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Spectroscopic studies in pure and Dy doped nanocrystalline CaF_2

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Abstract

Pure and Europium (Dy) doped Calcium fluoride (CaF_2) nanoparticles are synthesized by co-precipitation method and characterized by powder X-ray diffraction (PXRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM). Also, optical absorption (OA) and thermoluminescence (TL) results on gamma irradiated (γ-rayed) pure and Dy doped CaF_2 nanoparticles are reported. The XRD patterns confirmed the cubic crystallinity of the samples and the particle size is found to be ~25 nm. The purity of the synthesized nanoparticles is confirmed by FTIR spectrum. The morphological features studied using SEM revealed that the nanoparticles are agglomerated and porous. γ-rayed pure CaF_2 nanoparticles showed a prominent absorption with a peak at ~360 nm besides four weak but well separated absorptions at ~210, 267, 442 and 510 nm, whereas the γ-rayed Dy doped samples showed a series of absorption peaks at ~210, 293, 373, 468 and 573 nm. The various color centers responsible for the absorption peaks are identified. The TL studies of γ-rayed pure CaF_2 nanoparticles exhibited a strong and prominent TL glow with peak at ~145ºC whereas the Dy doped one showed a prominent glow at 143ºC along with a weak one at 243ºC. The results obtained are discussed in detail.

Keywords: Synthesis, Nanoparticles, X-ray diffraction, Optical absorption, Thermoluminescence

1. Introduction

CaF_2 is one of the well-studied alkali fluoride compounds for basic research [1]. It attracted researchers by its high stability and non-hygroscopic behavior. Rare earth doping to CaF_2 is used as a laser material. Number of novel routes are discovered to synthesize CaF_2 nanoparticles. Some of them are solvothermal, Co-precipitation, Hydrothermal, reverse micelle [2-4]. High energetic radiations are capable of creating defects in not only bulk crystals but also in nanocrystals. CaF_2 is one of the suitable materials to produce defects by synthesizing even in nanocrystalline form and produce defects similar to its bulk form [5,6]. Gamma radiations of low doses are also capable of creating defects in CaF_2 [7]. One of the scientific tools used to detect formed defects in crystals is Optical absorption in the UV-Visible region. Another technique that confirms the presence of defects is Thermoluminescence. It acts like a finger print to identify the defects created in the irradiated samples. In the present work nanoparticles of CaF_2 are synthesized by doping with Dy (2 mol%) using co-precipitation method. The prepared samples are characterized by XRD, SEM and FTIR. After γ-irradiation optical absorption (OA) and thermoluminescence (TL) studies are carried out.

2. Experimental

Stoichiometric quantities of the ingredients dysprosium nitrate ($Dy(NO_3)_2$), Calcium chloride ($CaCl_2$) and Ammonium fluoride (NH_4F) were taken in a 250ml conical flask and the mixture was dissolved in 100 ml of distilled water. The solution mixture was kept for constant stirring for about 2 hours on a magnetic stirrer. After stirring reaction mixture turned into opaque white suspension. The

stirred solution was subjected for centrifugation and a white residue was collected. The residue was washed thoroughly with ethanol to eliminate the residual chloride and the ammonium ions. The final product was extracted and dried on a sand bath at 100^0 C.

Figure 1: Powder X-ray diffraction pattern of Dy doped nanocrystalline CaF_2

mples was carried out using Philips X-pert PRO powder diffractometer with Cu-K_α radiation (λ=1.54056A) with a scan range 10-90°. The surface morphology of synthesized samples was analyzed by scanning electron microscopy (JEOL JSM-840A) using sputtering technique. FTIR studies were carried out using Nicolet Magna 550 spectrometer with KBr pellets in the frequency range from 400 - 4000 cm^{-1}. The characterized samples were irradiated by γ-rays from a Co^{60} source with an activity 3.89 KGy/hr in the dose range 0.079–7.78 KGy. The Optical absorption studies of γ-rayed samples were carried in the range 200 to 900 nm using V-570 UV/VIS/NIR double beam spectrophotometer. The TL measurements were made using an indigenously built TL set up by heating the samples with a heating rate of 5.5°C/s.

3. Results and Discussion

3.1 XRD, SEM and FTIR

The powder X-ray diffraction pattern of undoped nanocrystalline CaF_2 is shown in Figure1. The XRD peaks are indexed into cubic phase of the fluorite type structure with space group Fm3m (JCPDS Card no. 87–0971). The <h k l> values of the peaks are (1 1 1), (2 2 0), (3 1 1), (4 0 0), (3 1 1) and (4 2 2) [8]. The crystallite size was calculated from the full width at half maximum (FWHM) technique using Scherer's formula $D=K\lambda/(\beta \cos\theta)$ where K is the constant (0.99), λ is the wavelength of Cu-Kα (1.54A°) line, β is the FWHM and θ is the diffraction angle. The value of crystallite size was 25nm. The average value of lattice constant was found to be 5.454A°. Figure 2 shows the PXRD pattern of heat treated Dy doped CaF_2. It resembled that of as-prepared one. However, the intensity of the peaks was increased marginally. This indicates that Dy doping does not reveal any structural changes in the nanocrystalline CaF_2. The crystallite size was increased to 30 nm. This is due to the fact that when Ca^{2+} ions are substituted by a rare earth Dy^{3+}, the charge compensating F^- ions enter the fluorite structure in interstitial cubic sites and experience repulsion which leads to increase of the lattice parameter. The XRD pattern presents broad peaks revealing the small crystallite size of the synthesized samples.

The purity of the synthesized powder was checked by FTIR studies. The FTIR spectrum of undoped CaF_2 nanoparticles is shown in figure 3. There are two prominent absorption bands at ~3400 and 1550 cm^{-1}[9]. These are due to bending of water molecules. This indicates that the as-prepared samples contain hydroxyl groups. The band at ~364 cm^{-1} arises due to rotations of the hydroxyl ions. The 2357 cm^{-1} band is due to KBr pellets used for FTIR [10]. The FTIR spectrum of CaF_2:Dy nanoparticles is shown in Figure 4. The spectrum resembles that of the undoped samples with a slight shift in the peak position and a marginal increase in the intensity of the absorption bands.

Figure 5 shows the SEM photographs of as prepared Dy doped nanocrystalline CaF_2. As per the SEM pictures the nanocrystalline CaF_2 is agglomerated with polycrystals. The agglomeration ranged up to hundred microns. The nanoparticles have voids and pores. The fusion of smaller particles forms larger particles during precipitation. The morphological features match well with literature [11]. The CaF_2:Dy SEM pictures are shown in figure 6. It indicates that agglomeration is more and particles have gained large size. Also, there exists pores and voids in the samples.

3.2 Optical absorption studies

The absorption spectrum recorded in the UV-visible region for un irradiated and γ-rayed undoped CaF_2 nanocrystals is shown in Figure 7. In the pristine sample only a weak absorption band at ~360 nm is observed. Whereas in case of γ-rayed samples besides strong absorption at ~360 nm three weak absorptions are observed at ~210, 267, 442 and 510 nm. With increase in γ-dose the amount of absorption of the bands was found to increase marginally. However, increase in γ-dose did not alter peak positions. The absorption bands are accounted to various defect centers as discussed below. The large surface to volume ratio of nano particles results in voids over the surface of nanoparticles. These voids absorb UV light. In addition to this Schottky or Frenkel defects are pruned to exist on surfaces of nanoparticles. Such surface defects also absorb light. Literature reveals similar absorption bands in solvothermally synthesized nanocrystalline CaF_2. Absorption bands at 210, 267nm are attributed to the surface defects such as Schottky or Frenkel in nanocrystalline CaF_2[12]. The 360 nm absorption band in pure samples is attributed to the well-studied F-center which is consider to be the mother of all color centers. The 442 nm band is assigned to H-center. Absorption at 510 nm could be due to Mie absorption of nanocrystalline CaF_2[13].

Figure 8 shows absorption spectrum of Dy doped CaF_2 samples. The prominent absorption is peaked at ~373 nm besides the weak absorptions at ~210, 293, 468 and 573 nm. The 293 nm band is attributed to 4f→5d transitions of Dy^{3+} ions. The 373 nm absorption band is attributed to F-center whose peak position is shifted marginally when compared to that of undoped samples (360nm). Literature shows that 468 nm band could be due to self trapped exciton[19]. The weak absorption at 573 nm peak is attributed to formation of calcium colloids [14].

Figure 9: TL spectrum of pure nanocrystalline CaF_2

3.3 Thermoluminescence studies

The TL spectrum of pure nanocrystalline CaF_2 is shown in Figure 9. The TL glow was observed at ~145ºC. The intensity of the glow increased with γ-dose till 5.83 KGy and thereafter it decreased. The TL yield for low dose γ-rays is poor, due to low energy storage. The low dose γ-rays produce relatively less traps. The TL glow at 145ºC in pure CaF_2 nanoparticles is attributed to recombination of released electrons and holes at suitable lattice site. TL spectrum of Dy doped CaF_2 samples showed a strong TL glow at ~143ºC and a broad one at ~ 243 ºC (Figure 10).

The glow peak temperature appears to shift towards lower temperature with increase in γ-dose and the TL intensity increases till 5.835 KGy and thereafter it decreases. Compared to pure CaF_2 samples the TL intensity in Dy doped samples less. The TL glow at 243ºC in Dy doped CaF_2 can be explained in the following way. The dopant Dy exists in Dy^{3+} states. Due to γ-irradiation Dy^{3+} state reduces to Dy^{2+} by electron capture. Also the holes generate during γ-irradiation are captured by the host related defect centers. When the samples are heated to record TL, the holes to get released by emitting light. This produces TL glow at low temperature of about 143ºC[15]. The pictorial representation of the process is represented below.

During irradiation**:**

$Dy^{3+} + e^- \rightarrow Dy^{2+}$ and $F^- + \text{hole} \rightarrow V_k$

During heating :

$V_k \rightarrow F^- + F^+ + \text{hole}$ and $Dy^{2+} + \text{hole} \rightarrow Dy^{*3+} \rightarrow Dy^{3+} + TL$ Where Dy^{*3+} refers to Dy^{3+} in an excited state.

4. Conclusions

Pure and Dy doped CaF_2 nanoparticles were prepared by the cost-effective co-precipitation method. and characterized by XRD, SEM, FTIR, Optical absorption and TL. The average particle size of the synthesized samples as determined from XRD studies was found in the range 20-25 nm. The morphological features of samples as studied from SEM showed their agglomeration upto hundreds of microns. Also the samples are fluffy and porous. The FTIR results indicated the existence of hydroxyl groups in the as prepared sample. The large number of intrinsic defects formed in the γ-irradiated CaF_2 nanoparticles by the optical absorption spectra. The TL glows indicated the radiative recombination of released electrons and holes and also reduction of Dy ions from triply charged state to doubly charged state due to gamma irradiation. Compared to pure CaF_2 the TL intensity is increased by ten folds in Dy doped CaF_2.

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Figure Captions

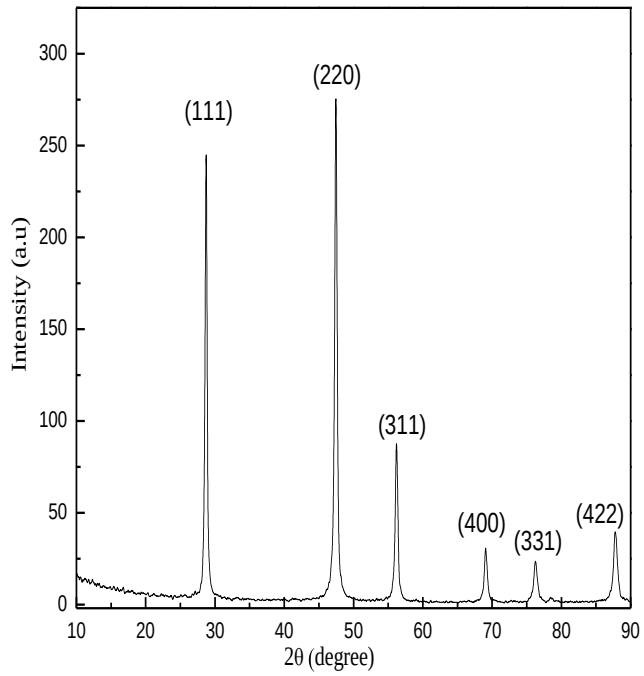

Figure1: PXRD pattern of undopedna nocrystalline CaF_2

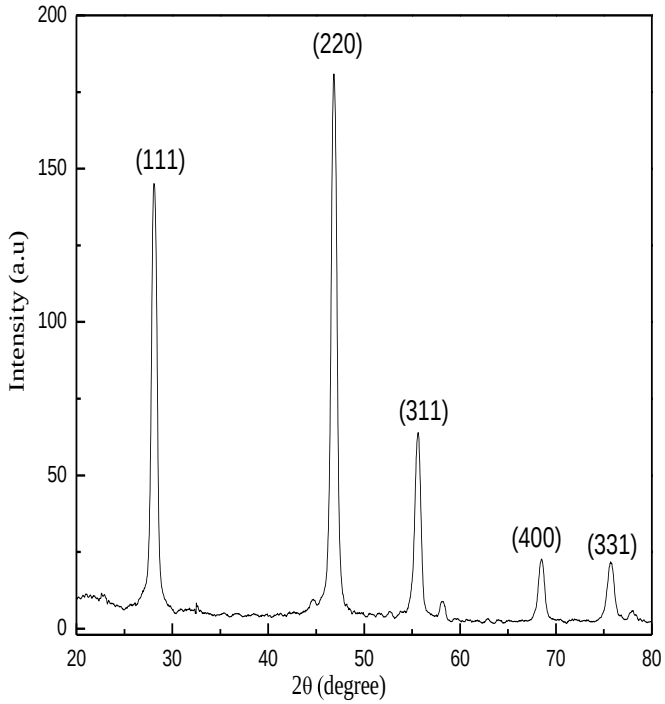

Figure 2: Powder X-ray diffraction pattern of Dydoped nanocrystalline CaF_2

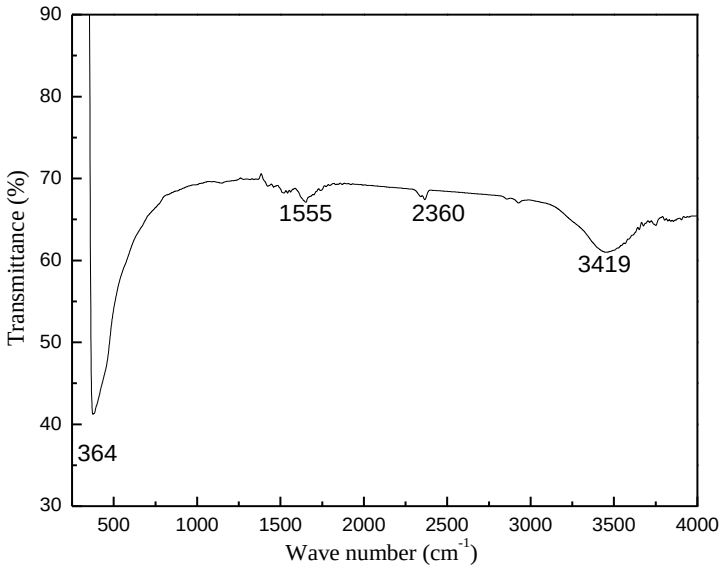

Figure 3: FTIR spectrum of undoped CaF_2 nanoparticles

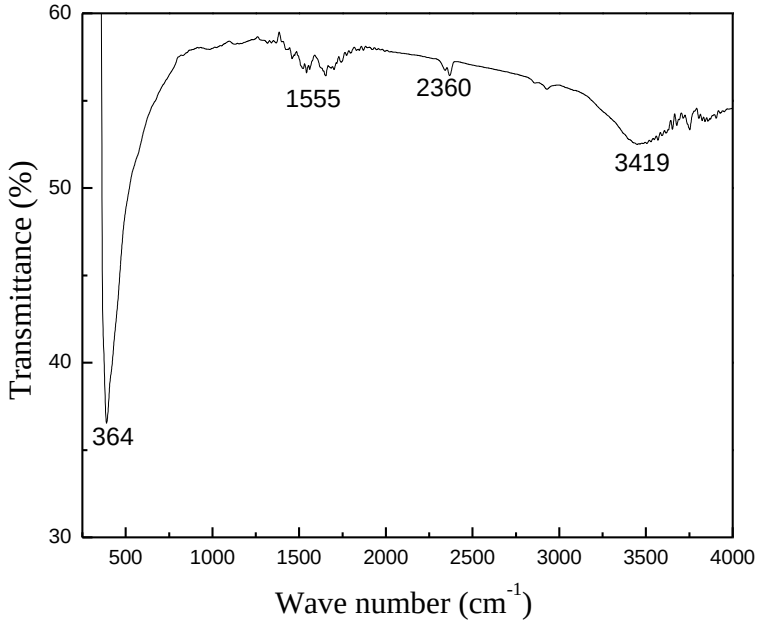

Figure 4: FTIRspectrum of Dy doped CaF_2 nanoparticles

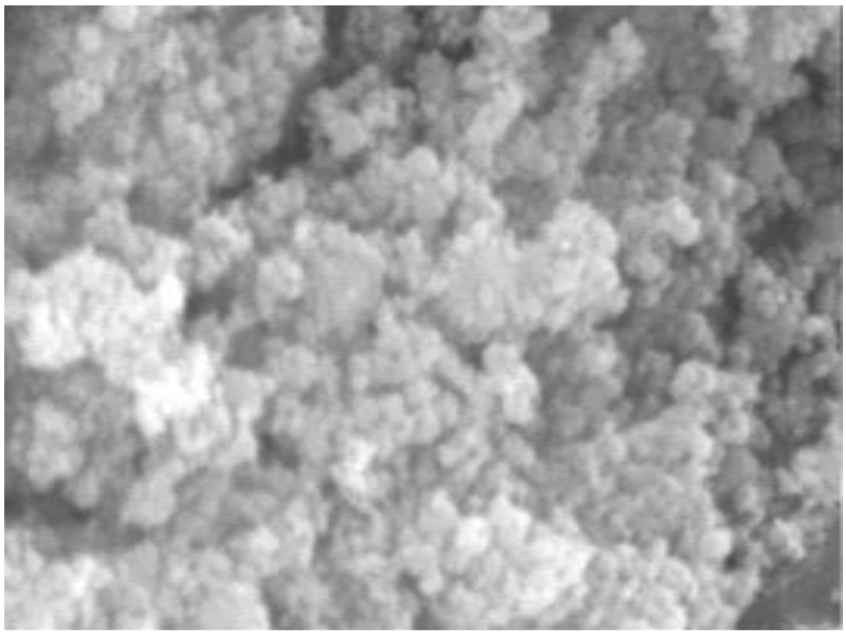

Figure 5: SEM photographs of undopednanocrystalline CaF_2

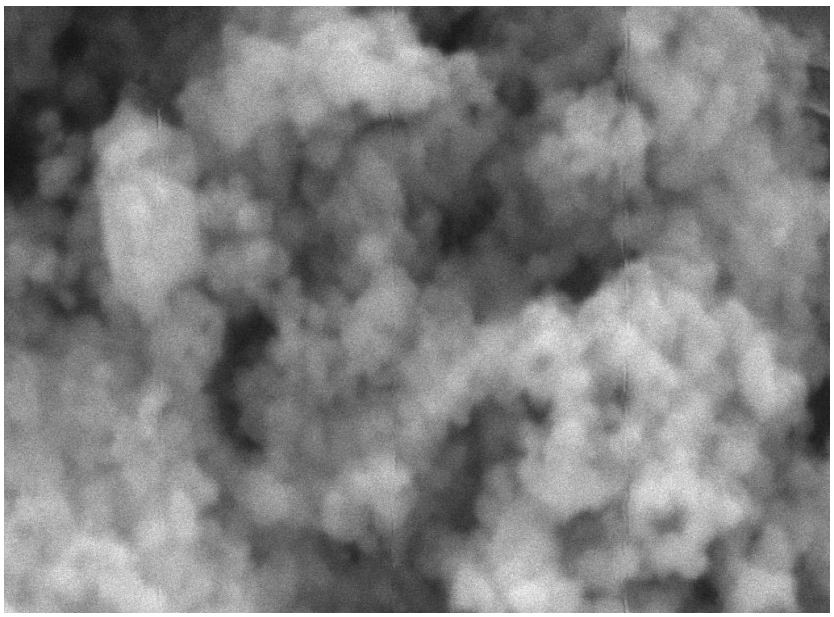

Figure 6: SEM picture of Dy doped nanoparticles

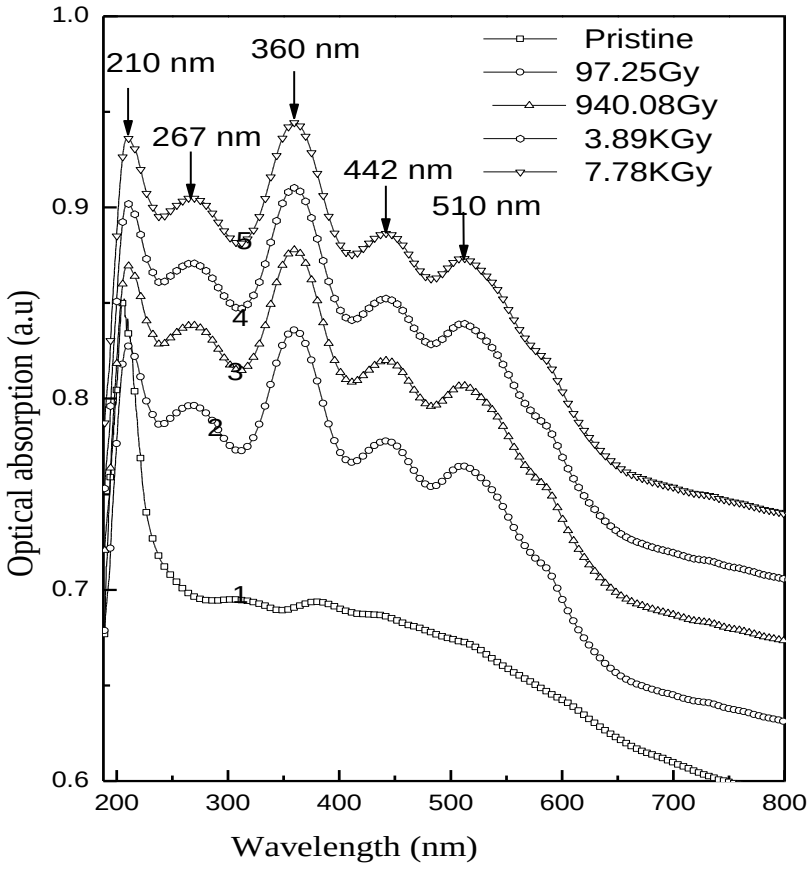

Figure 7: Optical absorptionspectrum of pure CaF_2 nanoparticles

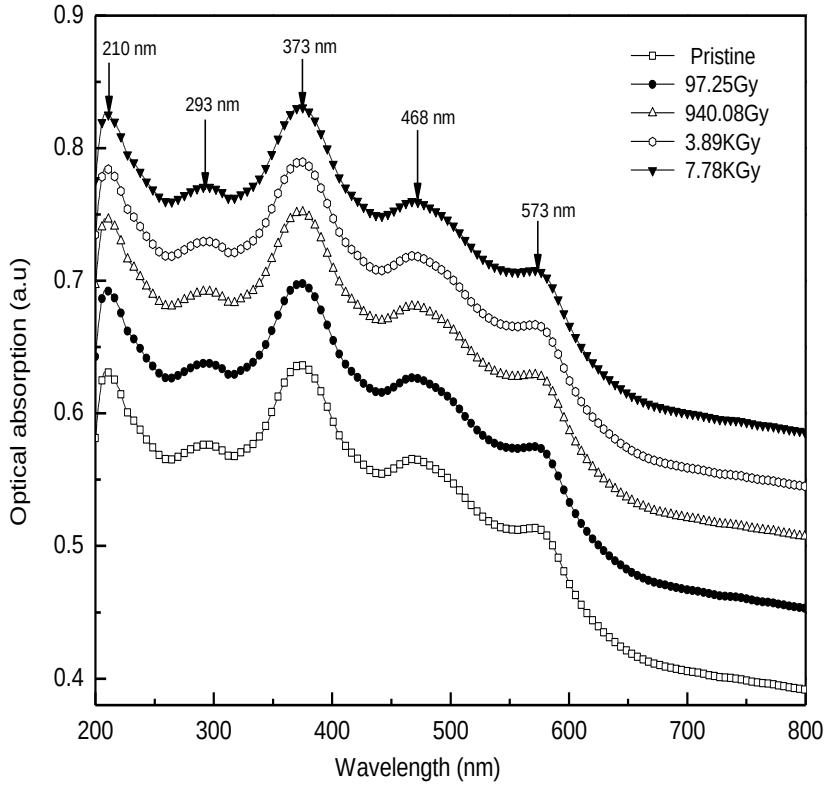

Figure 8: Optical absorptionspectrum of CaF_2: Dy nanoparticles

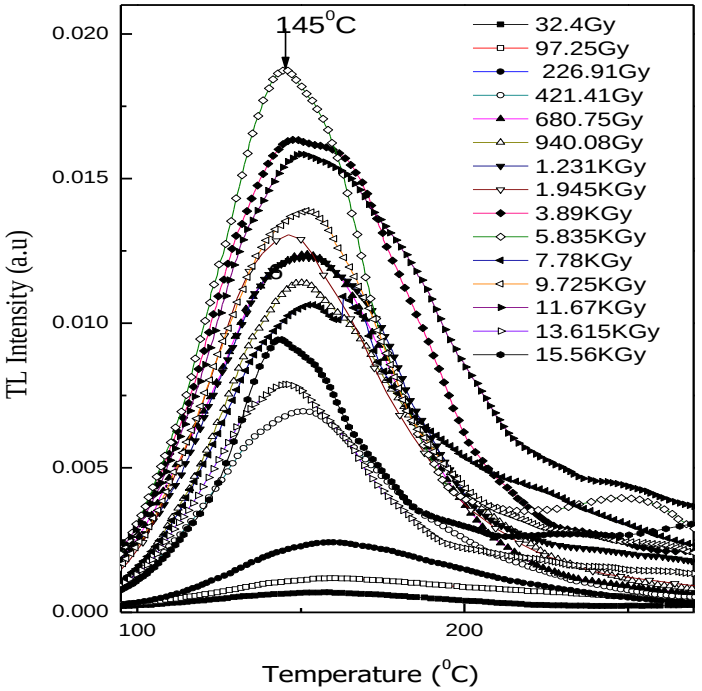

Figure 9: TL spectrum of Dy doped nanocrystalline CaF_2

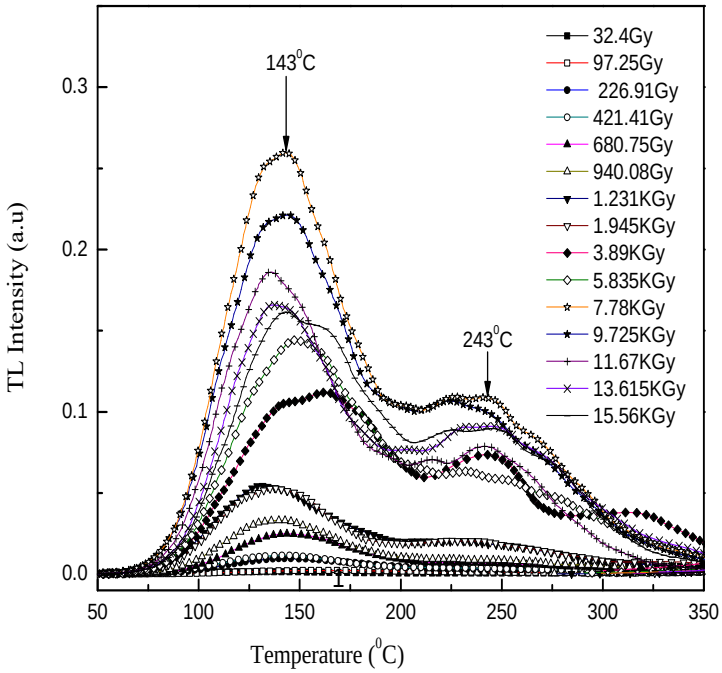

Figure 10: TL spectrum of Dy doped nanocrystalline CaF_2