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In-situ investigation of point defects kinetics in LiF using ion luminescence technique

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ABSTRACT

The present work reports the in-situ ion beam induced luminescence measurements using 2 MeV proton excitation of LiF single crystal with the aim of obtaining a further insight on F-type centers kinetics and its correlation with the self-trapped exciton (STE). It is found that the STE luminescence intensity decreases from the beginning of irradiation. While the dose-dependent evolution of $F_3{}^+$ and F_2 centers reveals three kinetic stages: (i) linear increase from the beginning of irradiation up to 10.1 MGy, followed by (ii) monotonic decrease to 18.1 MGy, and (iii) steady state from 18.1 to 26.2 MGy where the luminescence intensity remains constant. The STE luminescence completely extinguished at high dose; 18.1 MGy in our case. Whereas, the $F_3{}^+$ and F_2 luminescence persist and remain constant above 18.1 MGy. The latter behavior revealed in the present study can be useful for LiF application in radiation dosimetry and an imaging detector.

1. Introduction

Point defect in alkali halides materials often gives rise to different color centers when the materials are irradiated with protons, neutrons, electrons, charged particles, X-rays and gamma rays of various energies [1–12]. The different color centers are based on the absorption and luminescence of the materials, in which their intensities depend majorly on the kind of radiation, doses and the fluence range [10,13]. The optical properties of alkali halides scintillator materials were widely studied owing to their myriad applications in radiation detectors and dosimetry [14], thermo-luminescent dosimetry [10,11,15], active channel waveguides [12], tunable solid-state lasers [16,17], neutron imaging detectors [18] and optoelectronic light-emitting devices [19–21]. The main color center obtained in alkali halides, known as F-center, is a primary defect that can be produced when an electron is trapped at a vacant anion site. Moreover, $[V_K + e^-]$ excitons (self-trapped hole with an electron) and F-aggregate color centers F_2 (M − center) and F_3 (R-center) in which two and three electrons bound to two and three anion vacancies respectively, have been extensively observed in alkali halides scintillators. When the ion beam of high energy bombarded a crystal surface, it loses energy in the materials as results of the elastic collisions and electronic ionization and excitations. The processes occurring along the ion path (tracks) owing to a high energy loss are the most important ones. On the other hand, ion beams of different energies are also extensively studied for applications ranging from material modifications to radiobiology and radiotherapy [1,2,13,22–29]. LiF among the alkali halides has not been fully explored through the optimization of their properties [1–12]. Using optical absorption method, it was found that various irradiations induce absorption bands due to the F-type centers formation: F-centres (247 nm), F_2 center (445 nm), $F_2{}^+$ center (630 nm), F_3 center (316 nm, 374 nm), $F_3{}^+$ center (458 nm) and F_4 center (517 nm, 545 nm) in addition to Li colloids which absorb at 450 nm.

Ion beam induced luminescence (IBIL) is one of the most important techniques used to study in-situ defect formation in solids [30–35]. The IBIL technique is more efficient through *in-situ* study to explain the

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point defect mechanism and damage rate in solids lattice compared to other optical techniques like photoluminescence (PL) and UV–Visible absorption techniques [36]. Skuratov and co-workers studied in-situ luminescence in LiF by using swift heavy ion [30–33]. The luminescence spectrum observed shows a set of broad emission bands principally self-trapped exciton (STE) transitions, F_2 and $F_3{}^+$ centers. The authors revealed that the STE intensity decreases with increasing dose while that of F_2 and $F_3{}^+$ centers increases. Similar behavior was also reported by Quaranta et al. [37] in LiF excited by 2 MeV proton irradiation. In the present investigation and to avoid any track effects, the in-situ luminescence was performed using protons. The kinetic of point defect generated in LiF single crystal was investigated in a large fluence range.

2. Materials and experiment

In-Situ IBIL of pure single crystal of LiF with 10.0 × 10.0 mm^2 and 2.2 mm thickness was carried out at room temperature at 5 MeV pelletron Tandem accelerator at the national center for Physics Islamabad, Pakistan. The LiF sample exhibits no absorption band in the range 200–800 nm indicating the absence of impurities and excellent optical transmission [38]. The crystal was placed at the 45° angle on the sample holder at a distance of 3.0 cm from the collimating lens inside the chamber. The samples were irradiated with 2 MeV proton with different fluences ranging from 1×10^{14} to 1.3×10^{15} proton/cm^2 as shown in Table 1. The in-Situ luminescence spectra were collected in the wavelength range of 200–1000 nm at room temperature. The chamber working as a Faraday cup to measure the total charge impinging on the sample and the specified beam current (10nA) performed at $10^6 Torr$. The corresponding dose D (MGy) was calculated using the Eq.1 and reported in Table 1.

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

where φ, ρ and S are respectively, fluence (p/cm^2), density ρ = 2.635 (g/cm^3) and mass stopping power $\left(\frac{S}{\rho}\right)$ is in $(MeV \times cm^2/mg)$. D is in MGy. S is deduced from SRIM calculation [39]. The $\left(\frac{S}{\rho}\right)$ value taken from a depth near the surface is 0.126 $MeV \times cm^2/mg$.

The obtained luminescence was collected in the vacuum chamber by a silica fiber ≈ 500 µm diameter very close to the irradiated source in the beamline direction. The IBIL spectra were recorded using ocean view (QE65000) spectrometer coupled to the chamber via optic fibers. One hundred and twenty spectra were taken with 500 µsec of integrating time each.

3. Results and discussions

Fig. 1 shows the luminescence spectra of LiF crystal irradiated to a dose of 0.06 MGy. One can see two broad bands extended respectively from 280 to 450 nm and from 500 to 800 nm. The first one is contributed by the near-ultraviolet bands at 325 nm and 350 nm, which can be ascribed to the intrinsic self-trapped excitons and to the radiative recombination of $[V_K + e^-]$ excitons agitated by the lattice defects [32,33,35,40]. A band at 400 nm often attributed to the impurities [33], in particular to the divalent metal trace impurities responsible for the creation of vacancies in alkali halides [35]. It is interesting to note that the band at 280–296 nm attributed to STE and impurity observed in the case of heavy-ion irradiation is not observed in the present work. The second one consists of a band between 525 and 550 nm, which can be ascribed to the recombination of a hole associated with the F_3^+ center [40], and a band around 670 nm can be ascribed to the emission of F_2 centers [40]. One can also see a shoulder at about 760 nm, which can be attributed to F_4 centers.

Table 1
The fluence, dose and luminescence intensities of STE, F_3^+, F_2 and emission band at 890 nm for the investigated samples.

Fluence (p/cm^2)	Dose (MGy)	STE	F_3^+	F_2	890 nm
3×10^{11}	0.06	2244	377	1045	309
1×10^{14}	2.0	1665	428	1125	323
3×10^{14}	6.0	1123	476	1156	339
5×10^{14}	10.1	1121	687	1586	405
7×10^{14}	14.1	820	668	1405	401
9×10^{14}	18.1	355	492	923	564
1.1×10^{15}	22.2	302	387	693	399
1.3×10^{15}	26.2	321	462	839	432

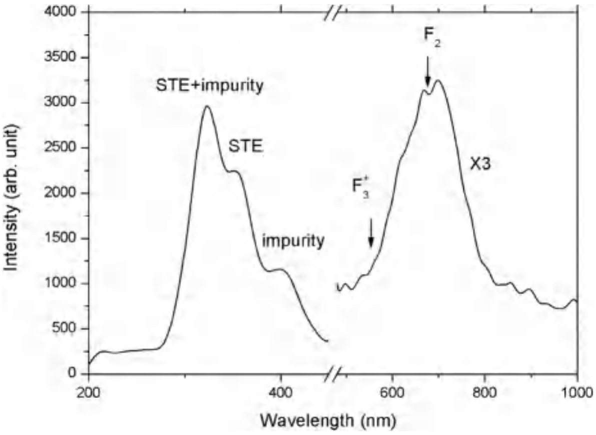

Fig. 1. Luminescence spectrum of LiF crystal irradiated to a dose of 0.06 MGy, showing the various point defects.

We reported in Fig. 2 the recorded in-situ spectra of LiF crystal irradiated up to 26.2 MGy. It is clear that the intensity of the emission band attributed to STE linearly decreases with dose whiles that of $F_3{}^+$ and F_2 centers increases, as shown in table 1. This is illustrated in Fig. 3, showing the evolution of each defect type separately. The STE intensity monotonically decreases from the beginning of the irradiation and reaches a minimum detectable value at a dose of 18.1 MGy. The same STE emission behavior has been reported by Skuratov et al. in the case of heavy-ion irradiation [32]. They attributed the STE decreases to the distortion of the LiF crystal lattice due to the accumulation of defects that provides non-radiative decay paths of $[V_K + e^-]$ excitons. Quaranta et al. also revealed a similar trend of STE in LiF irradiated with 2 MeV protons in the same fluence range [36]. We believe that the decrease of STE luminescence is due to the self-absorption effect, induced by F_3 centers, which absorb at 316 and 374 nm and also to the

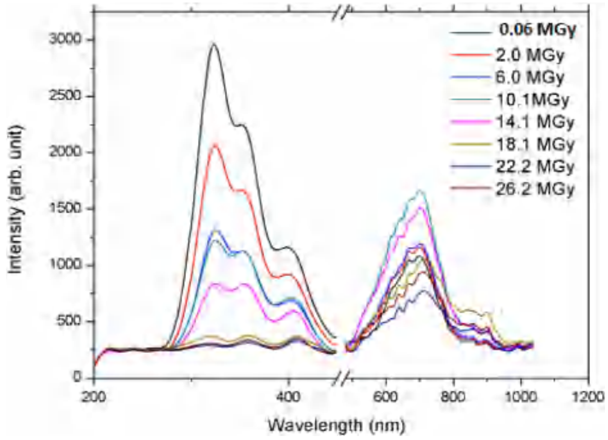

Fig. 2. Luminescence spectra of LiF crystal recorded at different doses.

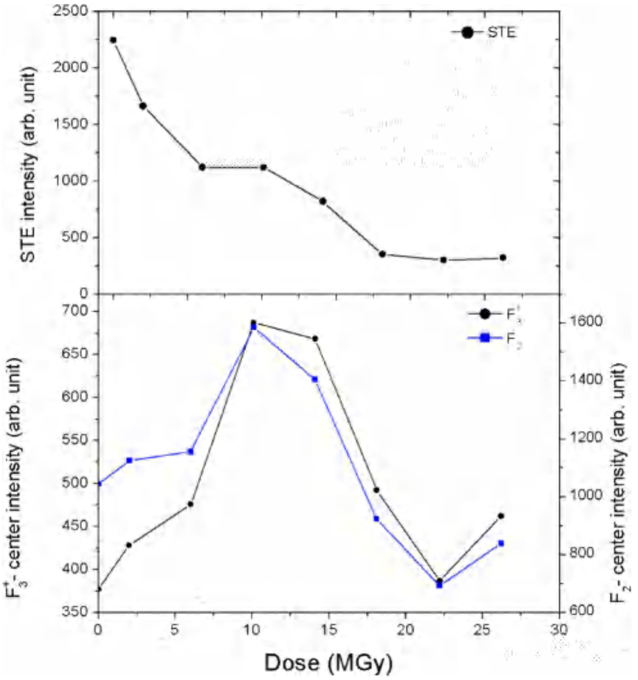

Fig. 3. The intensities of three major luminescence centers, STE, F_3^+ and F_2 vs. proton dose. The solid line is to guide the eye.

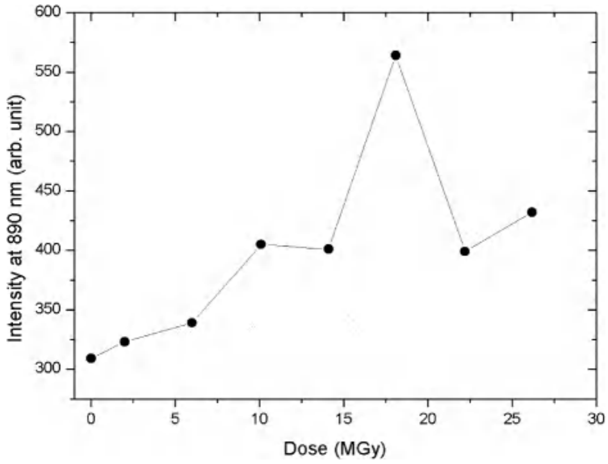

Fig. 4. Luminescence intensity at 890 nm versus dose. The solid line is to guide the eye.

nonradiative mechanism caused by the defect formation. It is interesting to mention that in ionic crystal-like LiF, the non-radiative STE recombination generates additional Frenkel defects (F- and H- center), a process also known as a non-impact mechanism [28].

From Fig. 3, one can see that the $F_3{}^+$ and F_2 centers exhibit exactly similar behavior. Both defects showed three kinetics stages. The intensity of both centers rapidly increases to a maximum intensity at 10.1 MGy followed by a more gradual decrease up to a dose of 22.2 MGy. Then it reaches a steady-state from 22.2 MGy to 26.2 MGy. While the data reported by Skuratov et al. for heavy-ion (figure 5 of ref. [31]) as well as that of A. Quaranta et al. [2] for 2 MeV proton, for approximately the same dose range, revealed only two kinetics stages. Skuratov et al. assigned the reduction of the $F_3{}^+$ intensity to the overlapping of track halo (halo is the point defects distributed around the ion track core), which causes a luminescence quenching. It is interesting to note that the same authors reveal that the $F_3{}^+$ generated by 20 keV He ions reaches a saturation value above 2.5 MGy up to 10 MGy. The comparison to the 2 MeV proton irradiation explains the importance of ionization and excitation process on the defects structure in LiF crystal. However, more recent data published by Meng-Lin Qiu using negative ion (20 keV H^-) found similar F_2 center luminescence behavior in the same fluence range [41]. We can also see from Fig. 2 that an emission band at 890 nm is growing as the dose increases. This band is attributed to $F_3{}^-$ and $F_2{}^+$ [2], indicating point defect aggregates formation. The evolution of this band versus doses is presented in Fig. 4. As can be seen, the band exhibits a linear trend up to 18.1 MGy, followed by a decrease to a stable intensity in good agreements with Meng-Lin Qiu [41]. The evolution of the F- center clusters ($F_3{}^+$, F_2, $F_3{}^-$ and $F_2{}^+$) observed in our study can be interpreted as follow: during irradiation, the F-center density increases and aggregates to form clusters (F2, F_3, F_4). With increasing dose, further aggregation occurs and leads to formation of more complex defects that contribute to the luminescence quenching. Moreover, the partial luminescence extinction observed is mainly due to the self-absorption effect caused by the complex point defect induced during irradiation, which absorbs in UV and visible wavelength range. In our opinion, the contribution of the crystal heating under proton beam irradiation to the F-type center's aggregates quenching is not important; otherwise, the emission intensity disappears at high doses and the stable intensity should not be observed.

4. Conclusion

The kinetic of point defects in lithium fluoride (LiF) crystal was investigated using *in situ* 2 MeV proton-induced luminescence (IBIL) technique in dose raging from 0.06 MGy to 26.2 MGy. The luminescence spectra revealed two broad bands at 280–450 nm and 500 – 800 nm attributed to STE and point defect aggregates ($F_3{}^+$ and F_2), respectively. At high dose, a shoulder at 890 nm growth attributed to the $F_3{}^-$ and $F_2{}^+$ centers. According to our experimental data, it is found that the STE luminescence monotonously decreases from the beginning of irradiation while the luminescence of F-type center aggregates ($F_3{}^+$ and F_2, $F_3{}^-$ and $F_2{}^+$) follow three kinetics stages. A stable luminescence intensity is observed at a high dose. The partial reduction of the luminescence during the second stage is attributed mainly to the self-absorption effect. These results reveal that the F-type center's aggregates are responsible for the LiF crystal luminescence property. However, the steady-state stage, revealed at a high dose (> 18.1 MGy), should be useful for radiation dosimetry and imaging detector applications.

CRediT authorship contribution statement

Abeeha Batool: Conceptualization, Data curation, Methodology, Software. **Samson O. Aisida:** Data curation, Software, Visualization, Investigation. **Javed Hussain:** Data curation, Software. **Shehla Honey:** Visualization. **Mahmoud Izerrouken:** Supervision, Software, Data curation, Validation. **Ayub Faridi:** Supervision, Validation. **Ishaq Ahmad:** Supervision, Visualization, Investigation. **Ting-kai Zhao:** Supervision, Visualization, Investigation.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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