ISSN : 0974 - 7486 Volume 13 Issue 8

Materials Science

An Indian Journal

Full Paper

MSAIJ, 13(8), 2015 [267-275]

Color centers in lithium fluoride irradiated with high energy heavy ions

H.Benhacine*, A.Meftah

LRPCSI, University 20 août 55 Skikda, route El-Hadaeik, 21000 Skikda, (ALGERIA)

E-mail: hbenhacine@gmail.com

ABSTRACT

Single crystal samples of lithium fluoride were irradiated at room temperature with different energy (144 - 255 - 544 and 840 MeV) Pb^{+53} ions in fluence range between 1×10^9 and 4×10^{12} ions/cm^2. The optical absorption and photoluminescence (PL) techniques were used for characterisation of the irradiated samples. The damage is dominated by the creation of simple defects (F centers) and aggregated defects (F_n centers). The concentration of F-center increases as a function of fluence and energy. On the other hand two very intense PL bands are observed at around 545 and 665 nm which correspond to the emission of F^+_3 and F_2 centers respectively and increase linearly in the same fluence range.

KEYWORDS

Lithium fluoride;
Swift heavy-ion irradiation;
Optical absorption;
Photoluminescence

INTRODUCTION

The formation of defects in lithium fluoride (LiF) and in other alkali halides created under various types of irradiation, e.g. photons, electrons, neutrons[1] and ions[2-4] has been studied for long time by several groups. In LiF primary radiation defects are F-centers (electron trapped by an anion vacancy) and H centers (interstitial halogen atom)[5]. At higher irradiation temperatures and higher fluences, these primary defects are transformed to more complex defects such as F_n-aggregation and Li colloids.

Using the chemical etching technique, Young[6] has observed damages due to tracks of fission fragments in irradiated LiF crystals with heavy ions. Perez et al.[7] studied LiF crystals, irradiated with different ions with energy between 30 and 60 MeV/u. Using optical absorption spectroscopy it was shown that the main defects in tracks are F and F_2 centers. Moreover, Balanzat et al.[8] studied various crystals (LiF, NaCl, and KBr) irradiated with heavy ions at low temperatures, demonstrated that the resulting exciton luminescence spectra and the dependence of the efficiency on temperature are the same as under x-ray or optical excitation. The fluence dependent behavior of F and F_2 color centers induced by SHI irradiation in LiF crystals has been studied by Trautmann et al[9].The number of F centers per unit volume initially increases and saturates at higher fluence, the estimated track radius from the saturation curve of F centers were found to be about 5–30 nm, depending upon ion energy.

The ion-induced damage on the surface inspected by scanning force microscopy is reported by Müller et al.[10, 11]. In this report, we concentrate on ion-induced defects in LiF by means of optical absorption spectroscopy, complementing studies performed with photoluminescence.

EXPERIMENTAL PROCEDURE

LiF samples of various thicknesses, between 0.5 and 1mm, were cleaved along of the (100) plane from a single crystal block of high purity. The crystals of LiF have been irradiated at room temperature under normal incidence with ^{208}Pb ions of 936 MeV energy delivered by the Medium Energy Line of the GANIL (Caen, France). The fluence extended from 1×10^{9} to 4×10^{12} ions.cm^{-2} and the flux was about 4×10^{8} ions cm^{-2} s^{-1} on a 1 cm^{2} surface. Thin aluminum foils of different thicknesses were placed in front of each sample in order to modify the initial energy of the ions and consequently the range R, and $(dE/dx)_e$. The ion rang was in all cases less than the sample thickness, the ion beam was stopped in the crystals. The main irradiation parameters, listed in TABLE 1, were deduced from TRIM 2005[12] code calculations.

The irradiated samples were analyzed by optical absorption spectroscopy (SHIMDZU 1700) in the spectral range 190 - 1100 nm and by photoluminescence (Perkin Elmer LS50B Luminescence Spectrometer). With the optical absorption spectroscopy technique it is possible to obtain information about the generated defects in the crystal by ion irradiation, and to calculate the concentration of defects. The concentration of defects can be determined by the Smakula formula, modified by Dexter[13]:

$$\mathbf{N\ (cm^{-3}) = A.\frac{n}{(n^2+2)^2}\,\frac{W}{f}\,\alpha_{max}} \qquad (1)$$

Where *f* is the oscillator strength of the optical transition, *n* the refractive index, α_{max} the absorption coefficient measured at the maximum of the band peak and *W* the band's full-width at half maximum (FWHM). A is a constant, which takes 0.87×10^{17} eV^{-1} cm^{-2} for Gaussian bands. The absorption coefficient α_{max} was determined from the optical spectra of each sample using the relation:

$$\alpha_{max} = 2.304\ \mathbf{OD/_R} \qquad (2)$$

where:

$$\mathbf{OD} = \log_{10}\left(\mathbf{I_0/_I}\right) \qquad (3)$$

Represents the optical density at band maximum and R is the ion range.

RESULTS AND DISCUSSION

Optical absorption spectroscopy

Typical optical absorption spectra obtained with LiF crystals irradiated with 2.6 MeV/u and 4.1 MeV/u Pb ions at different fluences are reported in Figure 1.a and Figure 1.b. Absorption bands show two predominant bands around 245 and 445 nm corresponding to F and F_2 centers (two electrons trapped in two neighboring anion vacancies) respectively. At higher fluence, of 2×10^{11} ions/cm^{2} the spectra become more complex due to track overlapping, two bands at about 315 and 375 nm, and two weak bands at about 515 and 545 nm. All these bands are well known, and are commonly labeled as, R_1, R_2 (F_3-center) and N_1, N_2 (F_4-center) absorptions respectively. The absorption band around 445 nm is a result of the overlapped band corresponding to the F_2 and F_3^+ centers (two electrons trapped in a three neighboring anion vacancies).

We observed the area of the absorption spectrum for LiF irradiated increase as a function of ion fluence and saturated at high fluences. The F and F_2

TABLE 1 : Irradiation parameters of Pb in LiF crystals

E(MeV) Ion ^{208}Pb^{+53}	$\left(dE/dx\right)_e$ (keV/nm)	$\left(dE/dx\right)_n$ (keV/nm)	Range (µm)	E/R (keV/nm)	Fluence Ions/cm^{2}
840	27	0.05	40	21	$1\times10^{9} - 4\times10^{12}$
544	27.5	0.075	29	18.7	$1\times10^{9} - 4\times10^{12}$
255	25	0.135	18	14	$1\times10^{10} - 4\times10^{12}$
144	20	0.215	13	11	$1\times10^{10} - 4\times10^{12}$

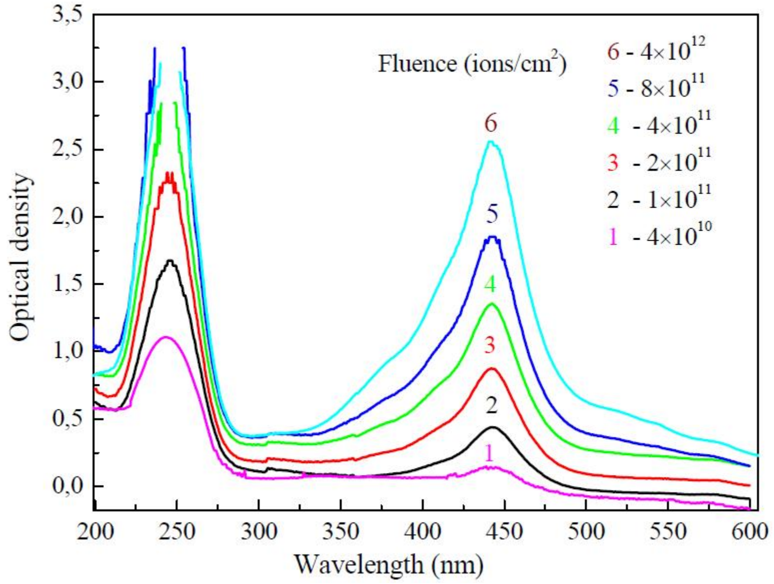

Figure 1.a : Optical absorption spectra of LiF irradiated with 540 MeV Pb ions of various fluences

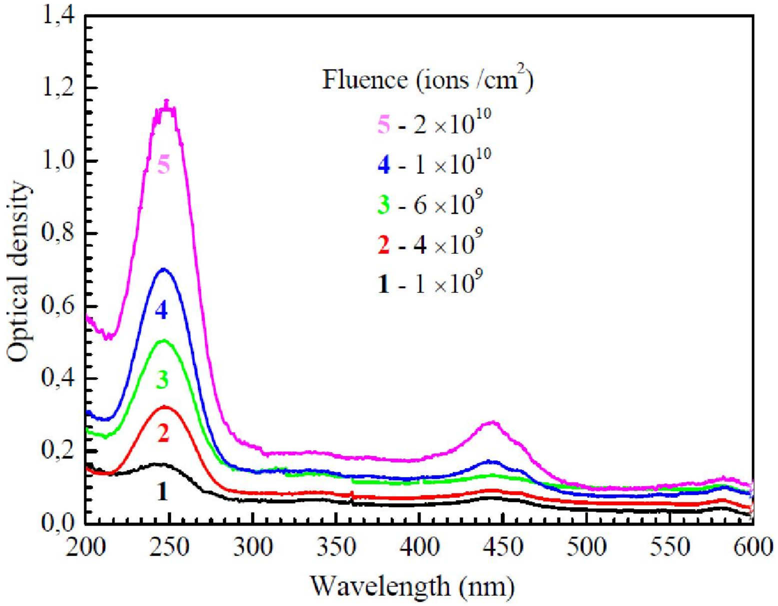

Figure 1.b : Optical absorption spectra of LiF crystals irradiated With Pb ions (4.1 MeV/u) of various low fluencies

centers bands of LiF were analyzed by means of Eq. (1). The evolution of N_F as a function of the ion fluence is presented in Figure 2. In the low fluence regime, N_F follows a linear increase. For fluences higher than 4×10^{11} ions.cm^{-2}, N_F saturates reaching a maximum value of 1×10^{19}.cm^{-3}.

Using the simple model proposed by Thévenard et al.[1], the situation can be simplified assuming that *F*-centers are homogeneously distributed in a cylindrical volume around the ion trajectory. The F-center creation obtained from this model is in the form:

$$N_F = N_s\ (1 - \exp[-(\pi r^2]\Phi)) \qquad (4)$$

where N_F (cm^{-3}) is the total F-center concentration obtained for an irradiation with an ion fluence Φ (ions.cm^{-2}), N_s (cm^{-3}) is the saturated concentration of F-centers in each individual track, and r_F is the radius of the track. Another interesting parameter deduced from the fit of the F-center curve in Figure 2 is the saturation level 6×10^{16} cm^{-2}, corresponding to a volume concentration of about 2.10^{19} cm^{-3}. The concentration of F_2 centres starts saturating at a fluence of 2×10^{12} ions.cm^{-2}. The resulting saturation was due to the overlapping of neighboring tracks[9].

We found that radii of the F-center halo increase

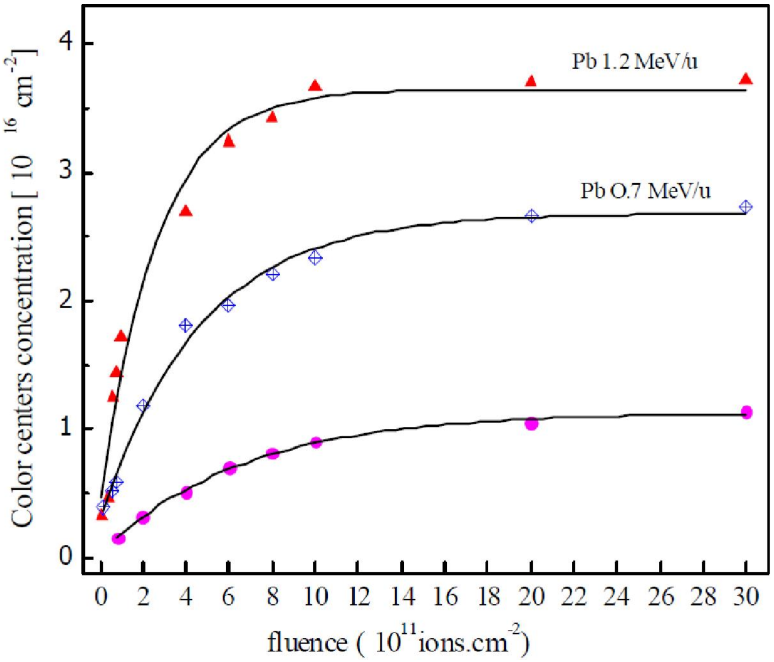

Figure 2 : Concentration of F-centers (triangles) and F_2-centers (circles) as a function of the fluence of Pb ions with an energy of 1.2 MeV/u, and concentration of F-centers (squares) at an energy 0.7 MeV/u

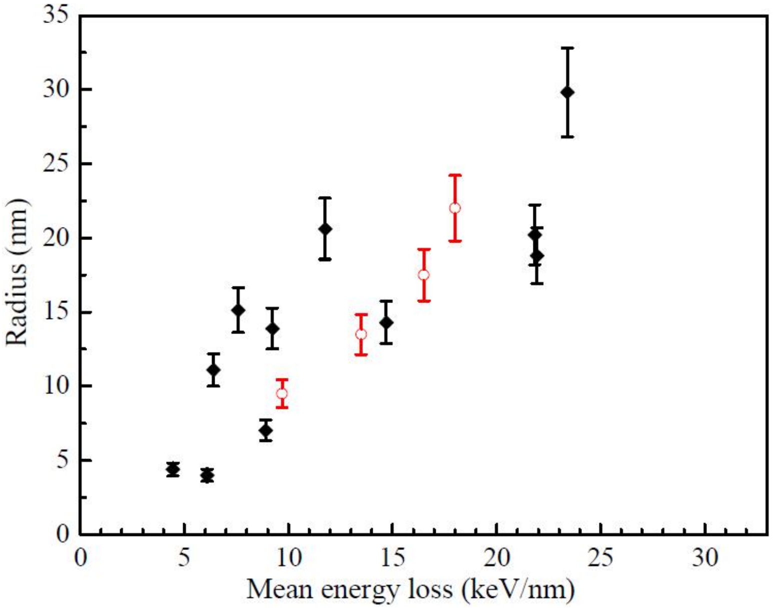

Figure 3 : Track radii in LiF deduced from optical absorption bands of F-centers plotted versus the mean energy loss (♦), track radii of this work (o)

with the mean energy loss of the Pb ion from 9 nm up to 22 nm. In Figure 3, the radii are presented as a function of the mean energy loss, i.e., the total ion energy is divided by the range. The track radii of F-centers in LiF irradiated with Pb at different energies are compared with those of LiF irradiated various ions species[9].

In order to compare the evolution of F and F_2 aggregate centers per track as a function of the fluence at the different energies, the number per single track of F center can be determined by:

$n_F^s = \frac{n_F}{\Phi}$[14],where n_F is given in cm^{-2}. Since the different bands in the 300–600 nm region strongly overlap were it is difficult to analyze individual contributions separately due to the unknown oscillator strength of the different centers. The creation of all

F_2 centers has been estimated from the parameter a^s which is deduced from the integrated absorption:

$$S = \int_{300}^{600} OD\, d\lambda \qquad (5)$$

normalised by the ion fluence

$$a^s = \frac{S}{\Phi} \qquad (6)$$

Where: a^s the integral absorption.

The dependences of n_F^s and a^s on the irradiation fluence and with different energies are displayed in Figure 4 and Figure 5. In all cases the number n_F^s and a^s per ion as a function of the fluence take the same evolution. At energies 144 MeV and 255 MeV the number n_F^s of color center produced per incident ion decreases with fluence. However, the F_n aggregate centers per ion increase in the first stage of the fluence, reach a maximum and finally decrease at higher fluences. This maximum appears at fluence 6×10^{11} ions.cm^{-2} at an energy corresponding to 0.7 MeV/u, and 2×10^{12} ions.cm^{-2} with 1.2 MeV/u. The number of color centers produced per ion track decreases at higher fluencies. This decrease gives an

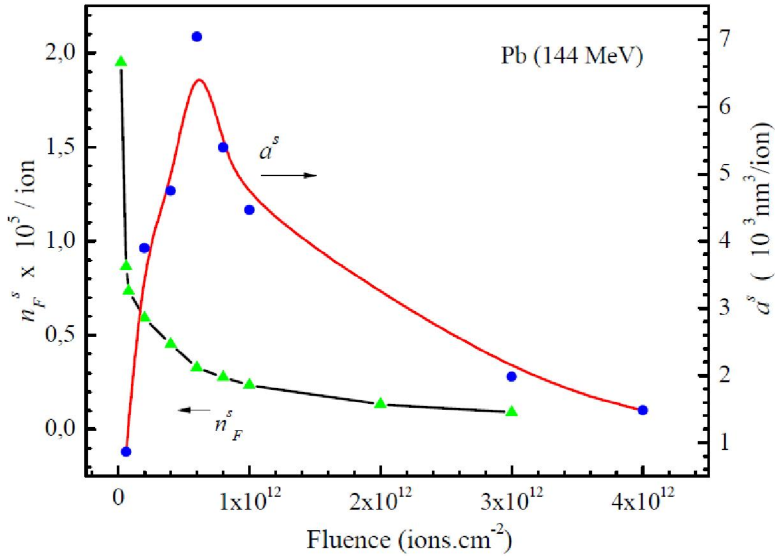

Figure 4 : Concentration of F-center (n_F^s) per ion track as a function of fluence for LiF crystals irradiated with Pb ions at different energies

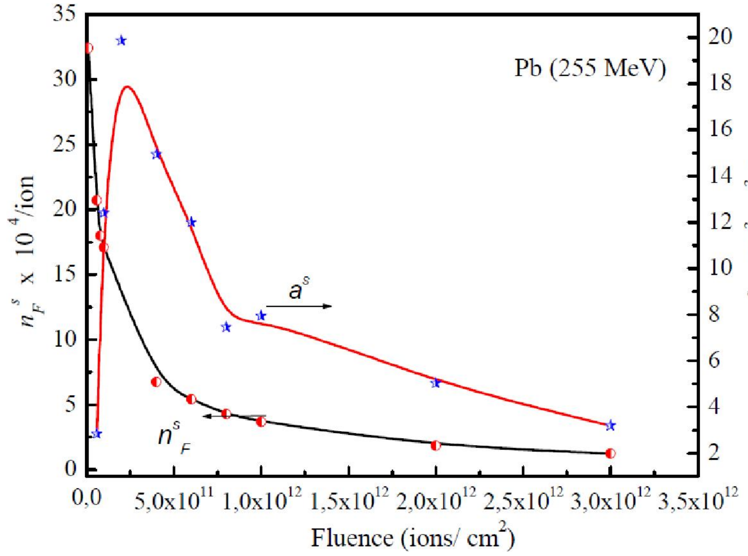

Figure 5 : Concentration of aggregates (a^s) per ion track as a function of fluence for LiF crystals irradiated with Pb ions at different energies

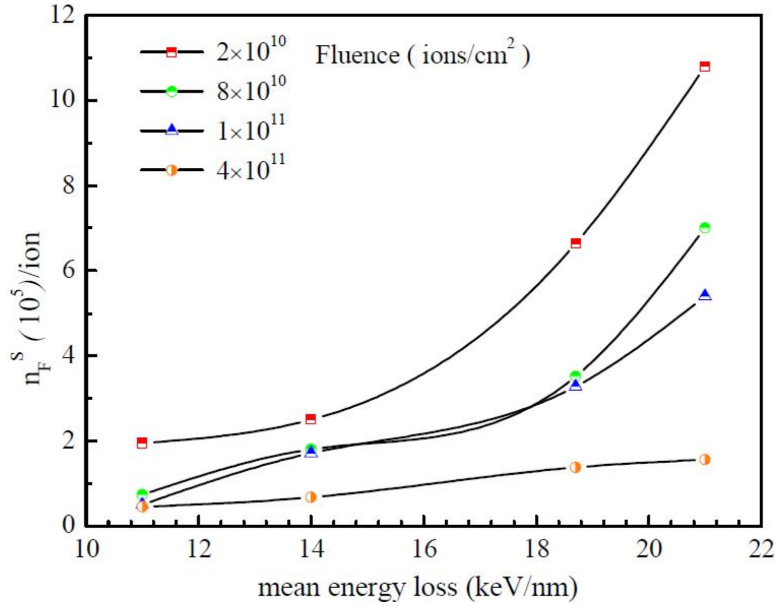

Figure 6 : Number of F centers n_F^s per ion as a function of the mean energy loss at high-fluence radiation (fluence is expressed in ions/cm^2)

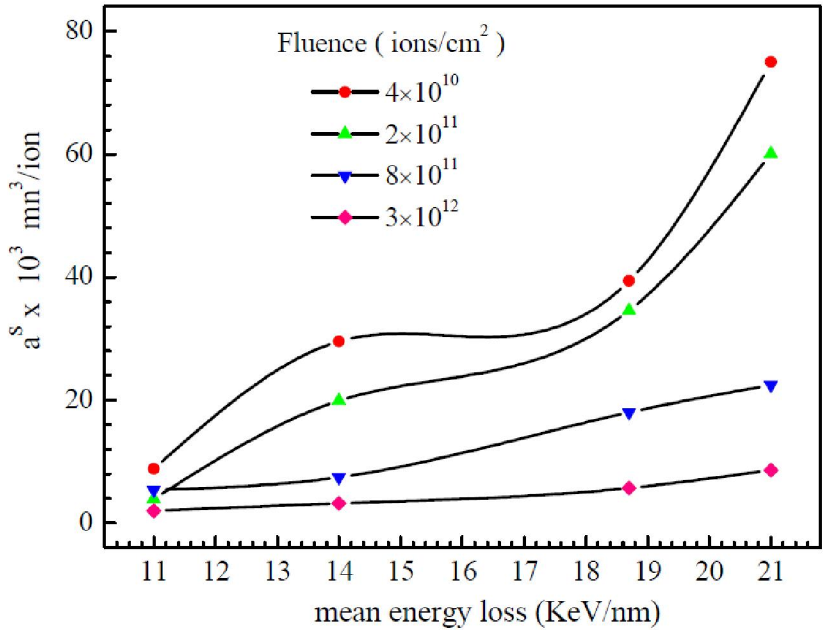

Figure 7 : Number of F_n aggregate centers a^s per ion as a function of the mean energy loss at high-fluence

indication that the recombination processes of electron and hole centers become dominant in this regime.

Comparing the results of LiF to those obtained earlier for LiF irradiated of Ni ion at 170 MeV and with Xe ion 300 MeV[15], we observe very similar effects. Also the evolution of n_F^s and a^s as a function of fluence is similar with MgF_2[15].

Figures 6 and 7, display F-center and F_n aggregate centers per track as a function of the mean energy loss at high ion fluence. The concentration of F-center (n_F^s) and aggregates (a^s) per ion track are proportional to the mean energy loss, and inversely proportional to the fluence.

It should be mentioned that the number of n_F^s and a^s per ion continues to increase with incident energy. The values of the energy 4.1MeV/u (S_e~27

KeV/nm) and 2.6 MeV/u (S_e ~ 27.4 KeV/nm) are situated on the right and the left of the Bragg's peak.

Photoluminescence measurements

The photoluminescence technique allows the possibility to study with more precision the F_3^+ and F_2 centers. The emission bands of and F_2 centers are well resolved contrary to their absorption bands. The excitation with a 445 nm wavelength-photon induces emission bands centred at about 553 nm and 680 nm assigned to and F_2 centers respectively[16, 17]. Moreover, The linear dependence between luminescence intensity and the number of related radiation defects is only valid at significantly lower values of optical density (<0.4). Thus only F_2 and F_3^+ with optical density lower than 0.5 is considered. Figure 8 shows an example of photoluminescence spectra of LiF single crystal irradiated with 144 MeV Pb ions at the values of fluence 6×10^9, 8×10^9, 1×10^{10}, 8×10^{10} and 1×10^{11} ions. cm^{-2}.

As mentioned above the spectra show two emission bands with maxima at about 2.17 eV (570 nm) and 1.95 eV (640 nm) due to the luminescence of F_3^+ and F_2 centers[18,19] respectively.

The line in the figures is the fit of the experimental data using two Gaussian peaks. The fit re-

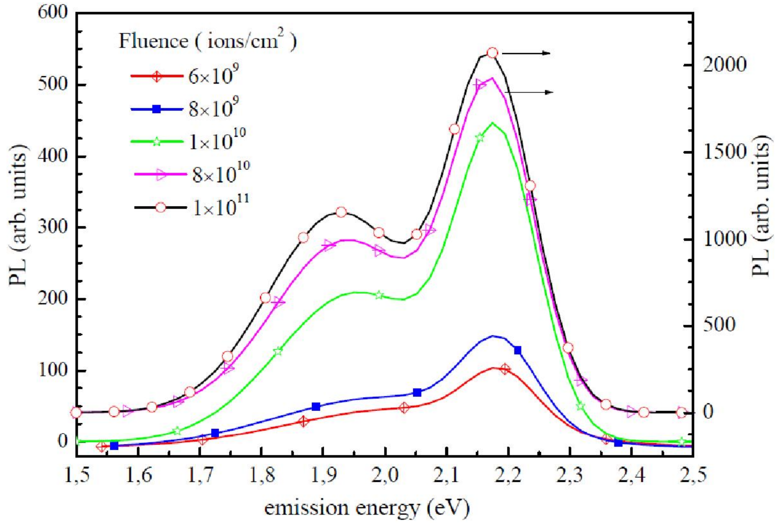

Figure 8 : Photoluminescence emission spectra of LiF crystals irradiated with 144 MeV Pb ions at different fluences (fluence is expressed in ions/cm^2)

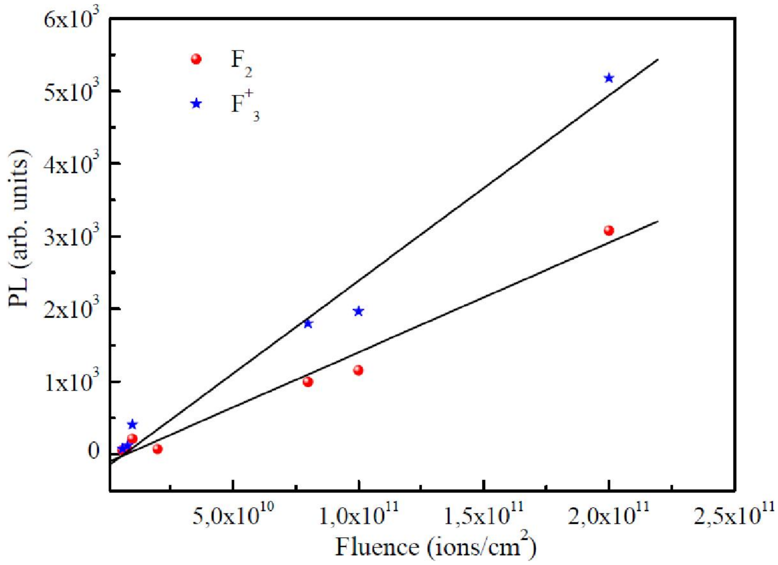

Figure 9 : PL intensity F_2 and F_3^+ color centers as a function of fluence

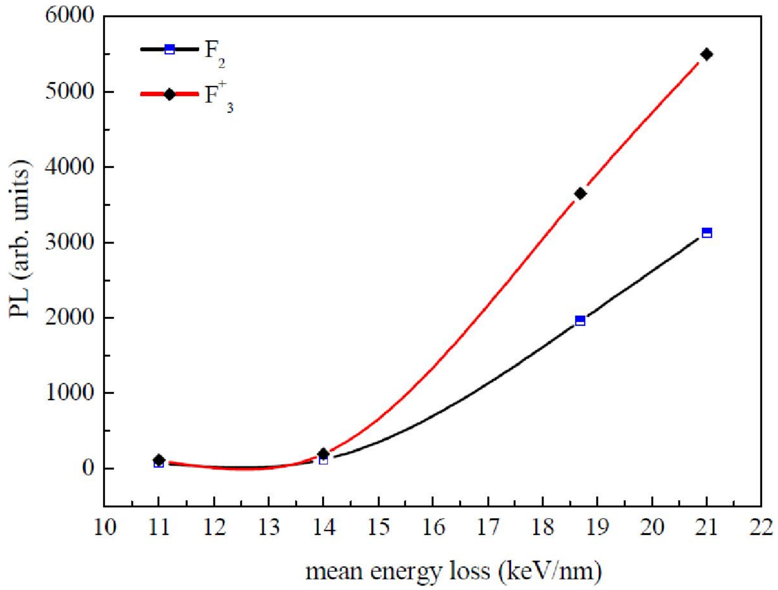

Figure 10 : PL intensity F_2 and color centers as a function of mean energy loss

veals approximately the same emission band width with increasing fluence and electronic stopping power. The F_2 and F_3^+ intensities linearly increase with increasing fluence as shown in Figure 9.

CONCLUSIONS

This paper reports on the damage produced in single crystals of LiF by irradiation with lead ions at different energies in the range of several hundred MeV. Single defects such as *F*-centers are produced in a large halo of 9–22 nm around the ion trajectory and track radii increase with the mean energy loss. Photoluminescence spectroscopy reveals that F centers aggregates (F_3^+, F_2) increase linearly with fluence, but not linearly with mean energy loss. Increase in PL intensity of the irradiated samples indicates an increase in high energy induced radiation defects in the samples.

ACKNOWLEDGEMENT

The authors are particularly indebted to Pr. A. Meftah to have placed at our disposal the single crystals of LiF used in this study within the framework of project CMEP, Tassil 03, MDU 573, and Dr. L. Gerbous from Nuclear Research Center of Algiers for photoluminescence measurements.

REFERENCES

[1] P.Thevenard, G.Guiraud, C.H.S.Dupuy, B.Delaunay; Radiat.Eff., **32**, 83 **(1977)**.
[2] K.Schwartz, G.Wirth, C.Trautmann, T.Steckenreiter; Phys.Rev.B**, 56**, 10711 **(1997)**.
[3] C.Trautmann, K.Schwartz, J.M.Costantini, T.Steckenreiter, M.Toulmonde; Nucl.Instr.and Meth.B**, 146**, 367 **(1998)**.
[4] C.Trautmann, K.Schwartz, O.Geiß; J.Appl.Phys, **83**, 3560 **(1998)**.
[5] N.Itoh, K.Tanimura; J.Phys.Chem.Solids, **51**, 717 **(1990)**.
[6] D.A.Young; Nature (London), **183**, 375 **(1958)**.
[7] A.Perez, E.Balanzat, J.Dural; Phys.Rev.B**, 41**, 3943 **(1990)**.
[8] E.Balanzat, S.Bouffard, A.Cassimi, E.Dooryhee, L.Protin, J.P.Grandin, J.L.Doualan, J.Margerie; Nucl.Instr.and Meth.B**, 91**, 134 **(1994)**.
[9] C.Trautmann, M.Toulemonde, K.Schwartz, J.M.Costantini, A.Müller; Nucl.Instr.And Meth.B**, 164**, 365 **(2000)**.
[10] A.Müller, R.Neumann, K.Schwartz, C.Trautmann; Nucl.Instr.and Meth.B, **146**, 393 **(1998)**.
[11] A.Müller, C.Müller, R.Neumann, F.Ohnesorge; Nucl.Instr.and Meth.B**, 166**, 581 **(2000)**.
[12] J.F.Ziegler, P.Biersack, U.Littmark; in: The Stopping and Ranges of Ions in Matter, J.F.Ziegler Pergamon, New York, **(1985)**.
[13] W.B.Fowler; Editor, *Physics of Color Centers*, Aca-

demic Press, New York London, **(1968)**.

[14] K.Schwartz, C.Trautmann, A.S.El-Said, R.Neumann, M.Toulemonde, W.Knolle; Phys.Rev.B**, 70**, 184104 **(2004)**.

[15] A.S.El-Said, R.Neumann, K.Schwartz, C.Trautmann; Nucl.Instr.and Meth.B**, 245**, 250 **(2006)**.

[16] V.A.Skuratov, S.M.Abu AlAzm, V.A.Altynov; Nucl.Instr.And Meth., **B191**, 251 **(2002)**.

[17] G.Baldacchini, R.M.Montereali; Opt.Mater., **16**, 53 **(2001)**.

[18] F.Bonfigli, B.Jacquier, R.M.Montereali, P.Moretti, V.Mussi, E.Nichelatti; F.Somma Opt.Mater., **24**, 291 **(2003)**.

[19] K.Kawamura, M.Hirano, T.Kurobori, D.Takamizu, T.Kamiya, H.Hosono; Appl.Phys.Lett., **84**, 311 **(2004)**.