Bull. Mater. Sci., Vol. 30, No. 1, February 2007, pp. 1–3.

Thermoluminescence characteristics of Sm^{3+} doped $NaYF_4$ crystals

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MS received 28 June 2006

Abstract. **Thermoluminescence (TL) characteristics of $NaYF_4$ crystals doped with Sm^{3+} have been studied after γ-ray irradiation. Dependence of luminescence efficiency on Sm^{3+} concentration and radiation dose has been measured and possible applications of $NaYF_4 : Sm^{3+}$ as a novel phosphor for TL dosimetry have been investigated. The efficiency of 0·3 mole% Sm^{3+} doped $NaYF_4$ crystal has been found to be maximum and comparable with commercial thermoluminescence dosimetric (TLD) materials.**

Keywords. **Thermoluminescence; fluoride crystals; traps; thermal bleaching; TLD-100; γ-ray dosimetry.**

1. Introduction

In recent years, a lot of attention is being paid towards the investigation of spectroscopic properties of rare earth ions incorporated into different inorganic host matrices from the view point of searching for new materials with applications in lasers, optical devices, solid state dosimeters, etc. Thermoluminescence (TL) studies help in understanding the emission of light during heating by the charge transfer processes in an already irradiated crystalline lattice. The fluoride crystals consisting of a single cation and doped with different rare earth ions are known to exhibit intense thermoluminescence and are thus useful for TL dosimetry (Kristainpoller *et al* 2001; Sangeeta *et al* 2001; Coeck *et al* 2002). Earlier studies have suggested that the complex fluorides of yttrium and alkali elements doped with certain rare earths may also be promising materials for TL dosimetry (Gopal Reddy *et al* 1988). In the present paper, TL studies have been carried out in undoped and Sm^{3+} doped $NaYF_4$ crystals from the point of view of investigating the practical applications of these crystals in TL dosimetry and to understand the energy transfer processes among the luminescent ions present in the lattice.

2. Experimental

A series of single crystals of $NaYF_4$, undoped and doped with 0·1, 0·3 and 0·5 mole% of Sm^{3+}, was grown by direct temperature gradient method. The preparation of $NaYF_4$ was reported earlier from our laboratory (Narasimha Reddy *et al* 1983). The rare earth dopant (Sm^{3+}) was added to melt in the form of fluoride. All the samples were γ-irradiated for different amounts of time using Co^{60} source with a dose rate of $1·8 \times 10^6$ rad h^{-1}. After irradiation the samples were transferred to the chamber of TL set up. The TL glow curves were recorded by heating the irradiated crystal at a constant rate of 30°C/min. The light output was detected by an EMI 6256S Photomultiplier.

3. Results and discussion

The TL curves of undoped and 0·1, 0·3 and 0·5 mole% Sm^{3+} doped $NaYF_4$ crystals are shown in figure 1. All the samples have been exposed to 10 min of γ-radiation dose of $1·8 \times 10^6$ rad h^{-1}. From the figure it can be seen that in

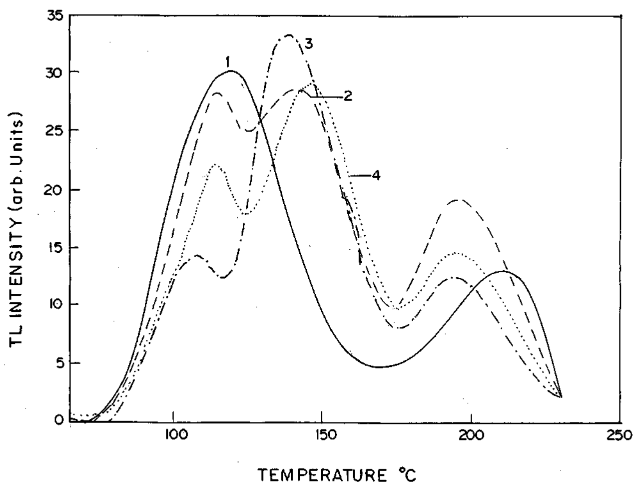

Figure 1. Thermoluminescence glow curves of undoped $NaYF_4$ crystal (curve 1), 0·1 mole% Sm^{3+} doped $NaYF_4$ (curve 2), 0·3 mole% Sm^{3+} doped $NaYF_4$ (curve 3) and 0·5 mole% Sm^{3+} doped $NaYF_4$ (curve 4).

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undoped $NaYF_4$ sample, a single main glow peak at 115°C, along with a shoulder peak on high temperature side at 210°C, is observed. The glow curves of the doped samples consist of three main peaks around 115°C, 145°C and 190°C. Comparison of TL glow curve of the undoped crystal with the Sm^{3+} doped crystals shows that additional glow peak around 145°C is observed in the Sm^{3+} doped $NaYF_4$ crystals and its intensity is considerably altered with the varying concentration of Sm^{3+}. As can be seen from figure 1, the intensities of both low temperature and high temperature peaks also vary in relation to the Sm^{3+} concentration in $NaYF_4$. This indicates a probable change in the trap structure of $NaYF_4$ with the doping concentration of samarium impurity. This observation is in conformity with the earlier studies (Narasimha Reddy *et al* 1987; Gopal Reddy *et al* 1988; Faria and Khaidukov 2001; Coeck *et al* 2002). From figure 1, it can also be seen that the 145°C TL glow peak in Sm^{3+} doped crystals has a maximum relative intensity at 0·3 mole% of Sm^{3+}. It is also observed that the intensity of this peak decreases with further increase in the concentration of Sm^{3+}. This is probably due to the formation of complex dopant aggregates that offer alternative non-radiative pathways for Sm^{3+} relaxation due to ion–ion interaction.

To understand the stability of the centres associated with the 0·3 mole% doped $NaYF_4$, the sample was irradiated for 10 min and kept in dark at room temperature for a prolonged period of 24 h and the TL glow curve was recorded, which is shown in figure 2. From this figure, one can notice that the first peak vanishes and the high temperature peak decreases drastically. The fading characteristics of 0·3 mole% Sm^{3+} doped $NaYF_4$ crystals have been further investigated by keeping the γ-irradiated samples in dark for 240 h at room temperature (figure 2, curve 3). One can see from this curve that no appreciable fading of TL is observed with enhanced annealing time. In comparison with the widely used TLD-100 (γ-ray dosimetry material) which fades about 10% per month (Kristainpoller *et al* 2001), this particular material appears to be more stable for γ-ray dosimetric applications. The dependence of TL intensity of 145°C glow peak in 0·3 mole% Sm^{3+} doped crystal on the time of γ-ray irradiation has been obtained and is shown in figure 3 and this is found to be linear. The assembly of the above characteristics makes this phosphor attractive for applications in TL dosimetry.

Earlier, it was shown that in undoped $NaYF_4$ powder samples two glow peaks, one around 115°C and another around 190–200°C, were observed and these were attributed to background impurities and F-centres, respectively. In $NaYF_4 : Sm^{3+}$ crystalline samples, irrespective of doping concentration, three glow peaks around 115, 145 and 190°C were observed. The nature of 115 and 190°C peaks can be understood comparing these peaks with those observed in undoped $NaYF_4$ crystals. Figure 2 shows that the centres responsible for 115°C peak are quite shallow and annealed out even at room temperature. From figure 1 it can be seen that the substitution of Sm^{3+} for Y^{3+} in $NaYF_4$ modifies the glow curve of the undoped crystal by giving rise to additional new intense peak at 145°C, and the intensity of this peak is also found to be sensitive to the percentage of Sm^{3+} present in the crystal. This suggests that the new traps which are responsible for 145°C are due to Sm^{3+} defect centres induced by γ-irradiation. To check the behaviour of these centres, we have performed experiments on thermal bleaching. It is found that if thermal bleaching is done up to 150°C the width of the remaining 190°C peak reduces to that of undoped $NaYF_4$. This result suggests that the cen-

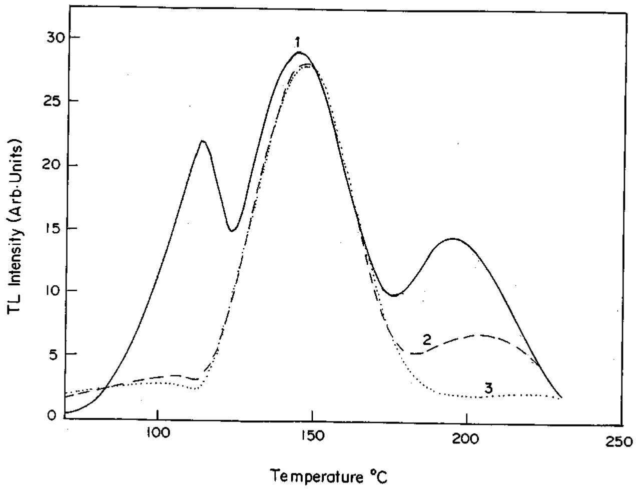

Figure 2. Thermoluminescence glow curves of $NaYF_4 : Sm^{3+}$ (0·3 mole%): curve 1 (γ-irradiated for 10 min), curve 2 (γ-irradiated for 10 min and kept at room temperature in dark for 24 h) and curve 3 (γ-irradiated for 10 min and kept at room temperature in dark for 240 h).

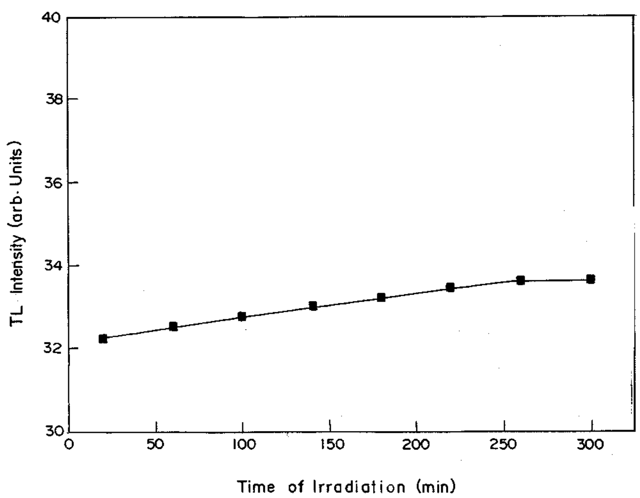

Figure 3. Dependence of TL intensity of 145°C glow peak of $NaYF_4 : Sm^{3+}$ (0·3 mole%) on the time of γ-irradiation.

tres responsible for 145°C peak are not stable after the temperature of 150°C. In undoped crystal, the F-centre peak appears around 200°C and in samarium doped crystals the F-centre peak appears around 190°C. This slight variation may be because of the presence of new centres responsible for 145°C peak, which seem to perturb the F-centre environment.

Acknowledgements

The authors are thankful to Prof. U V Subba Rao, Former Head, Department of Physics, Osmania University, Hyderabad, for his help and encouragement during the present work.

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