Spectroscopic studies of γ -rayed $\text{CaF}_2\text{:Sr}$

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ABSTRACT

Optical absorption spectra of gamma irradiated (γ -rayed) Strontium (Sr) doped Calcium fluoride (CaF_2) single crystals showed a prominent absorption peak at ~ 370 nm and two weak ones at ~ 463 and 524 nm. At higher γ -dose the two weak peaks merged into a broad one at ~ 520 nm. The Photoluminescence (PL) spectra showed a prominent emission at ~ 394 nm when the crystals were excited at ~ 240 nm. The excitation of samples at 370 nm showed strong emission at ~ 530 nm with a shoulder at ~ 465 nm. The optical absorption and PL intensities were found to increase with γ -dose. However, the optical absorption and PL intensities of $\text{CaF}_2\text{:Sr}$ are found to be less than those of undoped CaF_2 single crystals.

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1. Introduction

Study of radiation induced defects in inorganic insulators has become a subject of rapidly growing interest in the past few years. Pure alkaline-earth halides are transparent from far ultraviolet to far infrared region. Chemical impurities when incorporated in the alkaline-earth halides even in parts-per-million show their absorption bands in the normally transparent spectral region. Also, defects produced by irradiation of samples with high energetic radiations invariably give rise to absorption bands towards longer wavelength side of the ultraviolet region or in the region of normal transparency. In this respect CaF_2 is an ionic crystal with a cubic structure in the space group Fm-3m . The transmission range of CaF_2 is $190\text{--}1100$ nm. It leads to a variety of applications. These applications range from infrared monochromators [1] to lenses and windows. CaF_2 has been considered as a prime candidate for use as laser windows at both short and long wavelengths [2]. Its thermal and mechanical sensitivity led to strengthening of material without degrading the optical performance over its transparent range [3]. CaF_2 surfaces are highly resistant to water adsorption at room temperature. Earlier CaF_2 was used in thin film form as antireflection coating on glass lenses [4]. Much of the earlier research on CaF_2 was centered on studies concerning the determination of the electronic structure of CaF_2 and color-center phenomena. The concentration and

distribution of extrinsic defects in CaF_2 crystal influence the absorption properties and homogeneity of the refractive index [5]. Rare earth (RE) doped CaF_2 is well studied. The dominating luminescence features in CaF_2 samples investigated are found to belong to RE impurities in their RE^{3+} charge state. It has been shown that RE^{2+} ions are stable only if the ground state of the RE^{2+} ion is well below the edge of the conduction band. Charge transfer in the form of capturing an excited valence band electron by a RE^{3+} ion is proved to convert a RE^{3+} ion into a RE^{2+} ion [6]. However, reports on radiation induced changes of optical properties of CaF_2 single crystals doped with elements like Magnesium (Mg), Strontium (Sr) are very few. Gamma irradiation of $\text{CaF}_2\text{:Sr}$ has shown that the radiation stability of a system is an order of magnitude less than that of undoped CaF_2 . Also, the probability of generation of stable radiation defects is found to be reduced [7–9]. In the present paper optical absorption and PL results of γ -irradiated Sr doped CaF_2 single crystals are presented. The effect of Sr doping on optical absorption and PL intensity and their variation with γ -dose are discussed.

2. Experimental details

Sr doped (1 mol%) CaF_2 single crystals grown by Bridgman technique were procured from Bhabha Atomic Research Center, Mumbai. The procured crystals were of 10 mm diameter and 20 mm length. Crystal slices of ~ 1 mm thickness were cleaved from the bulk crystals and used for studies. The crystal slices were polished to high optical transparency. The structure of the procured crystals was confirmed by X-ray diffraction studies.

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Fig. 1. Powder X-ray diffraction pattern of Sr doped CaF_2 single crystals.

Fig. 2. Optical absorption of γ -rayed Sr doped CaF_2 single crystals.

Due to limitations of single crystal XRD facility, powder X-ray diffraction pattern of the samples was recorded for the studies. The single crystals of CaF_2 were ground into a fine powder and characterized by powder XRD using PA analytical XPert PRO diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$) in the scan range 10° – 90° . All the crystal slices were annealed at 500°C for 2 h. The annealed samples were irradiated with γ -rays from a Co^{60} source for doses ranging from 97 Gy to 9.72 kGy at room temperature. The irradiated samples were subjected to optical absorption measurements in the wavelength range 190–900 nm using JASCO V-570 UV/Vis/NIR spectrophotometer at room temperature. The PL emission spectra of the samples were recorded at room temperature using a spectrofluorometer (Jobin Yvon Fluorolog 3) equipped with a 450 W Xenon lamp as an excitation source.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns (PXRD) of Sr doped CaF_2 . XRD peaks obtained were indexed and it resulted in a cubic phase of the fluorite type structure with space group $\text{Fm}\bar{3}\text{m}$. The pattern was compared with JCPDS-772096 [10]. It was found to match exactly with those reported in the literature [11,12]. Thus the XRD pattern confirmed the cubic crystallinity of the procured samples. The displayed peaks correspond to $\langle h k l \rangle$ values (111), (220), (311), (400), (311) and (422). Using the $\langle h k l \rangle$ values the lattice constant (a) of the sample was calculated. The average value of lattice constant was found to be $5.45 \text{ \AA}$.

The optical absorption spectra of pristine and γ -irradiated Sr doped CaF_2 crystals are recorded at room temperature. They are shown in Fig. 2. The absorption spectra is measured in the wavelength range 190–900 nm. However, no absorption bands were found in the shorter $5.45 \text{ \AA}$ wavelength (higher frequency) range i.e. below 200 nm. The pristine samples showed minimal absorption indicating the defect free state of the crystals. The irradiated crystals showed a prominent absorption peak at $\sim 370 \text{ nm}$ and three weak ones at ~ 238 , 463 and 524 nm. The optical absorption increased with increase in γ -dose as shown in Fig. 3. The two peaks at 463 and 524 nm merged into a broad one at $\sim 520 \text{ nm}$ when the dose was increased to $\sim 9.725 \text{ kGy}$. To understand the observed optical spectra, it is important to compile spectroscopic information on defects identified in CaF_2 crystals from literature. Major sources of luminescence in CaF_2 crystals are F and F-aggregate centers created by irradiation,

Fig. 3. Variation of Optical absorption with γ -dose for Sr doped CaF_2 single crystals.

oxygen defects present in the fluorite lattice and rare earth ion impurities [13]. It is known that ultrapure CaF_2 crystals are not sensitive to low dose of γ -rays to form color centers. However, at high γ -doses CaF_2 crystals are reported to form F-centers at room temperature [14]. The F-center is a fluoride ion vacancy binding one electron. The electronic structure of the F-center has shown that the ground state of the $1s$ wave function of the F-center is restricted to the anion vacancy. The F-center absorption correspond to an electronic excitation from $1s$ state to $2p$ state. γ -irradiation produces free electrons. These electrons when get trapped at negative ion vacancies form F-centers. The F-center absorption peak in CaF_2 is reported to be at 375 nm [15,16]. However, considerable deviations in the absorption spectra are reported for crystals studied by different workers depending upon the nature of impurities, method of preparation and other varying factors. Hence, the absorption peak at 370 nm in the present study is attributed to F-center generated in Sr doped CaF_2 crystals during γ -irradiation. The absorption band at 238 nm is assigned

to a center associated with an electron trapped by a Ca^{2+} interstitial as explained by Scouler and Smakula [17].

Literature reveals that an absorption band at 460 nm in irradiated CaF_2 is due to a hole connected with neutral fluorine atoms in interstitial positions (H centers) located in the center of the cube formed by the sublattice of eight fluorine ions [14]. Hence, the 463 nm band is attributed to traps of H-center. In Sr doped CaF_2 crystal the doped Sr^{2+} ions ($R=1.4 \text{ \AA}$) substitute some of the Ca^{2+} ions ($R=1.26 \text{ \AA}$) in the CaF_2 lattice. This results in the local elastic deformation in the CaF_2 lattice. It is reported that the absorption spectrum of pure CaF_2 crystals consists of a peak at 520 nm due to M-center [18]. M-center consists of a pair of adjacent F-centers. However, in Sr doped CaF_2 due to local deformation of the lattice the M-center gets perturbed. This results in a slight shift of M-center absorption peak [19,20]. Hence, the 524 nm peak in the present study is attributed to perturbed M-center.

High energy irradiation increases the concentration of traps for electrons and holes. The increase in the intensity of optical absorption peaks with γ -dose indicates the increase of color centers due to increase in traps. Higher γ -dose is found to produce more defects. The optical absorption studies were also carried out on undoped γ -irradiated CaF_2 crystals simultaneously under identical conditions and the results are presented elsewhere. From these studies it is observed that undoped γ -irradiated CaF_2 crystals produce a prominent and strong absorption peak corresponding to the F-center at $\sim 374 \text{ nm}$ along with three weak ones at ~ 456 , 523 and 623 nm corresponding to H, M and R-centers, respectively. The intensity of absorption peaks was found to increase with increase in γ -dose. However, there was no significant change in peak position and shape with increase in dose. When the absorption spectra of undoped and Sr doped CaF_2 crystals are compared it is found that optical absorption in Sr doped crystals is reduced marginally. This shows that Sr does not enhance the optical absorption of CaF_2 crystals unlike rare earth elements which exhibit pronounced absorption with a number of absorption peaks characteristic of RE ions [21].

Fig. 4 shows the photoluminescence spectrum of γ -irradiated Sr doped CaF_2 single crystals under 240 nm excitation. A strong PL emission is observed with a peak at $\sim 394 \text{ nm}$. However, when the samples were excited at 370 nm a prominent emission was observed at $\sim 530 \text{ nm}$ besides a shoulder at 465 nm (Fig. 5). The PL intensity of 394 and 530 nm peaks increased with increase in γ -dose as shown in Fig. 6. The PL studies of undoped CaF_2 were also carried by the authors and results are discussed elsewhere. The PL results of undoped and Sr doped samples are compared. From the studies it is found that excitation of undoped CaF_2 samples at 240 nm showed PL emission at 390 nm whereas the Sr doped CaF_2 crystals have shown the PL emission at 394 nm for the same excitation as mentioned above. Thus there is small shift in the emission peak in Sr doped samples. Similar shift is observed in the emission wavelength corresponding to the 465 nm emission wavelength as explained below. Undoped CaF_2 crystals showed PL emission at $\sim 460 \text{ nm}$ whereas the Sr doped one showed similar PL emission at $\sim 465 \text{ nm}$. This shows that similar defects are created in undoped and Sr doped samples. The PL intensities of the emission peaks in Sr doped samples are less than that of undoped CaF_2 . This indicates that Sr doping reduces the emission efficiency of CaF_2 . In CaF_2 , the aggregation of point defects produced by energetic radiation plays an important role in the emission and absorption of energy. It is well established that irradiation of CaF_2 leads to the formation of F and F-aggregate centers in it. When the sample containing F-center is excited with UV light, due to electronic transitions in the sample the energy absorbed by the defects gets released in the form of photons leading to PL emission. The emission at 394 nm in the present studies is attributed to F-center [22]. It is well known that the PL spectra greatly depend on the nature of the dopants, their location in the host lattice and

Fig. 4. Photoluminescence spectrum of Sr doped CaF_2 single crystals for 240 nm excitation.

Fig. 5. Photoluminescence spectrum of Sr doped CaF_2 single crystals for 370 nm excitation.

charge compensating ions. The nature of the luminescence centers is a function of the host lattice, the dopant concentration and the thermal treatment of the samples. Because of the change in atomic radius the lattice of CaF_2 is slightly distorted. The 465 nm peak in the present study may be assigned to host lattice emission as it occurs in both undoped and Sr doped CaF_2 crystals [23]. The 530 nm emission in the present study is attributed to aggregate centers perturbed by the strontium ions in the lattice of CaF_2 . The PL emission at 390 nm in pure CaF_2 crystals is assigned to F-center. This indicates that doping the CaF_2 crystal with Sr results in an emission band in the higher wavelength region. The intensity of

Fig. 6. Variation of photoluminescence intensity with γ -dose for Sr doped CaF_2 single crystals.

emission increases with γ -dose. Many investigators have reported that as irradiation increases, some kind of coagulation of colloidal particles takes place with bigger particles being produced at heavier irradiations. As a consequence peak the emission intensity increases [24,25]. The broad feature of the emission peaks indicates the high defect concentration responsible for the PL emission.

4. Conclusion

Optical absorption studies of γ -rayed Sr doped CaF_2 crystals showed generation of F and F-aggregate centers. The PL spectra

revealed the presence of radiation induced defects in the irradiated crystals. The doping of CaF_2 with 1 mol% Sr does not create new defects. However, the optical absorption and PL intensities are reduced in Sr doped CaF_2 crystals. Hence, Sr doping decreases the optical absorption and the emission efficiency of CaF_2 crystals.

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