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Effect of Ca colloids on in-situ ionoluminescence of CaF_2 single crystals

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ABSTRACT

This work reports in-situ ion beam induced luminescence (IBIL) of CaF_2 crystals using 2-MeV proton excitation. The in-situ IBIL experiments were carried out at pelletron Tandem accelerator at the National Center for Physics, Islamabad, Pakistan. The spectrophotometry UV–Visible analysis revealed that proton beam induced Ca colloids. Their concentration increases with fluence, and the mean size reaches about 10 nm. The IBIL results showed a wide luminescence band extended from 230 to 450 nm and a new band at about 210 nm, attributed to the self-trapped exciton (STE) decay. It was found that the luminescence intensity increases linearly with dose. From the absorption measurements, indicating the colloid formation in CaF_2 by proton irradiation, we believe that the latter colloids are responsible for the luminescence improvement during proton beam irradiation.

1. Introduction

The point defects in alkaline earth fluoride crystals, among which calcium fluoride (CaF_2) scintillator crystal belongs, have caught the attention of many researchers. It is well established that ion beam passing through an alkaline earth fluoride materials, produces many color centers, like F (single electron trapped by a fluorine vacancy), F_2 (two nearby anion vacancies with two trapped electrons), F_3 (three anion vacancies with three trapped electrons) centers [1–7]. The absorption bands of such defects are reported in the Table 1. Studies of the point defects in CaF_2 have found applications in experimental and theoretical physics, chiefly in the environmental radiation dosimetry, optics, sensors and microelectronics [2,8]. At higher irradiation dose F centers aggregate to F_n, that leads to the colloid formation. Calcium colloid in ionic crystals has been well investigated (see [9] and references therein). Due to the technological interest, several studies were devoted to calcium colloids with nanoparticles size induced by laser light, X-ray, γ-ray, electron, neutron and ion irradiation in CaF_2 crystals [10–19]. Indeed, the presence of Ca colloids increases the luminescence intensity of the self-trapped excitons STE in CaF_2 single crystal employed in photolithography at 193 and 157 nm [20]. The main goal of the present study is exactly to demonstrate the effect of Ca colloid on the CaF_2 luminescence property. For this purpose, we used in-situ ion beam induced luminescence with 2-MeV proton excitation. UV–vis spectrophotometry is used to study the Ca colloid formation by 2-MeV proton irradiation and its evolution with fluence.

2. Materials and experiment

Samples used in this work were cut from a high-quality single crystal of calcium fluoride (CaF_2). They had a thickness of about 1.5 mm, with the main plane oriented (1 1 1), as controlled by X-ray diffraction analysis (XRD) (not shown). In order to check the Ca colloid formation, the samples were first irradiated with 2.5- and 3.5-MeV protons to fluence up to 4.0×10^{15} p/cm^2. In-situ IBIL experiments were carried out at room temperature at 5-MeV pelletron Tandem accelerator at the national center for Physics Islamabad, Pakistan. The crystal sample was positioned at 45° angle placed on the sample holder and at a distance of 3.0 cm from the collimating lens in the chamber. This direction enhanced the collimated proton ion beam from the source to focus on the crystal sample. The sample was irradiated with 2-MeV protons with different fluences ranging from 1.32×10^{14} to 3.18×10^{14} p/cm^2 with the corresponding doses D in (MGy) obtained using Eq. (1) presented in the Table 2. The accelerator chamber works as a Faraday cup to measure the total charge impinging on the crystal sample with a specified beam current of 10 nA performed at 10^6 Torr all

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Table 1
Absorption bands of point defects in CaF_2.

Crystal	Centre	Absorption band (nm) (eV)
CaF_2	F	379 3.27
	F_2	366 3.39
	F_3	670 1.85
	Colloids	550

Table 2
Irradiation parameters.

Fluence (P/cm^2)	Dose (MGy)
1.32×10^{13}	0.24
9.02×10^{13}	1.66
1.96×10^{14}	3.61
2.17×10^{14}	3.99
2.65×10^{14}	4.88
3.18×10^{14}	5.85

through the irradiation process.

$$D = 1.602 \times 10^{-13}\varphi\frac{S}{\rho} \quad (1)$$

where φ, ρ and S are respectively, the fluence (p/cm^2), density ρ = 3.18 (g/cm^3) and total stopping power. $\left(\frac{S}{\rho}\right)$ is in (MeV × cm^2/mg) deduced from SRIM calculation [21]. The value taken from a depth near the surface is 0.115 MeV × cm^2/mg. The in-situ luminescence data of each spectrum were collected in the wavelength range 200–1000 nm at room temperature in the vacuum chamber by a silica fibers ≈500 µm diameter close to the irradiated source in the beamline direction. The IBIL spectra analyses were recorded using ocean view (QE65000) spectrometer coupled to the chamber via optic fibers with 90 spectra taken at an interval of 500 µsec integrated times. The optical absorption measurements were carried out using Cintra 40 spectrophotometer, in the wavelength range 200–900 nm.

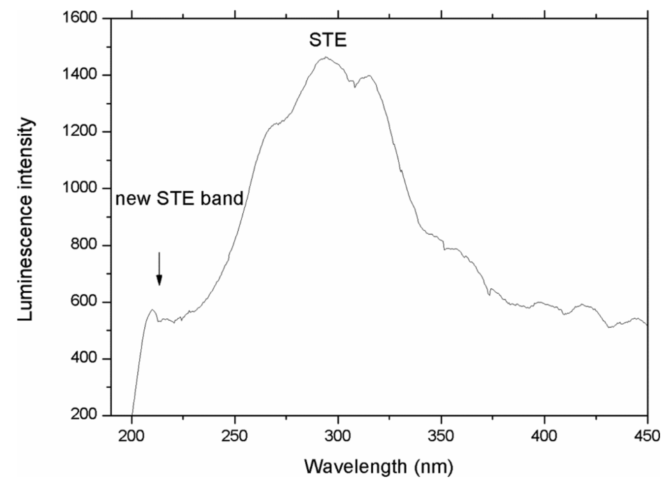

Fig. 2. IBIL spectrum recorded at low dose.

3. Results and discussions

UV–vis spectrophotometry measurements were made using an unirradiated sample as reference. We note that CaF_2 exhibits very good optical transmission in the region 200–900 nm, indicating the absence of impurities. The optical absorption spectra obtained after irradiation are depicted in the Fig. 1. From the figure, one can see four absorption bands centered at about 220, 340, 400 and 550 nm. The 220 and 340 nm absorption bands are probably due to the intrinsic defects, as suggested in our previous work [22]. The absorption bands at about 400 nm and 550 nm are well known and attributed to the F-center (electron trapped by anion vacancy) and Ca colloids [10,11,12,14].

It is clear from Fig. 1 that the absorption due to colloids (550 nm) increases rapidly with increasing energy compared to the F-center (400 nm). Moreover, for fixed energy, the absorption of colloid increases with increasing fluence and becomes predominant at high fluence. The same observation was made many years ago by Wilkins and

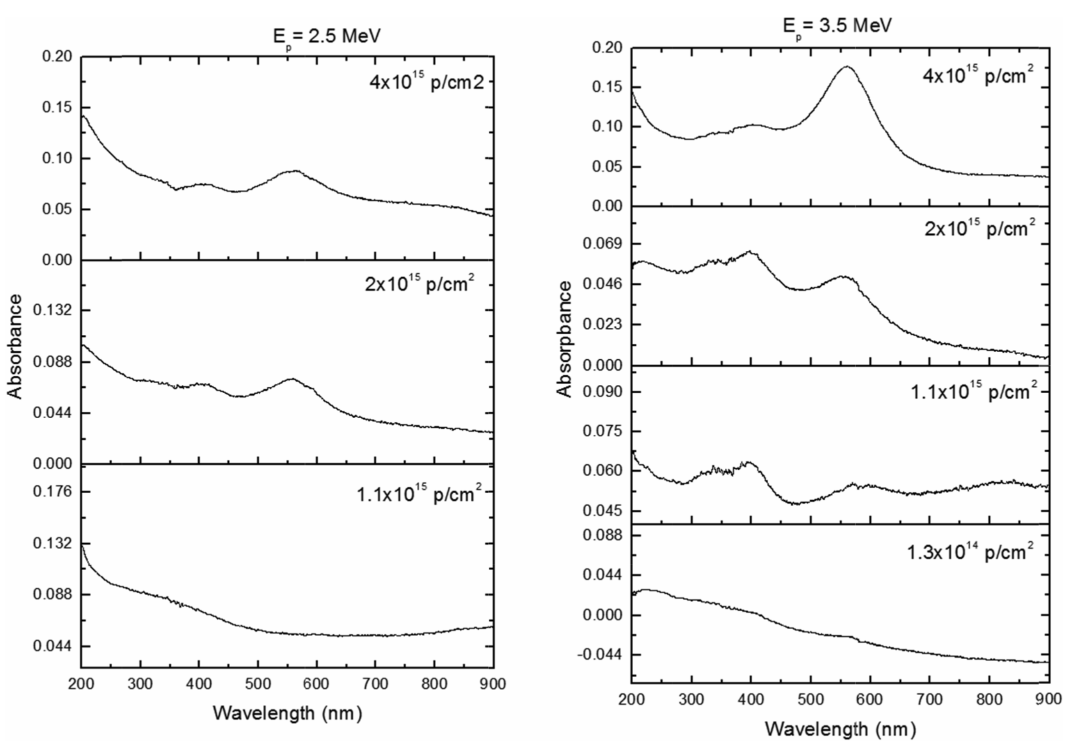

Fig. 1. Absorption spectra of CaF_2 crystals obtained after irradiation with 2.5 and 3.5 MeV at different fluences.

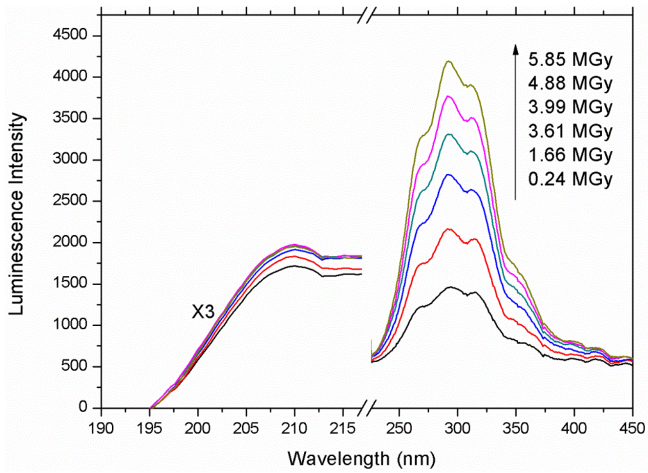

Fig. 3. IBIL spectra recorded at different doses.

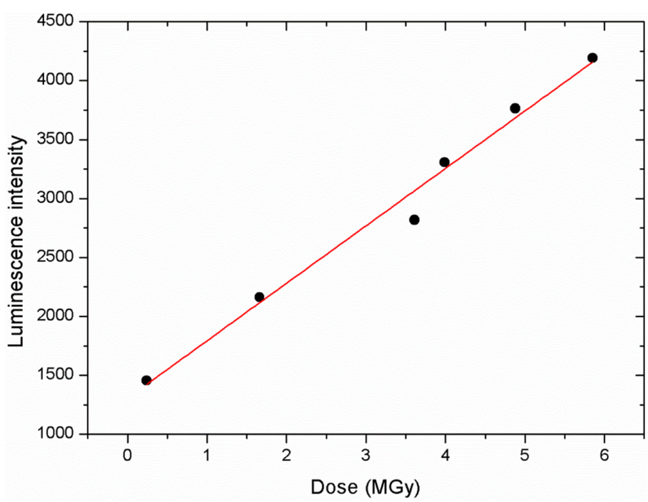

Fig. 4. Maximum intensity of the main luminescence band evolution as a function of doses. The solid line is the linear fit of the experimental data.

Bird [23] in 2.5-MeV proton irradiated calcium fluoride at higher fluence (> 1×10^{16} p $\times$ cm^{-2}). The size of such colloids can be deduced from the Orera and Alcala [24] theory. Using Mie theory, they evaluated the colloid radii as a function of positions and half widths (FWHM) of the absorption band. According to their approach, the absorption band at 550 nm with FWHM of 105 nm, obtained after 3.5-MeV irradiation up to 4×10^{15} p $\times$ cm^{-2}, corresponds to the colloid size of about 10 nm. The colloids of the same size were also observed in the electron-irradiated CaF_2 crystals [16]. According to these results, the efficiency of colloid formation in CaF_2 crystal is higher than that of the F centres, so the colloids are probably responsible for the luminescence increase under proton beam irradiation, observed in the IBIL measurements below.

Fig. 2 shows the in-situ IBIL luminescence spectrum of CaF_2 single crystal taken during 15 s corresponding to a dose of 0.24 MGy where the defects formation is very small. The spectrum shows a main characteristic line between 230 and 450 nm. It is a typical emission from a pure CaF_2 [25] and is interpreted as self-trapped exciton (STE) emission [26,27]. The STE is known as V_K + e, where V_K is a self-trapped hole, which consists of a F_2^- molecular ion with the bond axis oriented parallel to ⟨1 0 0⟩ [28]. In addition, it is interesting to mention a well-resolved emission band at about 210 nm. It can be interpreted as a new luminescence band of STE, found by Mysovsky and Radzhabov using *ab initio* calculation [29]. As it can be seen at Fig. 3, the intensity of both luminescence bands increases with increasing dose in contrast to our previous study, where the photoluminescence intensity decreases after gamma and neutrons irradiation and restored after thermal annealing [22]. It was attributed to the defect formation, which reduced the radiative decay of self-trapped exciton STE. Indeed, gamma-ray and neutron irradiation generate more F-centers compared to the Ca colloids. Cooke and Bennett suggest also that X-ray and neutrons irradiation generates mainly F and F- aggregates centers [30]. In addition, reactor neutrons induce transmutation reactions, which probably contribute to the decrease of the STE radiative decay.

Taking into account the above spectrophotometry results, we believe that the CaF_2 luminescence improvement is due to the Ca colloid formation induced by proton beam during irradiation. Furthermore, it is worthy to note the linear luminescence-dose dependent. The experimental data show a good fit to a linear equation (see Fig. 4).

4. Conclusion

Ion beam induced luminescence IBIL of CaF_2 crystals using 2-MeV proton excitation was investigated. The luminescence spectra reveal the presence of two bands: (i) a new STE band at about 210 nm, which confirms ab initio calculation of Mysovsky and Radzhabov [29], and a large band with a maximum at 290 nm. The latter band shows a good linear luminescence-dose dependent. According to our experimental data, the Ca colloids are the main defects generated in CaF_2 by proton beam irradiation. Their concentration and size increase with fluence. We believe that the colloid formation is responsible for the luminescence improvement observed in this study, when CaF_2 is excited with 2-MeV proton beam. According to the absorption measurements, the colloid size is larger for higher proton energy. So we expect more luminescence intensification for higher proton energy. This result can be useful in the applications where CaF_2 is being used as a scintillator.

Conflicts of interest

The authors declare that they have no conflicts of interest.

CRediT authorship contribution statement

Abeeha Batool: Conceptualization, Data curation, Methodology, Writing - original draft, Software. **Mahmoud Izerrouken:** Supervision, Writing - original draft, Writing - review & editing, Software, Data curation, Validation. **Samson O. Aisida:** Data curation, Writing - original draft, Software, Writing - review & editing. **Javaid Hussain:** Data curation, Writing - original draft, Software, Visualization, Investigation. **Ishaq Ahmad:** Supervision, Visualization, Investigation, Writing - review & editing. **M. Qadeer Afzal:** Supervision, Visualization. **Ayub Faridi:** Supervision, Validation, Visualization. **Ting-kai Zhao:** Supervision, Visualization, Investigation.

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