CHIN. PHYS. LETT. Vol. 34, No. 1 (2017) 016104

Ion-Beam-Induced Luminescence of LiF Using Negative Ions

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(Received 31 August 2016)

Negative ion-beam-induced luminescence (IBIL) measurements of a pure LiF crystal using 20 keV H^- are performed to monitor the formation and annihilation of luminescence centers during ion irradiation. Several emission bands are observed in the IBIL spectra and the evolvement mechanisms of the corresponding centers are identified. The difference between the IBIL measurements using positive ions and negative ions is that the intensities of luminescence centers can reach the maxima at lower fluences under negative-ion irradiation due to free charge accumulation.

PACS: 61.80.Jh, 41.75.Cn, 61.72.J– DOI: 10.1088/0256-307X/34/1/016104

The optical properties of luminescence centers in LiF have been widely studied for many applications such as thermoluminescence dosimetry,[1,2] tunable lasers,[3] and certain imaging detectors.[4] The formation of luminescence centers in LiF can be produced by many radiation sources, e.g., x-rays, gamma rays, ultraviolet (UV) light, ions, neutrons and electrons. Radiation type and fluence can have a significant impact on the luminescence yield of each center.[5–8] The main luminescence centers studied in LiF were self-trapped exciton (STE) recombination (in the UV range) at unstable defects or impurities,[9–13] F_3^+ centers (peaked at 540 nm) and F_2 centers (centered at 670 nm).[14–16] The studies of other luminescence centers, such as oxygen/magnesium impurities related centers (at 400 nm and 440 nm)[5,17] and the F-aggregate centers (F_4-like centers at 740 nm and F_3^-/F_2^+ centers at 890 nm)[6,17,18] still need to be improved. Thus it can be seen that F-type centers (anion vacancy or its aggregation, trapping different numbers of electrons) play an important role in the luminescence centers of LiF.

To have a clear understanding of luminescence centers generated by ion irradiation and the evolution of each center under irradiation, ion-beam-induced luminescence (IBIL; also called ionoluminescence, IL) measurements have been employed for decades because IBIL can provide *in situ* real-time measurements. IBIL spectra can offer detailed information about the evolution of emission band intensities as a function of fluence.[10,12,13,18] However, previous IBIL measurements were almost all using positive ions. It is difficult to avoid the charge accumulation effect on sample surfaces because the samples for the IBIL measurements are insulators or semiconductors. Charge accumulation on sample surfaces was caused by injected positive ions and outgoing secondary electrons. The charge accumulation effect may influence the intensities of incident ions and forms of defects. In the case of negative ion irradiation, the number of incoming and outgoing charges on the surface was well balanced.[19–23] Hence, it is worth studying the IBIL spectra of LiF under negative ion irradiation and making comparison with the previous IBIL measurements using positive ions.

In this Letter, the IBIL measurements of a pure LiF crystal using 20 keV H^- were carried out at the negative IBIL setup of GIC4117 tandem accelerator of Beijing Normal University. The obtained IBIL spectra, without charge-up of the sample, provide detailed information about the formation and annihilation of each luminescence center during the negative ion irradiation. Furthermore, the difference between the IBIL measurements using positive ions and negative ions was discussed.

The negative IBIL setup was built on the original negative-ion implantation system at the GIC4117 tandem accelerator of Beijing Normal University. The ion beam was produced by the GIC860A Cs sputtering negative ion source and then deflected by two 45° analyzing magnets. To collect more photons, the angle between the ion beam and the sample surface was adjusted at 45° and the optical fiber (diameter 600 μm) was perpendicular to the sample surface. We used an ocean optics spectrometer (QE PRO) for the IBIL measurements. The available wavelengths cover the range of 197–982 nm with an entrance slit size of 100 μm. A schematic diagram of the IBIL setup is shown in Fig. 1.

The pure LiF crystals ($10 \times 10 \times 0.95\,mm^3$, ⟨100⟩ orientation) with the incident face polished were purchased from MTI Corporation (KJ Group, China). The sample was irradiated by 20 keV H^- at room temperature. The beam current was 1 μA with a diameter of 8 mm, measured by a Faraday cup before irradiation. The integration time was 1 s for each spectrum,

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and 100 continuous spectra were collected. The total irradiation dose was approximately $1.3 \times 10^{15}\,\mathrm{cm}^{-2}$. The vacuum was kept below 3×10^{-6} Torr during the irradiation.

Due to the low count of light from the 20 keV H^- irradiation, the IBIL spectra shown in Fig. 2 were the integrated intensities of the first 5 s, 20–25 s and last 5 s during this measurement. The backgrounds of spectra were deducted automatically by software in the first step.

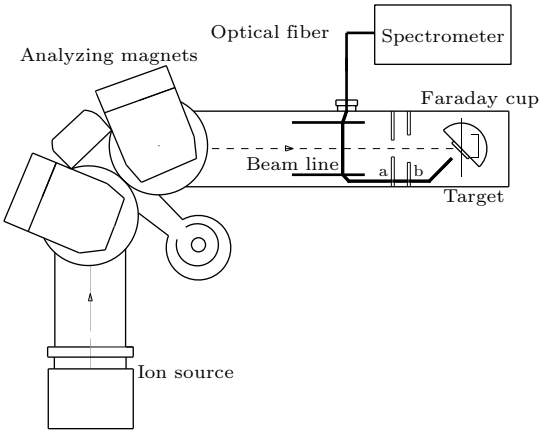

Fig. 1. Schematic diagram of the IBIL experimental configuration. (a) Beam aperture and (b) suppressor electrode.

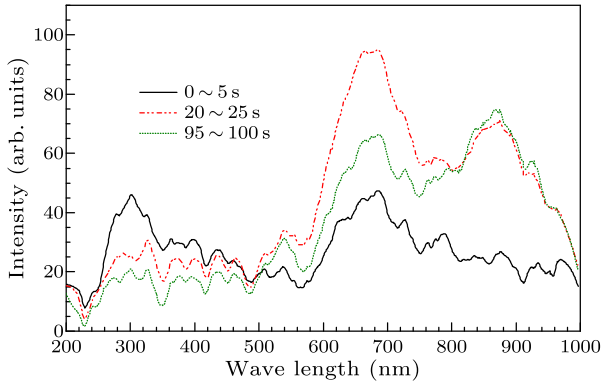

Fig. 2. IBIL spectra of LiF under 20 keV H^- irradiation at room temperature in the first 5 s, 20–25 s and last 5 s.

In the early stage, the main broad emission was observed in the UV range. With an increase in fluence, the emission in the UV range decayed evidently and then maintained a relatively constant intensity to the end of the measurement. During the irradiation, several luminescence peaks appear in the visible and near-infrared (NIR) range, with two main peaks centering at around 670 nm and 890 nm and some shoulder peaks were observed.

During the ion irradiation, numerous defects were formed from the single point defect in the initial period to complex aggregates in the high fluence. Each emission band is associated with a certain type of radiative recombination. According to the enormous amount of investigation about defects in LiF, the UV band centered at about 300 nm was caused by the recombination of STEs associated with lattice defects or impurities. The origin of the UV band is still in question.[9,10,13] The two luminescence peaks at 540 nm and 670 nm were attributed to the recombination of election–hole pairs at F_3^+ and F_2 centers, respectively. These luminescence centers were extensively observed and studied in many LiF luminescence measurements using different stimulated methods.[14–16] Other luminescence peaks observed in this study (located at around 400 nm, 740 nm, and 890 nm) were occasionally detected and studied in Refs. [5,16-18]. The luminescence peaks centered at about 400 nm and 440 nm were associated with impurities (O and Mg). The shoulder peak at 740 nm was caused by F_4-like centers, inconspicuous in many previous measurements. The broad emission located at around 890 nm results from F_3^- and F_2^+ defects, overlapping evidently.

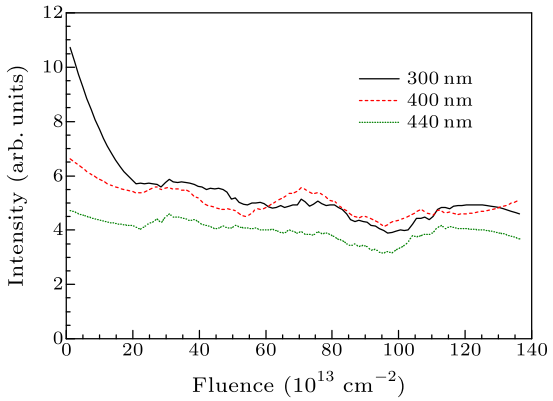

Fig. 3. Evolution of three emission band intensities (300 nm, 400 nm, and 440 nm) as a function of the fluence.

The UV band at around 300 nm, corresponding to the recombination of the STEs, showed a rapid decay in the early stage (fluence$\leq 4 \times 10^{14}\,\mathrm{cm}^{-2}$ approximately) and then kept a weak intensity consistently to the end of the measurement. Because the STE recombination was at unstable defects or impurities, it is understandable that the destruction of luminescence centers by ion bombardment led to the initial decrease. The UV band was well discussed under MeV positive ion irradiation.[9,10,13] The luminescence yield was enhanced by V_F+e recombination (where V_F denotes the hole trapped by a cation vacancy) and depended on the exciton density. The monotonic decrease with increasing fluence in the UV range may indicate that the emission was related to the STE recombination near impurities rather than point defects.[18]

The two peaks at 400 nm and 440 nm, caused by the impurities (O^{2-} and $Mg^{2+}O^{2-}$ centers), show a similar evolution from the beginning to the end. The intensities of 400 nm and 440 nm peaks change tinily during the IBIL measurement. The distinct influence of impurities (oxygen and metal ions) on luminescence spectra were present in the work of Baldacchini *et al.*,[17] even though the impurities in LiF were less than

10 ppm.

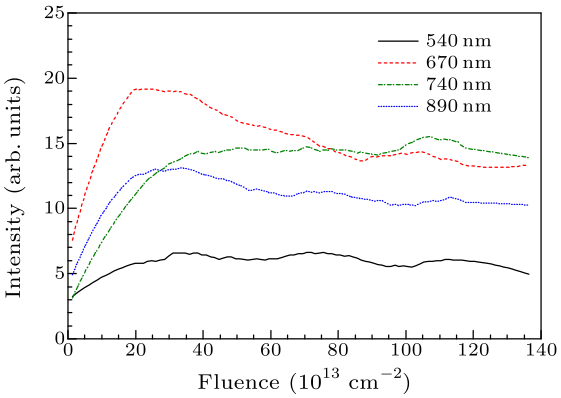

Fig. 4. Evolution of four emission band intensities (540 nm, 670 nm, 740 nm, and 890 nm) as a function of the fluence.

The 540 nm peak, caused by the recombination of election–hole pairs at F_3^+ centers, grows slightly in the early stage (fluence$\leq 3\times10^{14}$ cm^{-2} approximately) and then maintains an approximately stable intensity during the measurement. The intensity of the 670 nm peak, related to F_2 centers, increases distinctly to a maximum at the fluence of about 2.5×10^{14} cm^{-2}, then attenuates slowly. The formation and annihilation of F_3^+ and F_2 centers can be attributed to the clustering of single vacancies and the transformations between different F-type centers by the reactions v_a+F_2 $\rightarrow F_3^+$ (where v_a denotes the anion vacancy), F_2^++F$\rightarrow F_3^+$, F_3^++e$\rightarrow F_3$, F_3^++2e$\rightarrow F_3^-$, etc.

The F_3^+ and F_2 centers in LiF are common in each type of luminescence measurement and are extensively studied,[14–16] useful for researchers studying optical properties of these color centers and their applications. It is worth noting that the decrease in F_3^+ centers may also be caused by strong reabsorption of the green luminescence by the ion-induced F_n centers.[14]

The luminescence peak located as a shoulder at 740 nm, attributed to F_4-like centers, is rarely observed and studied in luminescence measurements.[6,18] The intensity evolution of F_4-like centers shows a behavior similar to the evolution of F_2 centers (670 nm). The saturation value occurs at a fluence of about 3×10^{14} cm^{-2}. Here F_3 centers can be regarded as the precursor of F_4-like centers. During the ion irradiation, F_4-like centers would be created and damaged with continuous formation and further aggregation of vacancies.

The NIR band peaked at around 890 nm, caused by the F_3^- and F_2^+ centers, and remains constant after growth in the initial stage (fluence$\leq 5\times10^{14}$ cm^{-2} approximately). The reactions for the formation and annihilation of F_3^- and F_2^+ centers are similar to the other F-type centers.[6,17] Recently, the evolution of the NIR F_3^-/F_2^+ band as a function of dose has been reported for the first time by Valotto *et al.*[18] The increase and decrease rates are slower than the other centers (F_4-like center is not involved), attributed to the more complex formation mechanisms and higher radiation difficulty.

The majority of luminescence centers are generated by ion bombardment because the main luminescence yield is caused by the production of anion vacancies during the ion irradiation, in addition to the minority present before irradiation. Apart from transformations between different types of anion vacancies, some common mechanisms are responsible for the intensity evolution of each luminescence center. The competition from non-radiative recombination mechanisms is one reason for the attenuation. The effect of stress produced by irradiation, resulting in minor changes in lattice symmetry, may be another mechanism for the decrease in luminescence intensity.[24] Self-absorption effects produced by heavy damage are also responsible for the decrease in certain luminescence centers.[14]

The IBIL study of LiF using negative ions is first employed in this work, and the major difference with respect to the IBIL studies of LiF using positive ions is the fluence reaching intensity maximums for each center. Compared with the IBIL studies of LiF using positive ions, the results presented in this work show that using negative ions we would reach saturated values at lower fluences.[18] The results may be attributed to charge accumulation. During positive ion irradiation, the positive ions are left in the material and take up a certain amount of electrons. Meanwhile, secondary electrons released from material surfaces during irradiation enhance the charge imbalance. The lack of electrons would reduce the formation rate of some electroneutral and negatively charged centers. In addition, with an increase in positive charge accumulation, the electric field on the sample surface would change the motion trail of incident positive ions and would consequently lead to a decrease in the actual injected fluence. If it is negative ion irradiation, the electric charge would be well balanced and these effects can be well avoided.

In summary, the IBIL measurements of a pure LiF crystal using 20 keV H^- have been performed to monitor the intensity evolution of each luminescence center at the negative IBIL setup of the GIC4117 tandem accelerator. The experimental results show that the setup can provide highly sensitive photon detection and real-time measurements with detailed information about the evolution of irradiation damage. The luminescence centers, related to STE recombination near impurities and trace impurities (O^{2-} and $Mg^{2+}O^{2-}$ centers), show a monotonic decrease. Other emission bands associated with anion vacancies (F_3^+, F_2, F_3^-/F_2^+ and F_4-like centers) increase evidently in the initial stage with different rates. After reaching the intensity maximum, F_2 and F_4-like luminescence cen-

ters decrease with a slow rate while F_3^+ and F_3^-/F_2^+ centers keep constant. The reactions for the formation and annihilation of F-type centers are given, and some attenuation mechanisms such as the growing nonradiative recombination mechanisms, effects of stress produced by irradiation, and self-absorption effects produced by heavy damage are discussed.

The difference between the IBIL studies using positive ions and negative ions is that the intensities of luminescence centers would reach saturated values at lower fluences when the IBIL work uses negative ions, due to being free of charge accumulation. The advantage of the IBIL using negative ions is to enhance charge balance.

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