simultaneous PL emission corresponding to Eu^{3+} and F_2 CCs

spanning from yellow to red color in gamma irradiated Eu doped LiF phosphors may be exploited as a promising red emitting phosphor.

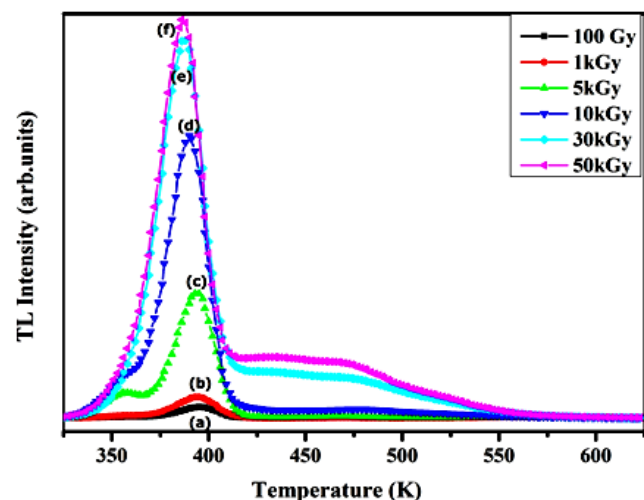


Fig. 10. TL glow curve for γ -irradiated LiF at (a) 100 Gy, (b) 1 kGy, (c) 5 kGy (d) 10 kGy (e) 30 kGy and (f) 50 kGy doses.

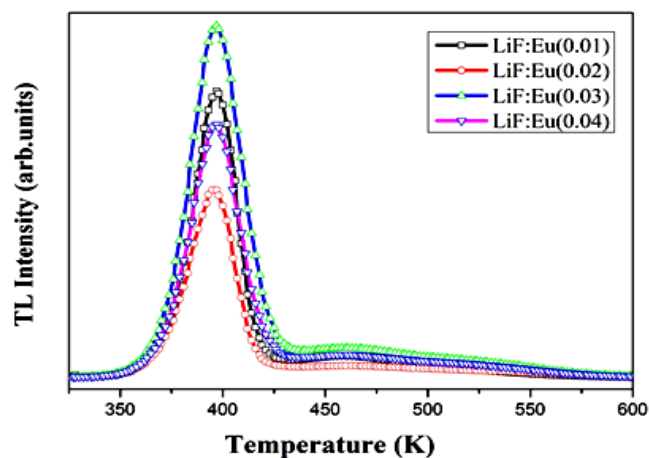


Fig. 11. TL glow curves for x mol %, where $x = (0.01, 0.02, 0.03$ and $0.04)$ Eu doped LiF exposed with γ -rays at 10 kGy dose.

Thermoluminescence studies

Thermoluminescence materials on irradiation exhibit glow curves having one or more glow peak(s), when trapped charges are released upon heating such material. The TL glow curve is a characteristic of the different localized trapping states present in the forbidden band of material. These trapping states or levels are characterized by certain physical parameters like trap depth (E) and frequency factor(s). In order to investigate the nature of such energy traps in γ -irradiated LiF at various irradiation doses in the range 100 Gy to 50 kGy, the typical TL glow curves acquired from 325 K to 625 K and are shown in Fig. 10. For low irradiation doses of 100 Gy and 1 kGy, a single prominent glow peak was observed at 395 K, whose TL intensity increases on increasing the irradiation dose. At irradiation dose of 5 kGy, another less intense glow peak at 357 K appeared which reduced to a shoulder one at 10 kGy dose and ultimately merged with main peak at all higher irradiation doses. The appearance of low temperature glow peak at low irradiation doses revealed the formation of

shallow traps. At 30 kGy irradiation dose, a less intensity broad band around 464 K was observed. The higher TL intensity of this band was observed on increasing the irradiation dose to 50 kGy. It might be attributed to the formation of complex impurity (activator) related defects at higher doses. It is worth mentioning here that low temperature peak(s) and high temperature peak(s) are well separated. It signifies that the low temperature peak and high temperature broad glow band may be related to different kinds of trapping states involved in the TL phenomenon. It can be attributed to fact that at higher irradiation doses, the activator energy levels may also reorganized giving complex TL glow curve. These results seems to be in good agreement with absorption studies where we have observed the formation of M and F₃ color centre for irradiation doses 30 kGy and 50 kGy respectively in LiF.

To study the effect of doping concentration on TL intensity, the single phase Eu doped LiF samples of different concentrations in the range 0.01 to 0.04 mol %, were exposed with γ -rays at fixed dose of 10 kGy. TL glow curves for Eu doped LiF are much similar to pure LiF except a minor shift in the main glow peak as shown in Fig. 11.

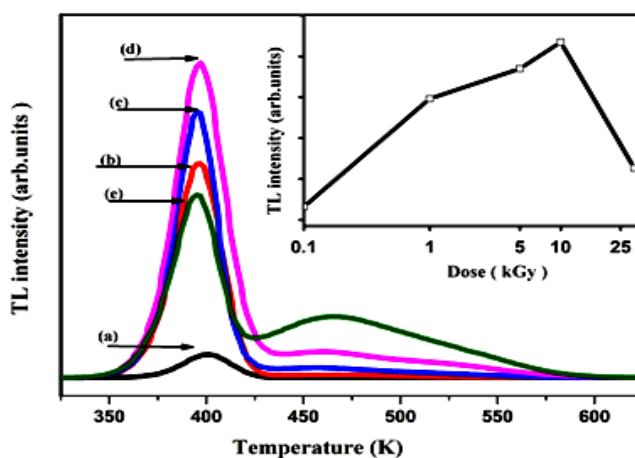


Fig. 12. TL glow curves of γ -irradiated LiF: Eu (0.03 mol %) at (a) 100 Gy, (b) 1 kGy, (c) 5 kGy (d) 10 kGy and (e) 30 kGy doses. The inset in the figure shows the TL intensity vs. dose response of LiF: Eu (0.03 mol %).

Except the variations in TL intensity, the TL glow curve exhibits a prominent intense glow peak of 396 K for all Eu³⁺ concentrations and is well separated from low intensity broad band around 462 K which, in fact consists of several overlapping peaks. It was further observed that these low temperature glow peak at 396 K and high temperature band at around 462 K are well separated. The maximum TL intensity was observed for LiF: Eu (0.03 mol %). The TL response for optimal sample LiF: Eu (0.03 mol %) at various irradiation doses is shown in Fig. 12. The TL intensity was found to be increased on increasing the irradiation dose and attained maximum value at 10 kGy then started decreasing on further increasing the irradiation dose. It may be due reason that available trapping states being filled to their capacity so that irradiation at higher dose(s) has no effect on the TL intensity [40-43].

The trapping parameters, namely activation energy E (eV), order of kinetics (b) and frequency factor S (sec⁻¹) for

pure and LiF: Eu (0.03) mol % samples were evaluated from the shape of experimental TL glow curve using Chen's peak shape method [17], which involves following empirical equations:

$$E_{\alpha} = C_{\alpha} \left(\frac{kT_m^2}{\alpha} \right) - b_{\alpha}(2kT_m) \quad , \quad \text{Where}$$

$$C_{\tau} = 1.51 + 3.0(\mu_g - 0.42) \quad ,$$

$$C_{\delta} = 0.976 + 7.3 (\mu_g - 0.42) \quad ,$$

$$C_{\omega} = 2.52 + 10.2(\mu_g - 0.42) \quad \text{and}$$

$$b_{\tau} = 1.58 + 4.2(\mu_g - 0.42) \quad , \quad b_{\delta} = 0 \quad , \quad b_{\omega} = 1$$

$$\frac{\beta E}{kT_m^2} = \text{sexp} \left\{ \frac{-E}{kT_m} \right\} [1 + (b - 1)\Delta_m] \quad , \quad \Delta_m = \frac{2kT_m}{E}$$

β is linear heating rate and k is Boltzmann's constant. This peak shape method is mainly based on the temperature T_m , T_1 and T_2 where T_m corresponds to temperature corresponds to maximum TL intensity ($I_{\max}$) while, T_1 and T_2 are temperatures correspond to half of maximum TL intensity on either side of $I_{\max}$. The peak shapes parameters involve in this method are; total half intensity width $\omega = (T_2 - T_1)$, high temperature half width $\delta = (T_2 - T_m)$ and low temperature half width $\tau = (T_m - T_1)$. To determines the order of kinetics (b), the form factor $\mu_g = \frac{\delta}{\omega} = \left(\frac{T_2 - T_m}{T_2 - T_1} \right)$, which involves T_1 and T_2 , the temperatures correspond to half of the maximum intensity on either side of maximum. Theoretically, form factor μ_g lies between 0.37 and 0.56. The value close to 0.42 for first kinetics and 0.52 for second –order kinetics. The value of μ_g for TL glow curves of γ -irradiated pure LiF and LiF: Eu (0.03 mol %) samples at various doses were close to 0.42, which revealed the first order kinetics and evaluated trapping parameters for are presented in Table 1 and Table 2 respectively.

Table 1. The trapping parameters of LiF (pure) namely symmetry factor, frequency factors, activation energy at various γ -irradiation doses.

Dose (kGy)	Symmetry Factor		Frequency Factor S (Sec ⁻¹)			Average S (Sec ⁻¹)		Activation Energy or Trap depth (eV)		Average Trap depth (eV)	
	μ_s	S_{τ}	S_{δ}	S_{ω}	S	E_{τ}	E_{δ}	E_{ω}	E		
0.1	0.44	6.03×10^{17}	2.83×10^{17}	6.36×10^{17}	5.07×10^{17}	1.39	1.41	1.41	1.40		
1	0.48	5.67×10^{19}	3.66×10^{19}	4.51×10^{19}	4.61×10^{19}	1.60	1.63	1.63	1.62		
5	0.43	1.59×10^{19}	1.67×10^{19}	1.45×10^{19}	1.57×10^{19}	1.48	1.52	1.52	1.51		
10	0.44	3.65×10^{17}	1.79×10^{17}	3.9×10^{17}	3.12×10^{17}	1.36	1.38	1.38	1.37		
30	0.46	7.41×10^{16}	5.83×10^{16}	9.09×10^{16}	7.44×10^{16}	1.31	1.33	1.32	1.32		
50	0.45	1.53×10^{15}	1.49×10^{15}	2.05×10^{15}	1.69×10^{15}	1.18	1.19	1.18	1.18		

Conclusion

Single phase pure and Eu (0.01 – 0.04 mol %) doped LiF samples having micro-cubical morphology were successfully prepared via co-precipitation method at constant pH value 8.00 and controlled reaction rate. Pure LiF doesn't exhibit any color centre formation at room temperature, however, γ -irradiation induced dose dependent

color centers (F, M and F₃) in LiF. The only F color centers were observed in Eu doped LiF without γ -irradiation. The γ -irradiated Eu doped LiF also exhibits dose dependant color centre formation as in case of pure LiF. The quantitative calculations of color centers using Smakula's formula shows that concentrations of both F and M color centers increases almost ten times for gamma irradiated Eu doped LiF in comparison to γ - irradiated LiF. Pure LiF doesn't shown any photoluminescence signal, however, $\square$ -irradiated LiF exhibits a broad emission in the red region which has been ascribed to radiations induced F₂ (M band) color centers. Eu doped LiF shows characteristic emission lines corresponding to Eu³⁺ transitions from ⁵D₀ to ⁷F_J level for (J=0, 1, 2, 3, 4). The γ -irradiated Eu doped LiF shows simultaneous PL emission of Eu³⁺ as well as that of F₂ color centers, makes it a promising candidate as red emitting phosphor. The natures of energy traps induced by $\square$ -irradiation in pure and in Eu³⁺ doped LiF were investigated through thermoluminescence studies. The trapping parameters namely activation energy E (eV), order of kinetics (b) and frequency factor (S) were also evaluated from the shape of experimental TL glow curve using Chen's peak shape method.

Table 2. The trapping parameters of LiF: Eu (0.03 mol%) at different γ -irradiation doses.

Dose (kGy)	Symmetry Factor		Frequency Factor S (Sec ⁻¹)			Average S (Sec ⁻¹)		Activation Energy or Trap depth (eV)		Average Trap depth (eV)	
	μ_s	S_{τ}	S_{δ}	S_{ω}	S	E_{τ}	E_{δ}	E_{ω}	E		
0.1	0.51	1.56×10^{19}	2.65×10^{18}	8.29×10^{18}	8.85×10^{18}	1.48	1.52	1.54	1.51		
1	0.46	1.09×10^{17}	8.30×10^{16}	1.33×10^{17}	1.08×10^{17}	1.37	1.39	1.38	1.38		
5	0.45	3.52×10^{18}	1.82×10^{18}	3.83×10^{18}	3.06×10^{18}	1.45	1.48	1.47	1.47		
10	0.52	3.5×10^{20}	2.5×10^{19}	1.17×10^{20}	1.64×10^{20}	1.54	1.59	1.63	1.59		
30	0.47	1.42×10^{16}	1.28×10^{16}	1.81×10^{16}	1.50×10^{16}	1.29	1.30	1.29	1.29		

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