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# Luminescence of $Eu^{3+}$ Ions in $LaF_3$ Laser Host

By

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Rare earth doped fluorides have been used in laser applications. Not much is known about the effect of ionizing radiation on the lasing and other properties of fluorides. The colour centre formation by $\gamma$-ray irradiation in pure and $Eu^{3+}$ doped $LaF_3$, studied by thermoluminescence measurements, is reported in this paper. It is shown that $LaF_3:Eu^{3+}$ is less sensitive to $\gamma$-ray irradiation. Characterization of this laser material using XRD and photoluminescence techniques is described.

## 1. Introduction

Oxide and fluoride laser host crystals have been grown extensively during the last 30 years. The spectroscopy and laser performance of these crystals have been studied in great detail. The most important amongst them is the $YAG:Nd^{3+}$ laser crystal. Of late, among the neodymium doped vanadium based crystals investigated are also $YVO_4$, $GdVO_4$, and $Sr_5(VO_4)_3F$ [1]. In the tysonite crystal family $LaF_3$ has attracted a great deal of interest as a host material for trivalent rare earth ions. Soloman and Muller [2] were the first to grow $Pr^{3+}$ doped $LaF_3$ and obtained the laser transition $^3P_0 \rightarrow {}^3H_6$; in $Er^{3+}$ doped $LaF_3$ the laser transition $^4I_{13/2} \rightarrow {}^4I_{15/2}$ obtained by Krupke and Gruber [3] and in $Nd^{3+}$ doped $LaF_3$ the laser transition $^4F_{3/2} \rightarrow {}^4I_{11/2}$ by Dmitruk and Kaminskii [4] were used in laser applications. Thereafter, spectroscopic and laser properties of rare earth doped lanthanum fluoride have been studied by a number of workers [5 to 11]. Many efficient lasers are developed on the basis of fluoride host crystals in recent years [12 to 15].

$Eu^{3+}$ exhibits the $^5D_0 \rightarrow {}^7F_2$ laser transition (611 nm line emission) in $Y_2O_3$ and $YVO_4$ hosts [16, 17].

Our investigation was also concentrated on $Eu^{3+}$ laser transitions in $LaF_3$ host material. Recently degradation of optical efficiency in 1.524 C/kg $\gamma$-irradiated $YAG:Nd^{3+}$ and $YLF:Nd^{3+}$ has been reported by Rose et al. [18], luminescence of defects in yttrium aluminium garnet by Rozenfeld and Rotman [19], and radiation damage in $YVO_4:Yb^{3+}$ by Pode et al. [20]. Not much is known about the effect of ionizing radiation and radiation damage in rare earth doped fluoride laser materials. The $\gamma$-irradiations are known to create structure and impurity defects in the anion and cation sublattices of the sample. In the present investigation, the formation of defects, colour centres, etc., by $\gamma$-irradiation in $LaF_3$ and $LaF_3:Eu^{3+}$ samples has been studied with the help of thermoluminescence measurements. The above samples are characterized by XRD and photoluminescence techniques. It is shown that $LaF_3:Eu^{3+}$ is much less sensitive to $\gamma$-rays.

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## 2. Experimental

The materials $LaF_3$ and $LaF_3:Eu^{3+}$ were prepared by a solid state diffusion method. Analar grade powders were used as starting materials. For preparing $LaF_3$, $La(NO_3)_2$ (5.00 g) and $NH_4F$ (1.28 g) were mixed thoroughly for one hour and then transferred into a porcelain crucible. In case of the doped sample, a known amount of $Eu(NO_3)_2$ (0.1 mol %) was added to $La(NO_3)_2$ (5.00 g) and $NH_4F$ (1.28 g). The mixture was thoroughly mixed for one hour and then transferred into a porcelain crucible. These powders were annealed in a resistive furnace by slowly raising the temperature, kept at about 800 °C for 24 h in air, and then cooled slowly to room temperature. The samples will be designated as $LaF_3$ (U)/ $LaF_3:Eu^{3+}$ (U) (U stands for unquenched). Some unquenched samples were annealed at 400 °C for 1 h and then quenched to room temperature by putting the crucible containing the powders onto a metal block. This sample will be designated as $LaF_3$ (400 Q)/ $LaF_3:Eu^{3+}$ (400 Q) (Q stands for quenched). Some unquenched samples were annealed at 750 °C for 1 h and then quenched to room temperature by the above method. These samples will be designated as $LaF_3$ (750 Q)/$LaF_3:Eu^{3+}$ (750 Q). The compounds were studied by XRD. It was found that the observed XRD pattern of $LaF_3$ agreed with the reported XRD data (JCPDS card number 32-483) [21].

Thermoluminescence (TL) glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (SQ response), dc amplifier, and millivoltrecorder. Five mg of a sample were heated every time at a rate of 150 K/min.

Exposure to γ-rays was made using a $^{60}Co$ source. Fluorescence from unirradiated samples was studied on a Hitachi F-4000 fluorescence spectrometer. Emission and excitation spectra were recorded with a spectral slit width of 1.5 nm.

## 3. Results and Discussion

The photoluminescence emission spectrum for the $LaF_3:Eu^{3+}$ (750 Q) sample is shown in Fig. 1. A prominent emission line is seen around 611 nm when excited by 250 nm light. This corresponds to a transition from the excited state of $Eu^{3+}$, $^5D_0 \rightarrow {}^7F_2$.

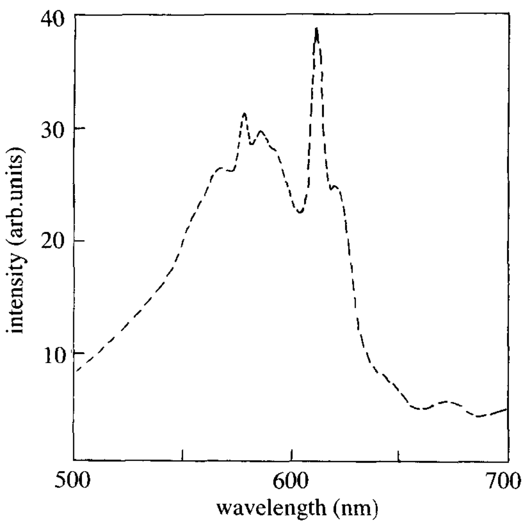


Fig. 1. Photoluminescence emission spectrum of the $LaF_3:Eu^{3+}$ (750 Q) sample ($\lambda_{ex} = 250$ nm)

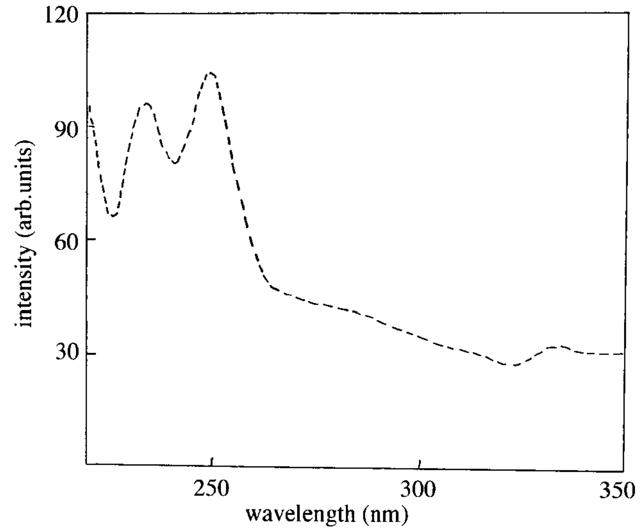


Fig. 2. Photoluminescence excitation spectrum of the $LaF_3:Eu^{3+}$ (750 Q) sample ($\lambda_{em} = 611$ nm)

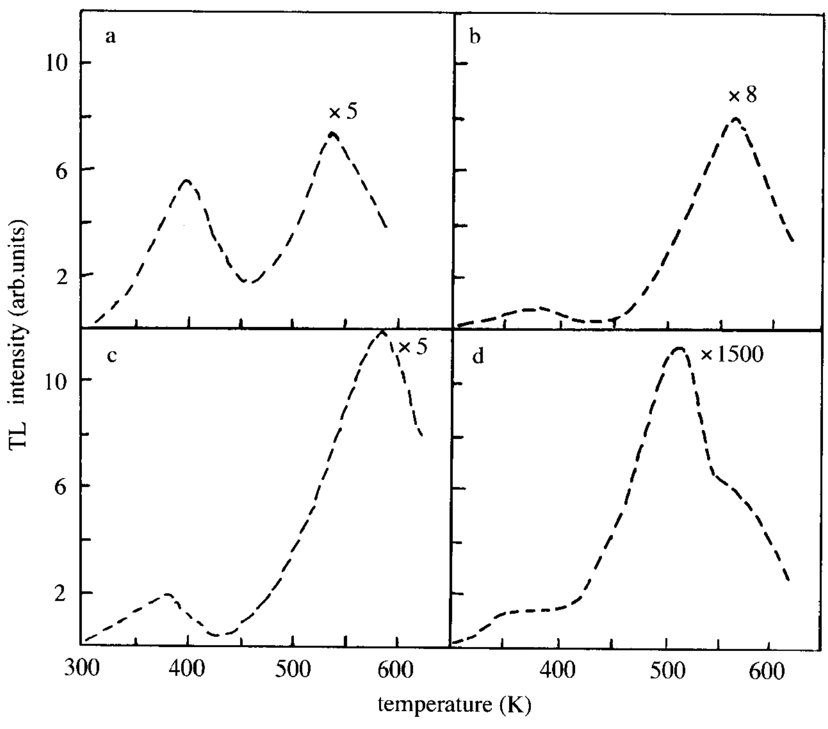


Fig. 3. Thermoluminescence glow curves for various $LaF_3$ samples exposed to 0.0604 C/kg; a) $LaF_3$ (U), b) $LaF_3$ (400 Q), c) $LaF_3$ (750 Q), and d) $CaSO_4:Dy^{3+}$. Numbers at the curves are the multipliers of the ordinate for obtaining the relative intensities

The corresponding excitation spectra of the sample $LaF_3:Eu^{3+}$ (750 Q) show a strong peak around 250 nm. This excitation may be attributed to $Eu^{3+}$ in crystalline state (Fig. 2).

In $LaF_3:Eu^{3+}$ (U) and $LaF_3:Eu^{3+}$ (400 Q) samples excitation and emission peaks are observed at the same positions and hence are not shown.

The glow curves of various $LaF_3$ samples exposed to 0.0604 C/kg are shown in Fig. 3. In all samples a prominent glow peak is observed around 580 K and another weak peak at 380 K. In $LaF_3$ (U), $LaF_3$ (400 Q), and $LaF_3$ (750 Q) samples glow curves are similar, only the TL intensity ratio between 380 and 580 K peaks varies according to Fig. 3a, b, and c, respectively. It is also seen that the sensitivity of $LaF_3$ samples is about 300 times lower than that of the well-known TLD phosphor $CaSO_4:Dy^{3+}$ (Fig. 3d).

The glow curves of various $LaF_3:Eu^{3+}$ (0.1 mol %) samples exposed to 0.0604 C/kg are shown in Fig. 4. In all samples a prominent TL glow peak is observed around 545 K and in $LaF_3:Eu^{3+}$ (400 Q) (Fig. 4b) and $LaF_3:Eu^{3+}$ (750 Q) (Fig. 4c) another low temperature peak is observed around 380 K. The sensitivity of the $Eu^{3+}$ doped samples is about 1500 times lower as compared to the $CaSO_4:Dy^{3+}$ TL dosimetry phosphor (Fig. 4d).

The intensity of the TL glow peak at 545 K in $Eu^{3+}$ doped samples is five times less sensitive as compared to the 580 K glow peak in pure samples. On the other hand, the $Eu^{3+}$ ion in the $LaF_3$ lattice quenches the TL or decreases the colour centre formation by irradiation. These properties are very useful in lasing materials.

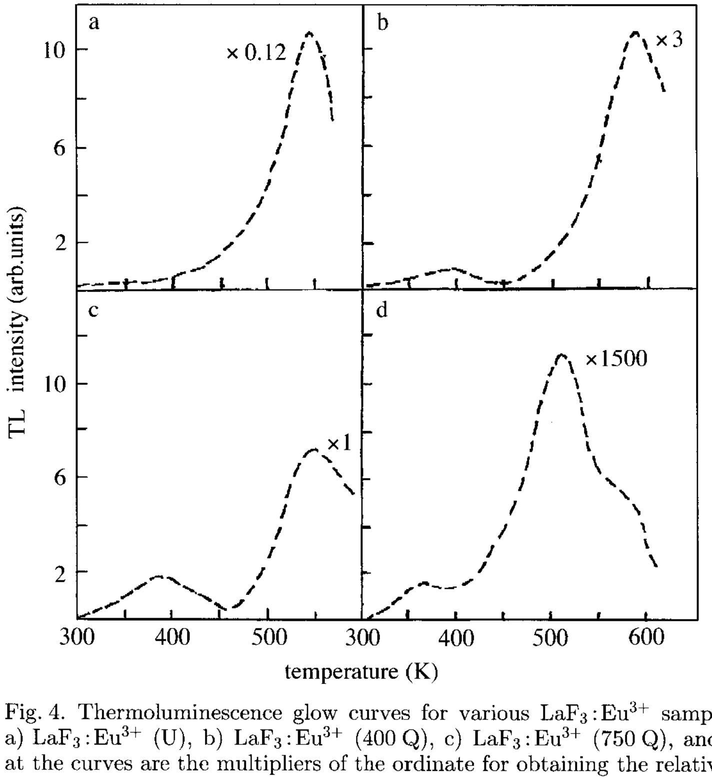


Fig. 4. Thermoluminescence glow curves for various $LaF_3:Eu^{3+}$ samples exposed to 0.0604 C/kg; a) $LaF_3:Eu^{3+}$ (U), b) $LaF_3:Eu^{3+}$ (400 Q), c) $LaF_3:Eu^{3+}$ (750 Q), and d) $CaSO_4:Dy^{3+}$. Numbers at the curves are the multipliers of the ordinate for obtaining the relative intensities

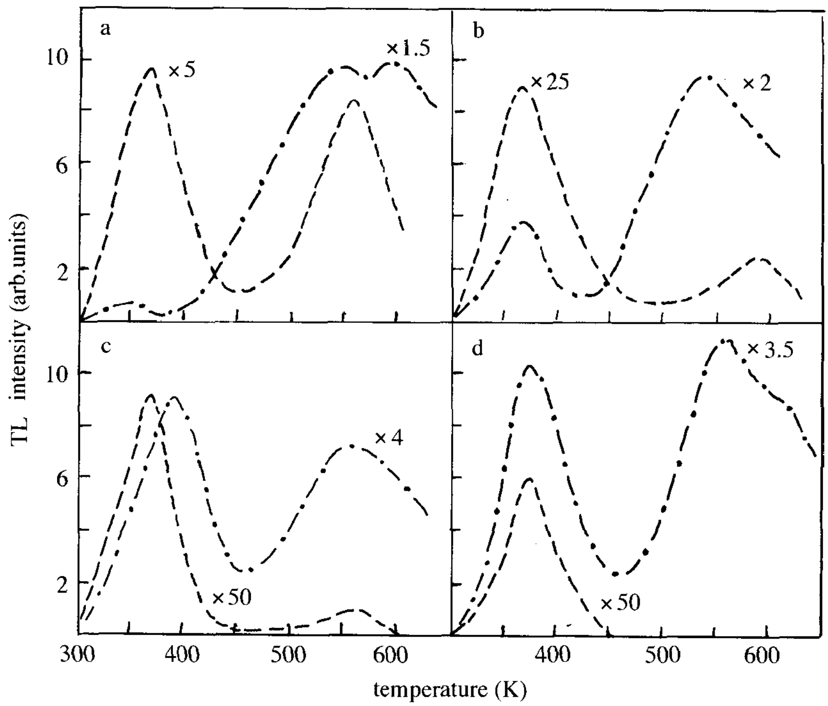


Fig. 5. Thermoluminescence glow curves of $LaF_3$ (750 Q) (dashed curves) and $LaF_3:Eu^{3+}$ (750 Q) (dash-dotted curves) at various γ-exposures; a) 0.28, b) 1.4, c) 2.8, d) 9.2 C/kg

The TL glow curves of pure and $Eu^{3+}$ doped $LaF_3$ (750 Q) samples at different exposures are shown in Fig. 5. It is observed that in pure $LaF_3$, the TL intensity of high temperature peak decreases with increasing γ-ray exposure as compared to the low temperature peak. However, in $LaF_3:Eu^{3+}$, the intensity of the low temperature peak showed an increase with the γ-ray exposure. The response curves of $LaF_3$ (750 Q) and $LaF_3:Eu^{3+}$ (750 Q) samples with γ-ray exposure are shown in Fig. 6. Curve a denotes

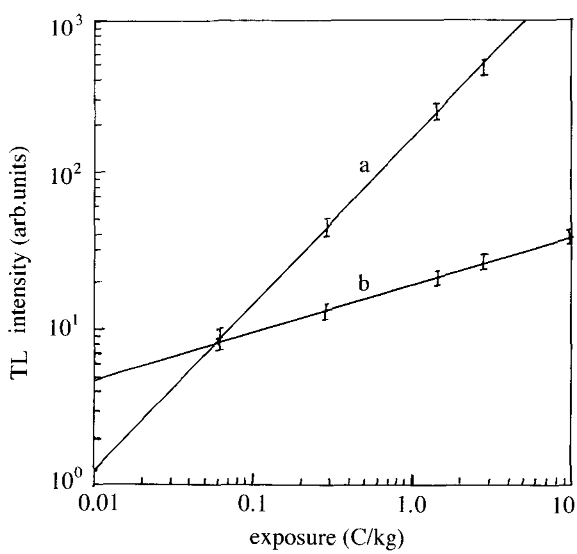


Fig. 6. Response curve for $LaF_3:Eu^{3+}$ (750 Q) samples (curve b). The height of the peak is shown as a function of γ-ray exposure. Curve a for $LaF_3$ (750 Q) (peak at 580 K) is also given for comparison

the TL glow peak (580 K) intensity variation with γ-ray exposure in the pure sample, whereas curve b represents the variation of the 545 K glow peak intensity variation in the $Eu^{3+}$ doped sample. Here the peak intensity is taken as a measure of particular colour centre formation [22]. The figure shows that colour centre formation is very low for increased γ-ray exposure and the increase in peak intensity with γ-ray dose for the $LaF_3:Eu^{3+}$ (750 Q) sample is not linear.

The above results indicate that Eu enters the $LaF_3$ lattice in trivalent state and the colour centre formation is much less than in the pure $LaF_3$ sample at γ-irradiation. $LaF_3:Eu^{3+}$ (750 Q) is also much less sensitive to γ-rays as compared to the well-known TLD phosphor $CaSO_4:Dy^{3+}$ [23]. The colour centres formed may act as scattering centres, which in turn reduces the efficiency of laser materials and optical properties may be degraded.

## 4. Conclusion

In conclusion, $Eu^{3+}$ emission in the red region of the spectrum around 611 nm is very useful in laser application. TL measurements give important information about colour centre formation in pure and $Eu^{3+}$ doped $LaF_3$. $LaF_3:Eu^{3+}$ is little sensitive to γ-ray exposure and the TL glow peak intensity is not linear with increasing γ-ray dose.

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