

C. Pandurangappa¹ and B.N. Lakshminarasappa^{2*}

¹Department of Physics, RNS Institute of Technology, Channasandra, Bangalore-560061

²Department of Physics, Jnanabharathi Campus, Bangalore University, Bangalore-560056

1. Introduction

Among alkali fluorides CaF₂ is a unique optical material that occurs naturally as the mineral fluorite. CaF₂ single crystals are used for variety of infrared and ultraviolet wavelength applications due to the fact that they are highly transmissive from 200-1100 nm. Rare earth doped CaF₂ exhibits a variety of novel properties. At low RE³⁺ ion concentrations, the dopants mainly form isolated centers whereas at higher RE³⁺ ion concentrations, the dopant ions aggregate and form complex clusters [1]. The Yb ion is interesting because of its strong IR luminescence.

2. Experimental

Yb (3 mol%) doped CaF₂ single crystal slices of 10 mm diameter and 1mm thickness were irradiated with γ -rays from a Co⁶⁰ source for doses ranging from 97Gy to 9.72 KGy at room temperature. The irradiated samples were subjected to optical absorption measurements in the wavelength range 190-900 nm using V-570 UV/VIS/NIR spectrophotometer at room temperature. The PL emission spectra of the samples were recorded using a spectrofluorometer (Jobin Yvon Fluorolog 3) equipped with a 450W Xenon lamp as the excitation source.

3. Results and Discussion

Figure1 shows the optical absorption spectra of pristine and γ -irradiated Yb doped CaF₂ crystals. The pristine samples showed minimal absorption indicating the purity of the procured samples. Two strong absorption peaks were observed in the irradiated samples at ~243 and 360 nm. The optical absorption was found to increase with increase in γ -dose. It is well established that when CaF₂ crystals are γ -rayed F-centers are formed at room temperature. γ -irradiation produces free electrons which get trapped at negative ion vacancies and form the F-centres. Literature reveals that electron irradiated CaF₂ crystals exhibit the fundamental absorption at 375 nm and it is attributed to F-center [2]. The absorption peak at 360 nm in the present studies is attributed to F-center [3]. The 243 nm peak is attributed to electron trapped by at Ca²⁺ interstitials [4].

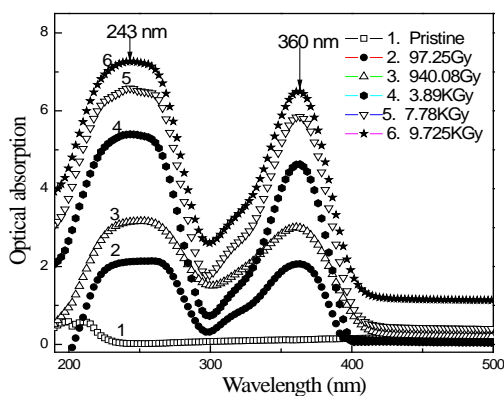


Figure 1. Optical absorption spectra of γ -rayed Yb doped CaF₂ single crystals

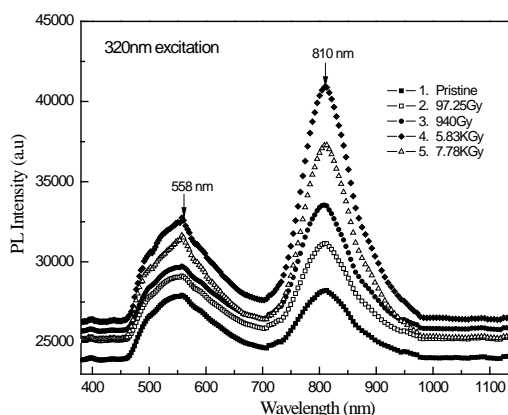


Figure 2. Photoluminescence spectra of γ -rayed Yb doped CaF₂ single crystals.

The photoluminescence emission spectrum of pristine and γ -irradiated pure CaF_2 crystals is shown in Figure 2. The spectrum shows two strong PL emissions – one in the visible region at ~ 558 nm and the other in the IR region with peak at ~ 810 nm when the samples were excited at 320 nm. The PL intensity was found to increase with increase in γ -dose. In CaF_2 , the aggregation of point defects produced by energetic radiation play an important role in the emission of energy. It is known that irradiation of CaF_2 leads to the formation of F and F-aggregate centers in it. The 580 nm emission peak is attributed to aggregation of F-centers to form Mie absorption [5]. It is known from the optical and magnetic resonance measurements that, when CaF_2 crystal was doped with Yb, the trivalent Yb^{3+} ions substitute the Ca^{2+} ions, resulting the Yb^{3+} ions surrounded by eight F^- ions [6]. The replacement by Yb^{3+} gives a contribution to the creation of charge compensation, such as an interstitial F^- ion. Since the doping CaF_2 with Yb requires a mixture of YbF_3 and CaF_2 powders the number of Yb^{3+} ions present during the crystal growth is much higher than the number of Yb^{2+} ions.

It is reported that γ -irradiation results in the conversion of Yb^{3+} ions to Yb^{2+} state and this results in the formation of Yb^{2+} associated centers which luminescence in the red region of visible spectrum. The excitation of Yb doped CaF_2 crystals with suitable wavelength gives rise to IR luminescence in the wavelength range 800- 900nm [7]. Thus the emission of 810 nm band in the present studies may be due to Yb^{2+} associated centers.

4. Conclusions

Gamma irradiated Yb doped CaF_2 single crystals showed the generation of F and F-aggregate centers. A strong IR emission was observed at ~ 810 nm due to Yb^{2+} centers. The PL studies revealed the transition of Yb ions from triply charged (Yb^{3+}) state to the doubly charged (Yb^{2+}) state upon γ -radiation. The increase in optical absorption and PL intensities with γ -dose indicated the enhancement of defects in the Yb doped samples.

References

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