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Electron–hole recombination luminescence in $\text{LiYF}_4: \text{U}^{4+}$ single crystal

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Abstract

Photoluminescence (PL), photostimulated luminescence (PSL), thermally stimulated luminescence (TSL) and electron paramagnetic resonance (EPR) studies were carried out on $\text{LiYF}_4: \text{U}^{4+}$ and pure LiYF_4 crystals. The PL and EPR investigations have identified the presence of Eu^{3+} , Tb^{3+} and Gd^{3+} ions in both of these crystals possibly due to their existence in the starting materials. The luminescence observed during afterglow, PSL and TSL revealed that emission occurs at wavelength positions 382, 413, 437 and 544 nm, which are characteristic of Tb^{3+} ions. The present investigations using PSL and TSL in combination with PL studies before and after gamma irradiation have revealed that selective energy transfer to Tb^{3+} ions occurs during electron–hole recombination processes like PSL and TSL. Even though other luminescent ions (U^{4+} and Eu^{3+}) are present in the system and $\text{U}^{4+}/\text{U}^{3+}$ ions are participating in electron capture/release processes, the selective energy transfer results in Tb^{3+} ions acting as luminescence centers.

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1. Introduction

Recently, there is a revival of interest in new phosphor materials for their possible application in next generation lamp phosphors, gas plasma devices for flat color panels, UV laser materials, and scintillator materials. In these devices, VUV/high-energy radiations are to be converted to visible output for lamp phosphors and panel devices and to UV output for scintillator materials. Investigations on LiYF_4 phosphor materials doped with different lanthanide ions using VUV radiation for excitation have been reported (Krupa and Queffelec, 1997; Meijerink and Wegh, 1999; Pieterse et al., 2002a, b). In this crystal, band-to-band transition is

reported at 10.55 eV. There has been some interest in investigating optical and luminescence properties of $\text{LiYF}_4: \text{U}$ for application as a solid-state laser. In this regard, the absorption, luminescence, synchrotron radiation-induced luminescence properties of U^{4+} and U^{3+} ions and radiation-induced changes have been studied in $\text{LiYF}_4: \text{U}^{4+}$ crystals (Hubert et al., 1994; Louis et al., 1995; Sangeeta et al., 2001; Kirikova et al., 2002; Godbole et al., 1992, 2001). These investigations have revealed radiation-induced conversion of U^{4+} to U^{3+} , laser action based on U^{3+} and UV luminescence arising from $f^1d^1 \rightarrow f^2$ transitions of U^{4+} with a fluorescence lifetime of 17 ns. In the present work, thorough investigations of nominally pure and uranium-doped LiYF_4 crystals were carried out using photoluminescence (PL) and electron paramagnetic resonance (EPR) to identify the intrinsic impurities present in base materials. In addition, the effect of the existence of various ions, on thermally stimulated luminescence (TSL) and photostimulated luminescence (PSL)

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processes were also investigated. Based on these investigations, the intrinsic impurities in the base materials were identified to be Eu, Gd and Tb ions. The PL, PSL and TSL studies have led to the conclusion that Tb^{3+} ions act as the predominant luminescent centers during e–h recombination process in spite of the presence of other luminescent ions due to selective energy transfer.

2. Experimental details

The crystals of $LiYF_4$ were grown by Prof. Gesland, University Du Maine, using Czochralski technique in an $Ar/CF_4/HF$ mixed atmosphere (Gesland, 1984). For preparing the doped crystals, a measured amount of UF_4 was added to the starting charge and the crystals on growth were found to contain around 800 ppm of uranium. For conducting various measurements, the crystal ingots were suitably cut and optically polished. Edinburgh FL-900 fluorescence-lifetime spectrometer and Hitachi F 4500 fluorescence spectrometer were used for luminescence determination. Bruker ESP 300 EPR spectrometer was used to record EPR spectra of the crystals. The afterglow observed due to the release of electrons from shallow traps at room temperature was recorded immediately after gamma irradiation without using the excitation source. PSL spectra were also recorded. Gamma irradiation was performed using ^{60}Co as gamma source and the crystals were irradiated for a cumulative dose of 100 Gray. TSL spectra were monitored using indigenously developed TSL setup suitable for coupling with Hitachi F-2000 fluorescence spectrometer. The coupling of TSL setup with spectrometer enabled the fast recording of entire emission spectra in the range of 220–800 nm at a scan speed of 1200 nm/min at various temperatures.

3. Results and discussion

3.1. Photoluminescence investigations

These studies were carried out on nominally pure and 800 ppm U^{4+} -doped $LiYF_4$ crystals. In our earlier investigations on these crystals, it was found that emission having short lifetime (~ 17 ns) was mainly observed in UV region only for U-doped sample, whereas, emission having long lifetime (~ 600 μs) was observed in visible region for both the crystals (Godbole et al., 2001). The analysis of spectra led to a conclusion that the visible emission observed in both the crystals was due to the presence of Eu^{3+} in the base material. Fig. 1 shows emission spectra recorded for these two crystals using 270 nm ($Eu^{3+}-O^{2-}$ charge transfer band excitation (Krupa and Queffelec, 1997)). Emission bands at 590, 620, 650 and 700 nm revealing presence of Eu^{3+} ions are observed. This figure also shows in the inset a resolved structure for 620 nm band in case of nominally pure crystal. Similar structure was observed in case of $LiYF_4: U^{4+}$

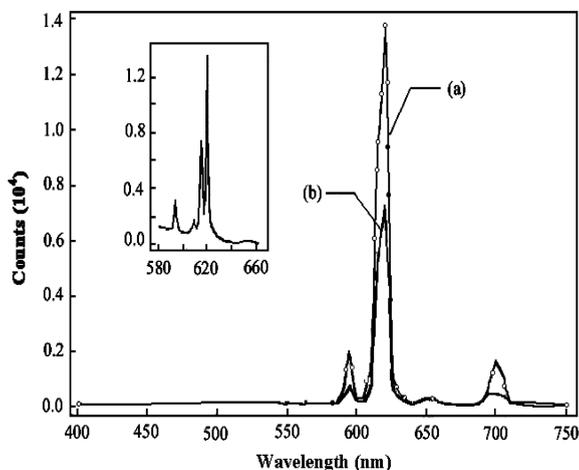


Fig. 1. Emission spectra observed on excitation with 270 nm for (a) $LiYF_4$ and (b) $LiYF_4: U$ crystals. Inset: resolved structure in 620 nm band for (a) $LiYF_4$.

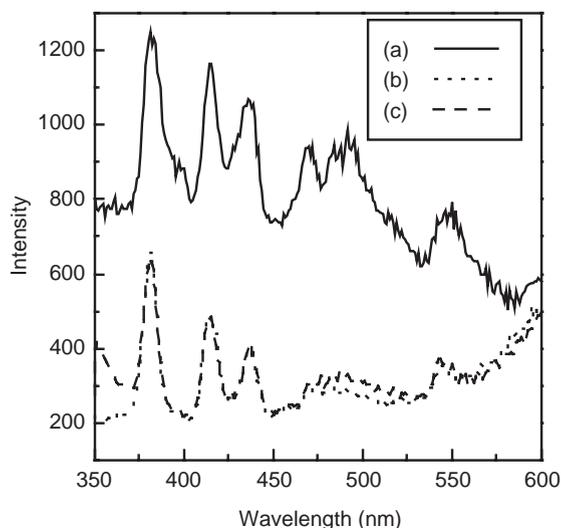


Fig. 2. Emission spectra observed on excitation with 270 nm (a) for nominally pure $LiYF_4$ crystal, (b) for $LiYF_4: U^{4+}$ crystal and (c) for $LiYF_4: U^{4+}$ crystal after gamma irradiation.

crystal also. No significant changes were observed in the spectra after gamma irradiation. Fig. 2 depicts the emission spectra observed (a) for $LiYF_4$ crystal, (b) for $LiYF_4: U^{4+}$ and (c) for $LiYF_4: U^{4+}$ crystal after gamma irradiation. The spectra were recorded with 210 nm excitation corresponding to f–d excitation band of Tb^{3+} (Krupa and Queffelec, 1997). The emission peaks at 382, 415, 437, 485 and 546 nm characteristic of Tb^{3+} ions were observed in all the three cases. As seen from the spectra, there is no significant difference brought about by gamma irradiation. Fig. 3 shows the emission spectra observed for U^{4+} -doped crystal (a) virgin

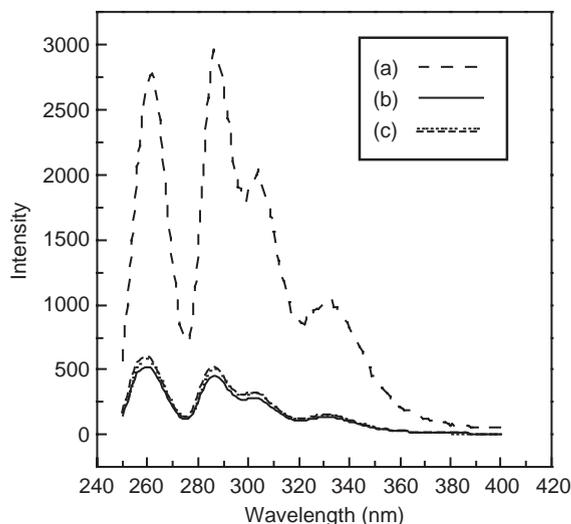


Fig. 3. Emission spectra observed on excitation with 240 nm (a) for LiYF₄: U⁴⁺ crystal (b) for γ -irradiated LiYF₄: U⁴⁺ crystal and (c) for γ -irradiated LiYF₄: U⁴⁺ crystal after photostimulation.

crystal (before gamma irradiation), (b) after gamma irradiation and (c) gamma irradiated crystal after photostimulation. The spectra were recorded with 240 nm excitation corresponding to f–d band of U⁴⁺ (Godbole et al., 2001). The emission peaks corresponding to $6d^15f^1 \rightarrow 5f^2$ at 260, 287, 302 and 331 nm are found in these samples. A significant reduction in luminescence intensity is observed after gamma irradiation. The observation reveals that reduction of U⁴⁺ ions occurred due to gamma irradiation. Based on absorption studies, the reduction of U⁴⁺ ions owing to their conversion to U³⁺ ions by electron trapping during gamma irradiation has been reported (Louis et al., 1995). A slight increase in luminescence intensity is observed after photostimulation of the gamma irradiated crystal. The increase in the intensity suggests that during photostimulation, U⁴⁺ ions were regenerated due to electron release from U³⁺ ions. A complete recovery of luminescence intensity of U⁴⁺ ions is observed only after thermal annealing at 300°C.

Immediately after gamma irradiation, the emission spectra for the crystals were recorded without any excitation on Edinburgh FL-900 spectrometer at room temperature. The afterglow spectra arise primarily due to electron–hole recombination at room temperature involving shallow traps for a period of few minutes. The afterglow spectra observed for LiYF₄: U⁴⁺ crystal are shown in Fig. 4. The peaks at 382, 415, 437, 485, 546 and 590 nm are characteristic of Tb³⁺ ions emission, while a weak emission around 620 nm can be probably due to Eu³⁺ ions. The fall in emission intensity was also detected for the consecutive measurements, confirming e–h recombination from shallow traps as the origin of spectra. No afterglow spectra were observed with nominally pure sample. The presence of afterglow emission only in tetravalent uranium-doped crystal clearly suggests that

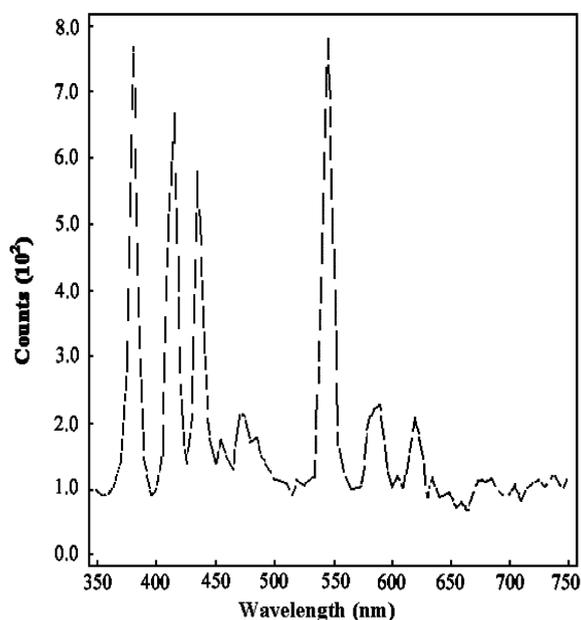


Fig. 4. Afterglow spectra for γ -irradiated LiYF₄: U⁴⁺ crystal.

the incorporation of these ions into the host matrix leads to the formation of some shallow traps.

3.2. Photostimulated luminescence investigations

TSL investigations (Godbole et al., 1992; Sangeeta et al., 2001) have revealed the presence of four TSL peaks due to e–/h– traps in LiYF₄ up to 600 K, while, backconversion of U³⁺ to U⁴⁺ was reported at 450 K (Louis et al., 1995). After the emptying out of the shallow traps, the deeper traps do exist in the crystal. The excitation spectra implying photostimulation, as shown in Fig. 5 were recorded for gamma irradiated LiYF₄: U⁴⁺ crystal by monitoring emission at 382 nm for Tb³⁺ ions on Hitachi F 4500 spectrophotometer. The excitation spectra recorded for the crystal before gamma irradiation are also shown in the same figure. The main excitation peak at 210 nm and a weak peak at 240 nm are observed before gamma irradiation. For gamma irradiated crystal, in addition to an increase in the intensity of 210 nm peak, additional strong peaks are observed at 247, 288, 300 nm. Fig. 5 also includes excitation spectra for gamma irradiated crystal monitored with 437 nm. The spectra clearly demonstrate the presence of 380 nm as the photostimulation peak. The absorption spectra of gamma irradiated pure LiYF₄ consist of two bands at 268 and 337 nm in UV region, while, gamma irradiated LiYF₄: U⁴⁺-doped crystal shows strong absorption bands between 300 and 550 nm region due to $5f^3 \rightarrow 5f^26d^1$ transitions of U³⁺ ions (Louis et al., 1995; Sangeeta et al., 2001). The photostimulation spectra can be attributed to the color centers in LiYF₄ crystal and U³⁺ ions. Furthermore, the absence of any excitation peak due to U⁴⁺ ions

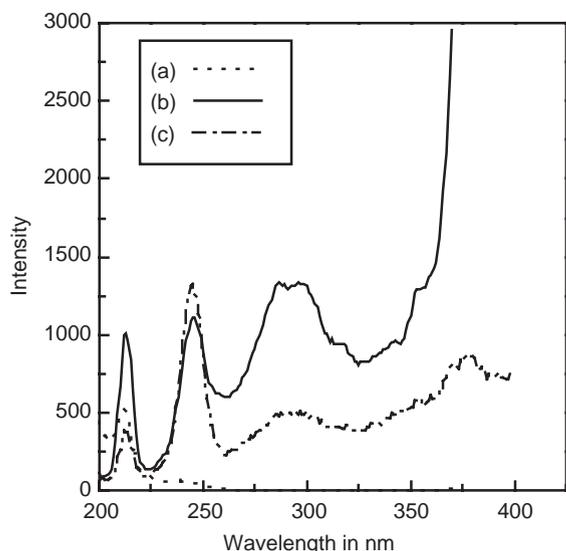


Fig. 5. Excitation spectra for Tb^{3+} ions (a) $\text{LiYF}_4:\text{U}^{4+}$ crystal (Emi. –382 nm), (b) γ -irradiated $\text{LiYF}_4:\text{U}^{4+}$ crystal (Emi. –382 nm) and (c) γ -irradiated $\text{LiYF}_4:\text{U}^{4+}$ crystal (Emi. –437 nm).

in the Tb^{3+} excitation spectra of virgin sample (i.e. before gamma irradiation) clearly suggests that no energy transfer is taking place from U^{4+} and Tb^{3+} ions. The photostimulation in the absorption bands of U^{3+} ions and the slight increase in luminescence intensity of U^{4+} ions after photostimulation suggest that U^{3+} ions formed by gamma irradiation convert back to U^{4+} ions by electron release during photostimulation. Similar conversion of U^{3+} ions (obtained by gamma irradiation) to U^{4+} ions was reported using YAG laser at 355 nm (Louis et al., 1995).

Fig. 6 shows the emission spectra observed on excitation with 288 nm (photostimulation band) for (a) $\text{LiYF}_4:\text{U}^{4+}$ and (b) gamma irradiated $\text{LiYF}_4:\text{U}^{4+}$. The spectra were recorded in the ranges of 200–350 and 300–600 nm with photostimulation bands at 380 and 288 nm, respectively. The spectra in the range of 200–350 nm did not reveal emission corresponding to U^{4+} ions. The spectra recorded in 300–600 nm clearly show the characteristic emission of Tb^{3+} ions. Fig. 7 shows the intensity variation observed as a function of time for Tb^{3+} emission at 382 nm on excitation in photostimulation band at 288 nm for gamma irradiated $\text{LiYF}_4:\text{U}^{4+}$ crystal. The intensity was observed to reduce continuously on excitation with 288 nm, thus, clearly indicating the dynamic nature of the emission process.

3.3. Thermally stimulated luminescence and electron paramagnetic resonance studies

TSL emission spectra were recorded for gamma irradiated LiYF_4 and $\text{LiYF}_4:\text{U}^{4+}$ crystals in the range of 300–600 K at different temperatures with a temperature

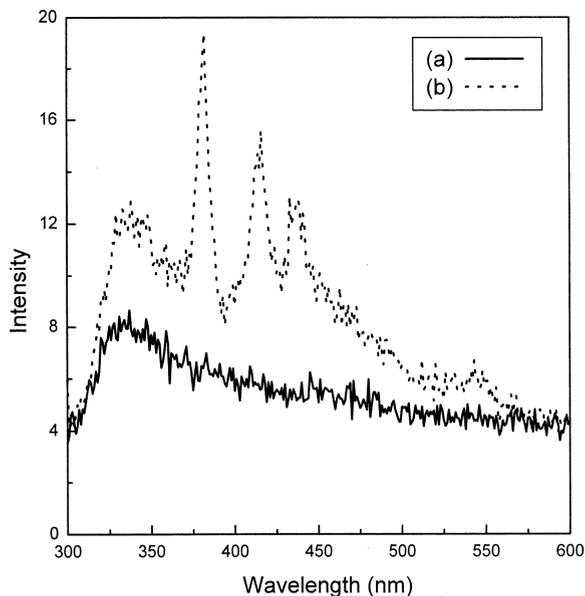


Fig. 6. Emission spectra observed on excitation with 288 nm (photostimulation band) (a) $\text{LiYF}_4:\text{U}^{4+}$ crystal and (b) γ -irradiated $\text{LiYF}_4:\text{U}^{4+}$ crystal.

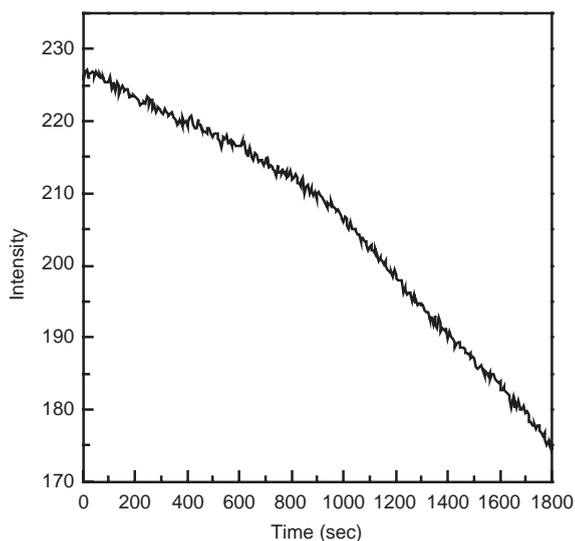


Fig. 7. Intensity variation as function of time (for 382 nm emission observed on continuous illumination in photostimulation band at 288 nm).

interval of 10 K. A typical TSL emission spectrum observed at 400 K for gamma irradiated $\text{LiYF}_4:\text{U}^{4+}$ crystal is shown in Fig. 8. The emission bands and their corresponding intensities are given in Table 1. As shown in the figure and table, major emission intensity is observed for the bands characteristic of Tb^{3+} ions along with minor emission owing to U^{4+} and Eu^{3+} ions. In the entire tem-

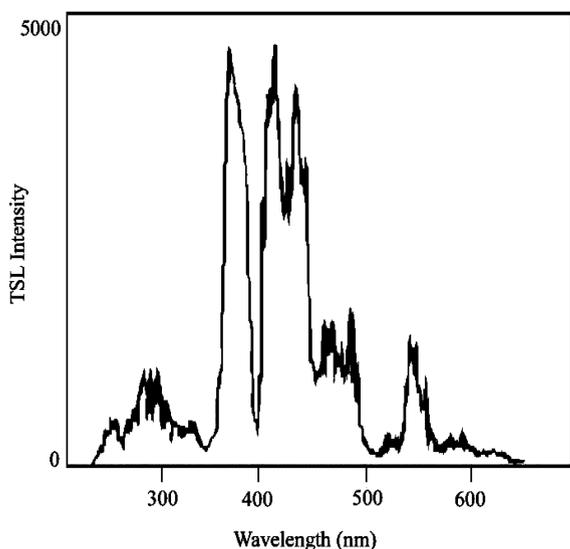


Fig. 8. Thermally stimulated emission spectra for γ -irradiated LiYF₄:U⁴⁺ crystal.

Table 1

Emission bands and their intensities observed for gamma irradiated LiYF₄:U⁴⁺ crystal

Sl. no.	Emission band (nm)	Peak intensity (Arb.units)	Emission due to
1	265	360	U ⁴⁺
2	300	575	U ⁴⁺
3	335	267	U ⁴⁺
4	382	5034	Tb ³⁺
5	415	3836	Tb ³⁺
6	437	3905	Tb ³⁺
7	485	1567	Tb ³⁺
8	546	2908	Tb ³⁺
9	620	191	Eu ³⁺

perature range investigated, the emission pattern remained the same except for the uniform changes in intensity with temperature for all of the emission groups observed. For gamma irradiated LiYF₄ crystal, no emission was detected in the entire temperature range. The observation of identical emission patterns from YF₃ and LiYF₄:U⁴⁺ crystals, and the absence of any definite emission from pure LiYF₄ crystal (Sangeeta et al., 2001) were reported in some earlier studies on fluoride crystals.

EPR studies carried out at room temperature have revealed the presence of characteristic S state ion spectra which can be attributed to Gd³⁺ ions. The spectra observed in the two crystals were similar, suggesting that in addition to Eu³⁺ and Tb³⁺ ions, Gd³⁺ ions also exist in both crystals because of their presence in the starting base materials. The emission due to Gd³⁺ ions was not observed in any of PL, PSL and TSL investigations.

3.4. Discussion

The present investigations clearly identify the emission bands as being associated with specific ions and also reveal that major TSL/PSL emission is due to Tb³⁺ ions present in the crystal at very minute level (< 100 ppm) in comparison to that of dopant U⁴⁺ ions (800 ppm). Earlier investigations on TSL emission characteristics were mostly restricted to singly doped compounds and were used to identify luminescent centers as well as the role of dopant ions in TSL process (Nambi et al., 1974; Morgan and Stoebe, 1989; Natarajan et al., 2002). In few cases, investigations involving codoping of different impurities were also reported (Nair et al., 2000; Atone et al., 1993). In these investigations, the PL enhancement through energy transfer mechanism was found to be not correlating with TSL yield and in most of the cases, emission from both dopants was observed.

The excitation spectra of Tb³⁺ ions do not reveal energy transfer from U⁴⁺ ions. The changes found in PL emission after gamma irradiation and photostimulation indicate that U⁴⁺ ions act as electron traps during gamma irradiation, while electrons are released during PSL/TSL process. The Eu³⁺, Tb³⁺ and Gd³⁺ ions are observed due to their presence in the base materials and are at concentrations much lower than that of intentional dopant U⁴⁺ ions. The observed major emission intensity is associated with Tb³⁺ ions only when luminescence is occurring due to e–h recombination processes like afterglow, PSL and TSL. When electrons and holes recombine, the recombination energy of the order of band gap can be reabsorbed by various color centers and impurity ions and can result in the observation of luminescence from different ions. The observation of emission from Tb³⁺ ions during PSL and TSL, strongly indicates the possibility of the selective transfer of energy to Tb³⁺ ions. The observation of TSL/PSL emission only from U⁴⁺-doped crystal and its absence in nominally pure crystal suggest that uranium doping helps to stabilize greater number of traps. Even though other luminescent ions viz. U⁴⁺, Eu³⁺ and Gd³⁺ ions are present in the crystal, major PSL/TSL emission occurs from Tb³⁺ ions only. The observation suggests the involvement of selective energy transfer in these e–h recombination processes. The band gap for LiYF₄ crystal was reported to be 10.55 eV (Krupa and Queffelec, 1997). VUV excitation studies of these ions in LiYF₄ (Krupa and Queffelec, 1997; Kirikova et al., 2002) reveal that Tb³⁺ ions have excitation bands over a wider range in comparison to Eu³⁺ and U⁴⁺ ions. The selective energy transfer observed in the present studies may be possibly associated with the differences in the VUV excitation bands of these ions.

4. Conclusions

In conclusion, on gamma irradiation U⁴⁺ ions act as electron trapping centers getting reduced to U³⁺ ions and on photostimulation with color center bands/U³⁺ f–d bands,

electron are released from U^{3+} ions thereby converting these ions back to U^{4+} ions. Even though uranium ions play a role in recombination process, the recombination energy migration occurs selectively to Tb^{3+} ions resulting in the emission being mainly characteristic of these ions. Further, the enhancement of overall traps by incorporation of U^{4+} ions in $LiYF_4$ crystal results in observation of afterglow due to shallow traps.

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