Optical absorption and thermoluminescence studies in 100 MeV swift heavy ion irradiated CaF_2 crystals

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ABSTRACT

Pure and Ytterbium (Yb) doped Calcium fluoride (CaF_2) single crystals were irradiated with 100 MeV Ni^{7+} ions for fluences in the range 5×10^{11} – 2.5×10^{13} ions cm^{-2} . The irradiated crystals were characterized by Optical absorption (OA) and Thermoluminescence (TL) techniques. The OA spectra of ion irradiated pure CaF_2 crystals showed a broad absorption with peak at ~ 556 nm and a weak one at ~ 220 nm, whereas the Yb doped crystals showed two strong absorption bands at ~ 300 and 550 nm. From the study of OA spectra, the defect centers responsible for the absorption were identified. TL measurements of Ni^{7+} ion irradiated pure CaF_2 samples indicated a strong TL glow with peak at ~ 510 K. However, the Yb doped crystals showed two TL glows at ~ 406 and 496 K. The OA and TL intensity were found to increase with increase of ion fluence upto 1×10^{13} ions cm^{-2} and thereafter it decreased with further increase of fluence. The results obtained are discussed in detail.

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1. Introduction

Defects in alkali halides under various types of irradiations are studied extensively during the past few decades. A wide range of potential applications exists for these materials and the development of various new techniques is directly related to the progress in this field. Irradiations with energetic ion beams play a vital role in the field of defect studies in inorganic materials. The energetic ions lose their energy during their passage through the material. This energy is spent either in displacing atoms of the sample by elastic collisions or exciting the atoms by inelastic collisions. Low energy ions up to a few hundred KeV have been used in the modification of surface and interface. The loss of energy by the ions in exciting or ionizing the atoms by inelastic collisions is called as electronic energy loss. Electronic stopping is dominant at high energies where the displacement of atoms due to elastic collisions is insignificant. Swift heavy ions (SHI) irradiation is a technique for modification of structural, optical and electrical properties of solids due to intense interaction of incident ions with the target atoms [1–3].

Inorganic fluoride materials are found to be sensitive to SHI irradiation with generation of metallic inclusions and induction of tracks [4,5]. Among the popularly known fluorides, CaF_2 single

crystals are excellent optical window materials because of their high transmissivity over a wide range from UV to IR region of the electromagnetic spectrum besides their use in dosimetry [6,7]. Nevertheless, there is much current interest in crystalline CaF_2 due to its use in deep UV lithography [8]. It is well established that when ionic crystals are irradiated with energetic radiations, they give rise to color centers [9]. These centers have been identified from various experimental techniques like optical absorption, luminescence, Raman and electron spin resonance [10]. Rare earth doped CaF_2 exhibits a variety of novel properties. When CaF_2 is doped with trivalent rare-earth (RE^{3+}) ions, the excess of charge is compensated by interstitial F^- ions, leading to several kinds of luminescent centers [11]. At low RE^{3+} ion concentrations, the dopant ions mainly form isolated centers whereas at higher concentrations, they aggregate and form complex clusters [12–14]. In the present work, OA and TL behavior of pure and ytterbium (Yb) doped CaF_2 single crystals irradiated with 100 MeV Ni^{7+} ions for fluences in the range 5×10^{11} – 1×10^{13} ions cm^{-2} are studied at room temperature (RT) and the results obtained are discussed.

2. Experimental

Pure and 3 mol% Yb doped CaF_2 single crystals were procured from Shanghai Institute of Optics and Fine Mechanics, China. CaF_2 crystal slices of about 1 mm thickness were cleaved from the big block grown along [1 1 1] direction. The cleaved slices were

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cut into number of small pieces of size 5×5 mm using a high precession saw with a diamond coated blade. The samples were irradiated with 100 MeV Ni^{7+} ions for fluences in the range 5.0×10^{11} – 2.5×10^{13} ions cm^{-2} using 15 UD pelletron at Inter University Accelerator Center, New Delhi. The irradiated samples were subjected to optical absorption measurements in the wavelength range 189–900 nm using V-570 UV/VIS/NIR spectrophotometer at RT. The TL studies of irradiated samples were carried out using a TL reader (Nucleonix system) by heating the sample from room temperature to 350 °C at a constant heating rate of 10 K s^{-1} and the resulting TL glow curves were recorded.

3. Results and discussion

Fig. 1 shows the optical absorption spectra of the pristine and Ni^{7+} ion irradiated CaF_2 crystals in the range 189–900 nm. The pristine CaF_2 sample showed minimal absorption throughout the spectral region. The ion irradiated samples exhibited a strong absorption with a peak at ~ 556 nm. Also, the figure indicates the possibility of a weak absorption at ~ 375 nm. The optical absorption was found to increase with increase of Ni^{7+} ions fluence till 1.0×10^{13} ions cm^{-2} and thereafter it decreases with further increase of fluence as shown in Fig. 3. However, the peak positions of these color centers remained unaltered with ion fluences. Literature on O^{16} and Pb^{208} ions irradiated [3] and neutron irradiated [15] CaF_2 crystals showed similar absorption spectra with a prominent absorption peak at ~ 550 nm. The results in the present study are in good agreement with the literature.

Cooke and Bennett reported that irradiated pure CaF_2 single crystals show absorption at 320, 376, 525 and 670 nm due to the formation of V_K -center, F-center, M-center and R-center respectively [16]. However, the absorption band at ~ 550 nm was also reported to be associated with the formation of M-center [16,17]. The 556 nm absorption peak in the present studies may be attributed to M-center. The weak absorption at ~ 375 nm indicates the possibility of formation of F-centers with low concentration.

Fig. 2 represents the optical absorption spectra of pristine and Ni^{7+} ion irradiated Yb (3 mol%) doped CaF_2 single crystals. Two prominent absorption bands with peak positions at ~ 300 and 550 nm are observed. The pristine sample shows weak absorption. The absorption at these wavelengths increased with Ni^{7+} ions fluence up to $\sim 1.0 \times 10^{13}$ ions cm^{-2} and thereafter it decreased with

Fig. 2. Optical absorption spectra of 100 MeV Ni^{7+} ion irradiated Yb doped CaF_2 single crystals.

further increase of fluence as shown in Fig. 3. It is observed that for lower fluence, the 550 nm band is stronger than 300 nm band. However, with increase in fluence, the 300 nm band grows and becomes equally strong as 550 nm band. On comparison of the absorption spectra of pure and doped samples, it is found that the 550 nm band in Yb doped CaF_2 samples is stronger than those observed in pure samples.

The absorption band at ~ 300 nm is attributed to Yb^{3+} ions in the doped CaF_2 samples. Kaczmarek et al. observed a similar absorption band at ~ 310 nm in Yb doped γ -irradiated CaF_2 crystals and attributed it to the Yb^{3+} ions [18]. 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 [19,20]. The replacement by Yb^{3+} gives a contribution to the creation of charge compensation, such as an interstitial F^- ion. The probability of formation of Yb^{3+} ions is more than that of Yb^{2+} ions in the as grown

Fig. 1. Optical absorption spectra of 100 MeV Ni^{7+} ion irradiated pure CaF_2 single crystals.

Fig. 3. Variation of peak position of optical absorption with Ni^{7+} ion fluence.

crystal and it may be explained based on the ionic radii of Yb. The ionic radii of Yb^{3+} and Yb^{2+} are 0.112 and 0.128 nm respectively in the eightfold coordination, while the ionic radius of Ca^{2+} in the same coordination is 0.126 nm [21]. This shows that the smaller Yb^{3+} ion can substitute for Ca^{2+} ion in CaF_2 more easily than the larger Yb^{2+} ion. The number of Yb^{3+} ions present during the crystal growth is much higher than the number of Yb^{2+} ions since for the doping of Yb ions a mixture of YbF_3 and CaF_2 powders was used.

Thermoluminescence glow curves of ion irradiated pure CaF_2 crystals are shown in Fig. 4. A strong and prominent TL glow was observed at ~ 510 K. The TL intensity of these glow peaks are found to increase with increase of Ni^{7+} ions fluence up to 1.0×10^{13} ions cm^{-2} and thereafter it decreased with further increase of fluence indicating the saturation of defects in the system. Variation of TL intensity is shown in Fig. 6. TL in pure CaF_2 crystals is found to arise due to radiative recombination of released electrons and holes at suitable lattice sites or stable defect sites. When CaF_2 crystals are subjected to high energetic radiations, electrons rise to the conduction band and get subsequently trapped by certain defect centers. Such defect centers with captured electrons form color centers. There exist some stable trapping states, formed due to the movement of trapped holes. When the crystal is heated most of the electron traps become unstable and undergo radiative recombination with holes at suitable lattice sites and emit the stored energy thereby accounting for TL emission. It is well established that high energy irradiation increases the concentration of electrons and hole traps due to lattice distortion and subsequently they annihilate during later stages. In the present study this is revealed by the increase in TL intensity with increase of ion fluence. Considerable deviations in the glow peak temperatures are reported for pure CaF_2 samples by different workers depending upon the crystal growth conditions, irradiation atmosphere and heating rate [22–26]. Rao reported that electron irradiated pure CaF_2 single crystals showed TL glow at ~ 513 K [23]. Sangeeta et al. reported that γ -irradiated pure CaF_2 single crystals showed TL glow with peak positions at ~ 513 K [24]. Manrique et al. proved that electron irradiated CaF_2 crystals show TL glows at 100 and 250 K [25]. Fukuda showed that pure CaF_2 crystals exposed to UV ray radiation exhibit two glows at ~ 350 and 450 K [26]. The TL glow at 510 K in the

present study is attributed to recombination of F-center and/or M-centers electrons with holes at suitable lattice sites.

Fig. 5 shows the TL glow curves of ion irradiated Yb doped CaF_2 crystals. Two strong and prominent TL glows were observed at ~ 406 and 496 K. Also Figs. 4 and 5 indicate another glow in the high temperature region at $\sim 350^\circ\text{C}$. However, due to experimental limitations it could not be recorded with the present instrument. Variation of TL intensity is shown in Fig. 6. The TL glow at ~ 406 K in the Yb doped crystals may be attributed to Yb ions. Merz and Pershan observed a TL glow at ~ 403 K in electron irradiated Yb

Fig. 5. TL glow curves of 100 MeV Ni^{7+} ion irradiated Yb doped CaF_2 single crystals.

Fig. 4. TL glow curves of 100 MeV Ni^{7+} ion irradiated pure CaF_2 single crystals.

Fig. 6. Variation of TL glow peak intensity with Ni^{7+} ion fluence.

doped CaF_2 single crystals [27]. According to the Merz and Pershan model of rare earth (RE) doped CaF_2 , the Yb ions are stable in their trivalent state. Irradiation reduces the trivalent (Yb^{3+}) ions to the divalent state (Yb^{2+}) through an electron capture. On heating, the trapped hole Centers produced during irradiation become mobile and migrate in the lattice. When such Centers approach a Yb^{2+} ion, they recombine with trapped electrons leaving the Yb ions in an excited Yb^{3+} state.

4. Conclusions

Swift heavy Ni^{7+} ion irradiated pure CaF_2 single crystals showed a strong absorption ~ 556 nm and it is attributed to M-center. Yb doped SHI irradiated CaF_2 crystals exhibited an additional absorption with a peak at ~ 300 nm due to Yb^{3+} ions. A strong TL glow is observed in pure as well Yb doped sample at ~ 510 K. It is attributed to the recombination of F-center and/or M-centers with hole centers. The TL glow at 406 K in the Yb doped samples indicated the charge transition of Yb ions from Yb^{3+} to Yb^{2+} state on irradiation and back to the triply charged state on subsequent heating.

References

- [1] I.V. Vorobyova, J. Kopniczky, MeV-atomic-ion-induced tracks on the surface of CaF_2 single crystal, *Nucl. Instr. Meth. Phys. Res. B* 237 (2005) 593–601.
- [2] Ning Yu, Michael Nastasi, Kurt E. Sickafus, Kazuhiro Yasuda, Joseph R. Tesmer, In situ study of ion-beam induced lattice damage in calcium fluoride crystals, *Nucl. Instr. Meth. Phys. Res. B* 127/128 (1997) 591–595.
- [3] M. Boccanfuso, A. Benyagoub, K. Schwartz, C. Trautmann, M. Toulemonde, Study of the damage produced in CaF_2 by swift heavy ion irradiation, *Nucl. Instr. Meth. Phys. Res. B* 191 (2002) 301–305.
- [4] J. Jensen, A. Dunlop, S. Della-Negra, Microscopic observations of metallic inclusions generated along the path of MeV clusters in CaF_2 , *Nucl. Instr. Meth. Phys. Res. B* 146 (1998) 399–404.
- [5] J. Jensen, A. Dunlop, S. Della-Negra, Tracks induced in CaF_2 by MeV cluster irradiation, *Nucl. Instr. Meth. Phys. Res. B* 141 (1998) 753–762.
- [6] K.E. Sickafus, H.J. Matzke, K. Yasuda, P. Chodak, R.A. Verrall, P.G. Lucuta, R.H. Andrews, A. Turos, R. Fromknecht, N.P. Baker, Radiation damage effects in cubic-stabilized zirconia irradiated with 72 MeV I^+ ions, *Nucl. Instr. Meth. Phys. Res. B* 141 (1998) 358–365.
- [7] D.E. McCarthy, Transmittance of Optical Materials from 0.17 μ to 3.0 μ , *Appl. Opt.* 6 (1967) 1896–1898.
- [8] R.A. Smith, F.E. Jones, R.P. Chasmar, The Detection and Measurement of Infrared Radiation, Oxford University Press, London, 1957. p. 341.
- [9] N. Senguttuvan, M. Aoshima, K. Sumiya, H. Ishibashi, Oriented growth of large size calcium fluoride single crystals for optical lithography, *J. Crystal Growth* 280 (2005) 462–466.
- [10] A. Smakula, Color centers in calcium fluoride, barium fluoride crystals, *Phys. Rev.* 77 (1950) 408–409.
- [11] W. Hayes, Crystals with Fluoride Structure, Clarendon, Oxford University press, London, 1974.
- [12] J. Corish, C.R.A. Catlow, P.W.M. Jacobs, S.H. Ong, Defect aggregation in anion-excess fluorites. Dopant monomers and dimmers, *Phys. Rev. B* 25 (1982) 6425–6438.
- [13] V. Petit, P. Camy, J.-L. Doualan, R. Moncorgé, Refined analysis of the luminescent centers in the $\text{Yb}^{3+}:\text{CaF}_2$ laser crystal, *J. Lumin.* 122–123 (2007) 5–7.
- [14] E. Nikiforov, A. Yu Zakharov, M. Yu Ugryumov, S.A. Kazanski, A.I. Ryskin, G.S. Shakurov, Crystal fields of hexameric rare-earth clusters in fluorites, *Phys. Solid State* 47 (2005) 1431.
- [15] S.A. Kazanski, A.I. Ryskin, A.E. Nikiforov, A.Y. Zaharov, M.Y. Ougrumov, G.S. Shakurov, EPR spectra and crystal field of hexamer rare-earth clusters in fluorites, *Phys. Rev. B* 72 (2005) 014127–014138.
- [16] D.W. Cooke, B.L. Bennett, Optical absorption and luminescence of 14-MeV neutron-irradiated CaF_2 single crystals, *J. Nucl. Mater.* 321 (2003) 158–164.
- [17] W. Hayes, R.F. Lambourn, Production of F and F-aggregate centres in CaF_2 , and SrF_2 by irradiation, *Phys. Stat. Sol. (b)* 57 (1973) 693–699.
- [18] Slawomir M. Kaczmarek, TaijuTsuboi, Masahiko Ito, Georges Boulon, Grzegorz Leniec, Optical study of $\text{Yb}^{3+}/\text{Yb}^{2+}$ conversion in CaF_2 crystals, *J. Phys. Condens. Matter* 17 (2005) 3771–3786.
- [19] J. Kirton, S.D. McLaughlan, Correlation of electron paramagnetic resonance and optical-absorption spectra of $\text{CaF}_2:\text{Yb}^{3+}$, *Phys. Rev.* 155 (1967) 279–284.
- [20] U. Ranon, J.S. Hyde, Electron–nuclear-double-resonance and electron-paramagnetic-resonance analysis of the ytterbium–fluorine superhyperfine interaction in $\text{CaF}_2:\text{Yb}^{3+}$, *Phys. Rev.* 141 (1966) 259–274.
- [21] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. A* 32 (1976) 751–767.
- [22] D.R. Rao, Thermoluminescence of electron-irradiated CaF_2 , *Phys. Stat. Sol. (a)* 22 (1974) 343–348.
- [23] D.R. Rao, On the analysis of thermoluminescence glow pattern, *Phys. Stat. Sol. (a)* 22 (1974) 337–341.
- [24] Sangeeta, S.C. Sabharwal, B. Ghosh, M.K. Gupta, Thermoluminescence from Europium doped calcium fluoride crystals, *Phys. Stat. Sol. (a)* 121 (1990) 657–665.
- [25] J. Manrique, S. Angulo, M.P. Pardo, R. Gastesi, A. De la Cruz, A. Perez, Thermoluminescence spectra of natural CaF_2 irradiated by 10 MeV electrons, *Radiat. Meas.* 41 (2006) 145–153.
- [26] Y. Fukuda, Thermoluminescence in calcium fluoride doped with terbium and gadolinium ions, *Radiat. Meas.* 43 (2008) 455–458.
- [27] J.L. Merz, P.S. Pershan, Charge conversion of irradiated rare-earth ions in calcium fluoride, *J. Phys. Rev.* 162 (1967) 217–235.