Electron-irradiation-induced defects in BaLiF$_3$ crystals

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Abstract.   We report preliminary results on the production of colour centres in BaLiF$_3$ crystals, subjected to electron irradiation. The dependence of the colour-centre creation on the temperature and dose of the irradiation, as well as on the direction of crystal growth, was studied. Our experimental results concerning absorption, emission and excitation spectra measurements show that defect formation in BaLiF$_3$ crystals depends strongly on the conditions of crystal growth and preparation of the samples. By comparing BaLiF$_3$ with KMgF$_3$ and LiF crystals, we were able to attribute the absorption bands at 260, 420, 632, 386 and 480 nm to F, F$_2$, F$_2^+$, F$_3$ and F$_3^+$ centres. Theoretical evaluations of the absorption energies for these defects were made, and they supported these assignments. Room temperature electron irradiation of crystals grown in $\langle 100 \rangle$ and $\langle 111 \rangle$ directions favours the formation of different kinds of F-aggregate centre for each of these two cases. In particular, for $\langle 100 \rangle$ crystals we were able to observe the formation of F$_2^+$ centres with one absorption band at 632 nm and a corresponding emission at 702 nm.

1. Introduction

The demand for developing new tunable laser sources has revived the interest in investigating colour-centre formation in fluoroperovskites. Our recent work concerning the spectroscopic characterization of Pb$^+$(1) centres as a potential laser-active medium in BaLiF$_3$ doped with Pb^{2+} ions [1–3] led to the necessity of undertaking a study of controlled defect formation induced by radiation in both pure and doped BaLiF$_3$ crystals. Although some work has recently been reported on x-irradiated [4, 5], γ-irradiated and UV-irradiated [5] BaLiF$_3$ crystals, centred around understanding them as possible scintillator materials, knowledge about colour centres in BaLiF$_3$ is still very scarce. This crystal is an inverted perovskite which has the same structure as the KMgF$_3$ crystal (figure 1). The crystal has a cubic symmetry where both cations occupy local sites of O$_h$ symmetry but with different coordination numbers n. For Ba^{2+} sites, n is 12 and for Li$^+$, n is 6. The fluorine ions occupy the centres of the cube faces and have D$_{4h}$ symmetry. In this paper we present a study of the primary defect formation in pure BaLiF$_3$ crystals as a function of the temperature and dose of high-energy electron irradiation. Crystals grown in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions were investigated. The more usual defect products in BaLiF$_3$ have been tentatively identified by optical techniques, by making a comparison of our measured absorption bands with those corresponding to the analogous defects in KMgF$_3$ and LiF. This analogy is possible because the absorption bands, corresponding to several F-aggregate centres, depend essentially on the anionic-vacancy distances. Moreover a modified H$_2$, H$_2^+$, H$_3$ and H$_3^+$ model has been used to predict the absorption bands for the F$_2$, F$_2^+$, F$_3$ and F$_3^+$ centres in BaLiF$_3$.
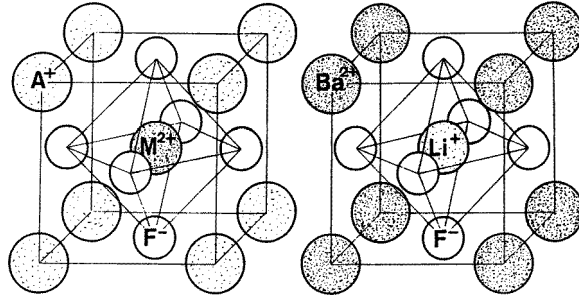
Figure 1. The crystalline structure of a normal perovskite (on the left) and of BaLiF$_3$ crystals.

2. Experimental procedure

BaLiF$_3$ crystals with good optical and crystalline quality were grown in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions by using the Czochralski growth method [6]. The samples were sawed from the crystal boules with faces perpendicular to the crystal growth direction. Specimens with 0.3 to 1.5 mm thickness were carefully polished, sealed in aluminium foil and irradiated in a Dynamitron accelerator with high-energy electrons (at 1.5 MeV and a current of 0.3 mA). The samples were irradiated at three different temperatures: 77, 173 and 300 K. The low-temperature irradiation was accomplished by placing the crystals in a copper boat floating in a liquid nitrogen pool under the electron beam. After the irradiation, the crystals were stored at liquid nitrogen temperature to avoid centre degradation. The radiation doses used were 250, 500 and 1000 kGy.

In this work we measured absorption, emission and excitation spectra. The absorption spectra were taken using a double-beam Cary 17D spectrophotometer and a home-made cryostat which enables the sample temperature to be reduced to 77 K within fifteen minutes. The emission and excitation apparatus has been described in detail in a previous report [1]. For the luminescence spectra a helium closed-circuit refrigerator cryostat was employed.

3. Experimental results

3.1. Effects of the temperature and dose of the electron irradiation

Figure 2 shows the irradiation temperature dependence of the absorption spectra for $\langle 100 \rangle$ and $\langle 111 \rangle$ crystals (figures 2(a) and 2(b) respectively). In these cases the radiation dose was fixed at 250 kGy and the curves were measured at 77 K. Before the irradiation, the crystals were completely transparent over the whole spectral range monitored. Two main absorption bands were observed at 260 and 420 nm and a non-distinct one at 305 nm overlapping the 260 nm band, for all of the irradiation temperatures. The first two absorption bands probably correspond to absorption of F and F$_2$ centres respectively. These assignments are supported by the comparison of BaLiF$_3$ results with those for KMgF$_3$ and LiF crystals reported in the literature. This is reasonable, since the distances between two nearest anionic vacancies are nearly the same for all three crystals considered. We will return to this point in the next section. It is also interesting to remark that room temperature irradiation of KMgF$_3$ produces F centres predominantly and only a small number of F$_2$ centres. However, this usual behaviour is not preserved in BaLiF$_3$ crystals.

The increase of irradiation temperature produces an enhancement in the concentration
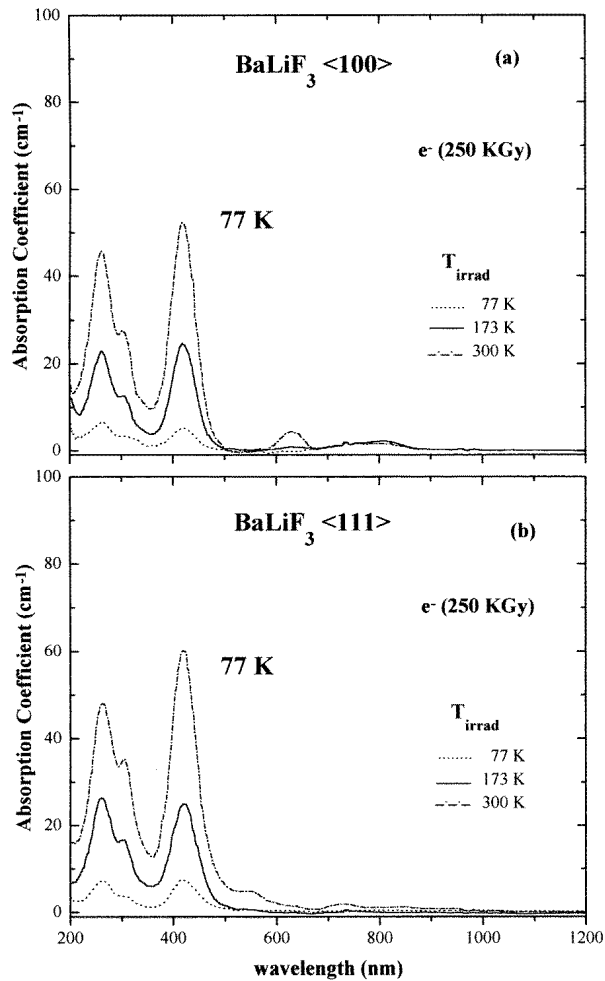
Figure 2. Optical absorption spectra of electron-irradiated BaLiF$_3$ crystals grown in the (a) $\langle 100 \rangle$ and (b) $\langle 111 \rangle$ directions. The radiation dose was fixed at 250 kGy. The curves were taken at 77 K. The irradiation temperatures were 77 ($\cdots\cdots$), 173 (——) and 300 K (— $\cdot$ —).

of the ultraviolet-absorbing defects. For room temperature irradiation we can also observe weak absorption bands between 500 and 1000 nm corresponding probably to F-aggregate-centre absorptions. It is also interesting to note that different kinds of F-aggregate centre are created in $\langle 100 \rangle$ and $\langle 111 \rangle$ crystals subjected to identical irradiation conditions. In $\langle 100 \rangle$ crystals, the room temperature irradiation produces mainly a 630 nm absorption band, while in $\langle 111 \rangle$ crystals, defects absorbing at 570 and 730 nm are produced in larger quantities. Storage of crystals in the dark for 72 hours contributes to the growth of the 630 and 730 nm absorption bands.

In figure 3 we can see the results for the irradiation dose dependence of the most prominent absorption bands observed in the ultraviolet region in BaLiF$_3$ crystals. Each curve corresponds to a specific irradiation temperature. Results concerning the crystals grown along the $\langle 100 \rangle$ direction are shown in this figure on the left-hand side and vice versa for $\langle 111 \rangle$ crystals. For irradiation at 77 K, nearly the same concentrations of defects
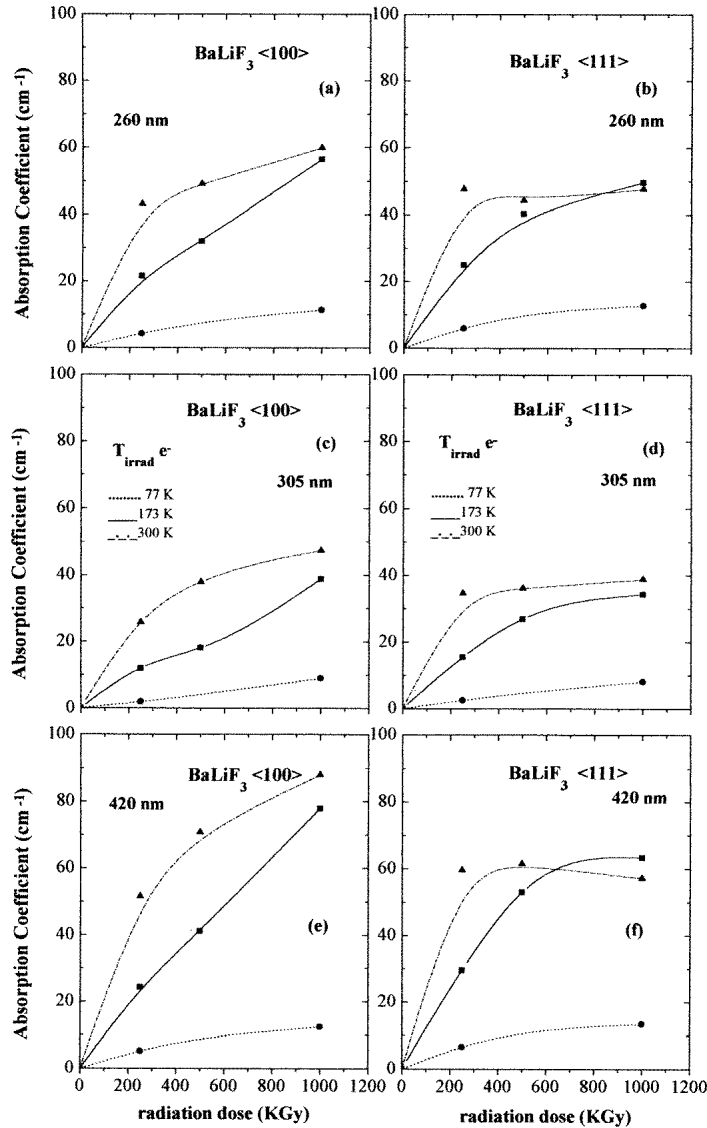
Figure 3. The radiation dose dependence of the 260 ((a), (b)), 305 ((c), (d)) and 420 nm ((e), (f)) wavelength positions for crystals grown in the ⟨100⟩ ((a), (c), (e)) and ⟨111⟩ ((b), (d), (f)) directions. The absorption measurements were taken at 77 K.

are produced in the ⟨100⟩ and ⟨111⟩ crystals. On the other hand, for irradiation accomplished at room temperature we can verify a distinct behaviour for each case. In ⟨111⟩ crystals the dose curves, for all of the wavelengths studied, attained saturation between 250 and 500 kGy. For ⟨100⟩ crystals, doses greater than 500 kGy still contribute to the defect concentration increase.

In order to verify the photonic stability of the defects observed immediately after the end of the irradiation, ⟨111⟩ crystals were illuminated at room temperature, with ultraviolet light (260 nm) and blue light (420 nm). The results are summarized in figure 4. Both the
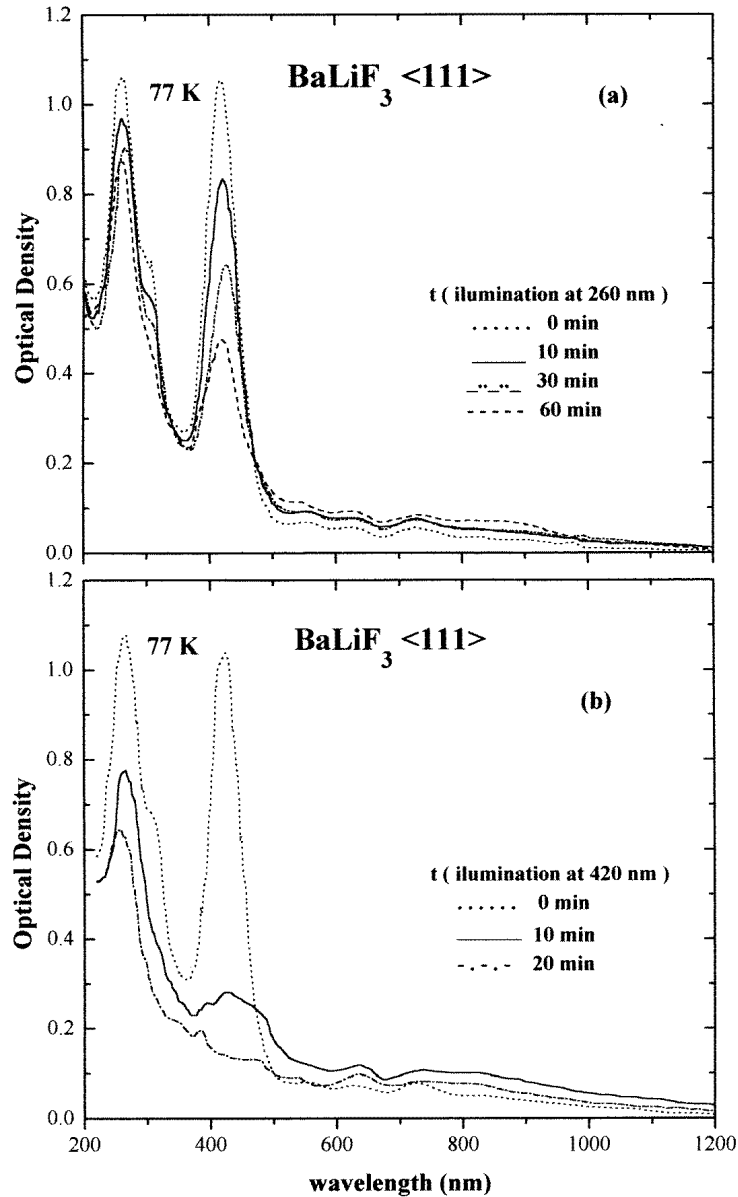
Figure 4. Optical spectra measured at room temperature after illumination of irradiated ⟨111⟩ crystals with (a) 260 and (b) 420 nm light. The times of light exposure were zero (······), 10 (——), 20 (— · —), 30 (— · · —) and 60 (- - - -) minutes.

UV and blue lights produce a pronounced decay of the 420 nm absorption band. Just ten minutes of blue light is sufficient to destroy most of the resonant band. Simultaneously, we observe that the absorption increases in the spectral region around 480 and 630 nm, and a very large absorption from 700 to 1100 nm shows up. We can also distinguish an absorption band at around 386 nm. On the other hand, we verified that the 260 nm absorption band is more stable under illumination.
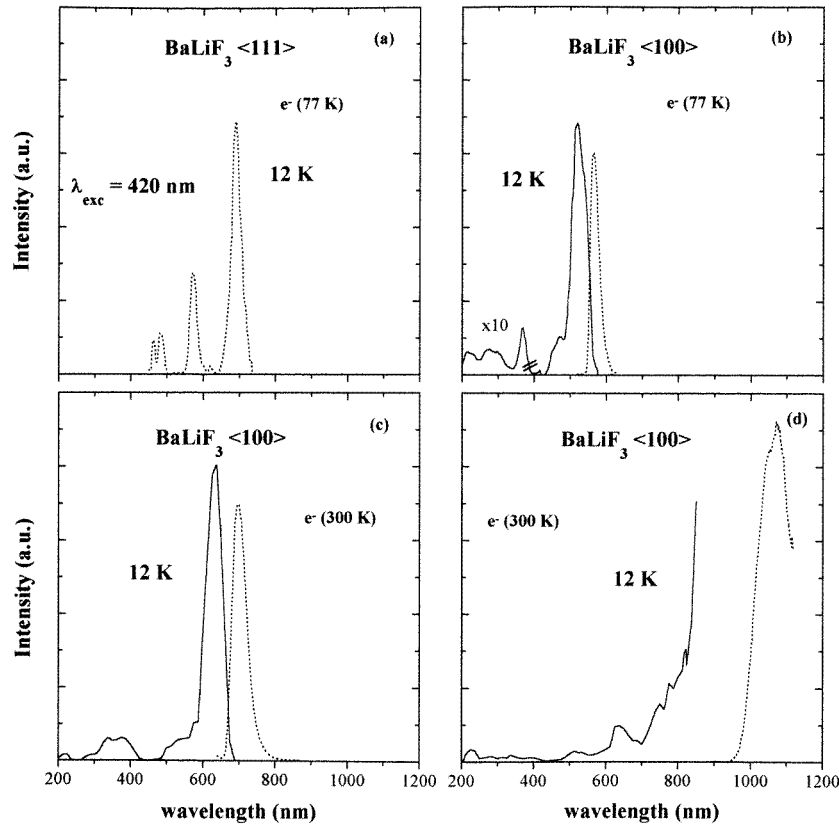
Figure 5. Excitation (——) spectra corresponding to 565 nm (b), 702 nm (c) and 1068 nm (d) emission (- - - -) bands observed for electron-irradiated BaLiF$_3$ crystals. In part (a) we can see the emission spectrum obtained by excitation at 420 nm. All of the curves were measured at 12 K in order to improve resolution.

3.2. Luminescence of defects

In order to obtain a deeper insight into the defect properties produced by irradiation, we optically excited the crystals in the region of the main absorption peaks and tried to determine the corresponding emission bands. The measurements were made at 12 K in order to improve the spectral resolution. Although the absorption bands in the ultraviolet region are very strong, illumination of ⟨111⟩ crystals irradiated at 77 K with 250 and 420 nm radiation results in very weak emissions. Excitation of the crystal with 250 nm radiation, at 12 K, gives rise to a very weak emission band with a maximum at 321 nm and a long tail which extends throughout the visible region. For excitation at 420 nm we observed four weak emission bands at 462, 482, 572 and 691 nm, as is shown in figure 5(a). This fact suggests the existence of an overlap of different types of defect absorbing in this region. Otherwise, excitation at 340 nm results in a more intense emission being observed at 433 nm with a halfwidth at half-intensity of 2400 cm^{-1} (12 K).

The visible bands were excited in the crystals irradiated at room temperature after storage in darkness for 72 hours. The 630 and 720 nm band excitation induces emissions at 702 and 1062 nm (12 K) respectively. These emissions and their corresponding excitation spectra

Table 1. Experimental positions of the principal emission bands and their respective excitation bands (the most intense) for colour centres in BaLiF$_3$.

Emission band (12 K)		Most intense excitation band (12 K)	
Peak position (nm)	Halfwidth (cm^{-1})	Peak position (nm)	Halfwidth (cm^{-1})
433	2400	350	2010
565	880	519	1835
702	963	632	1400
1068	814	720, 820	—

can be seen in figures 5(c) and 5(d). The excitation spectrum for the 572 nm emission band is shown in figure 5(b). All of the measured excitation spectra show a complex profile involving several weak absorption bands in the UV region. These results can explain most of the emissions reported above for the 420 nm excitation. The remaining induced emission at 482 nm is most probably due to the 420 nm absorbing defect. In fact, the corresponding excitation spectrum shown weak absorption bands at 360 and 425 nm. Table 1 summarizes the most intense emission and excitation bands observed in our experiments.

4. Discussion

Colour centres in pure fluoroperovskites received a detailed treatment for KMgF$_3$ [7–9] and RbMgF$_3$ [10, 11] crystals. BaLiF$_3$ crystals have received up to now only a brief examination. We can find some results concerning thermally stimulated processes (TSL and TSC) [12, 13]. More recently, some data concerning magnetic properties of x-irradiated crystals [4] and optical properties of x-, γ- and UV-irradiated crystals [5] have been published.

We believe that it is possible to identify some of the defects observed in this work for BaLiF$_3$ crystals by comparison of our results with those obtained for KMgF$_3$ [7–9] and LiF [14, 11]. The experimental absorptions for F, F$_2$, F$_3$ and V$_K$ centres are assembled in table 2. This procedure is valid because the absorption positions of F-aggregate centres depend mainly on the distances between the anionic vacancies. In BaLiF$_3$, KMgF$_3$ and LiF crystals the nearest-anion distances are 2.83, 2.81 and 2.84 Å respectively. So we can tentatively ascribe the 260, 420, 386, 480 and 632 nm absorption bands in BaLiF$_3$ to F-,

Table 2. Spectral characteristics of colour centres in fluoride crystals. The references are given in square brackets.

Centre	LiF Absorption (nm)	LiF Emission (nm)	KMgF$_3$ Absorption (nm)	KMgF$_3$ Emission (nm)	BaLiF$_3$ Absorption (nm) Experiment (our results)	BaLiF$_3$ Absorption (nm) Prediction (present work)	BaLiF$_3$ Emission (nm) Experiment (our results)
F	243 [23]		270 [7, 8]		260		
F$_2$	445 [14]	670 [14]	445 [7]	590 [9]	420	490	
F$_2^+$	630 [14]	910 [14]			632	627	702
F$_3$	380 [11]		395 [7]	465 [9]	386	452	
F$_3^+$	458 [14]	539 [14]			480	455	
V$_K$	340 [23]		340 [7]		345 [12]		

F_2-, F_3-, F_3^+- and F_2^+-centre absorption respectively.

We can also estimate the absorption energies for the defect centres referred to above by means of a theoretical method used by Herman *et al* [15] to calculate the energy levels of F_2 and F_2^+ centres. In their model they considered F_2^+ and F_2 centres as one and two electrons, respectively, moving in the field of two positive point charges immersed in a dielectric medium. This is equivalent to considering a hydrogen molecular ion, in the case of the F_2^+ centre, or a hydrogen molecule (F_2 centre), immersed in a dielectric medium k_0. The energy $E(r_{ab}, k_0)$ of a given electronic state of the hydrogen molecular ion in a dielectric medium can be related to the energy $E'(R)$ of the same state of the same molecule in free space by means of the expression

$$E(r_{ab}, k_0) = 1/k_0^2 E'(R) \tag{1}$$

where

$$R = r_{ab}/k_0 \tag{2}$$

where r_{ab} is the distance between the positive charges. So for given values of k_0 and r_{ab} it is possible to calculate R by means of expression (2). The energy $E'(R)$ can be extracted from data curves found in the literature for the energies of the H_2^+ [16], H_2 [16, 17], H_3 [18] and H_3^+ [18] molecules in free space over a range of internuclear distances.

This theoretical approach has been employed with success by Aegerter and Luty [19] to explain the absorption of F_2^+ centres in KCl and by Podinsh and Sibley [11] to estimate the absorption energies of F_2, F_3 and F_3^+ centres in $RbMgF_3$ crystals. Those authors obtained a good fitting by using not the real values, but effective values for both the dielectric constant and internuclear distances. Our results for the estimation of F-aggregate-centre absorptions in $BaLiF_3$ crystals are shown in table 2. For these evaluations we have considered an effective dielectric constant of 2.35 (the real value is 2.25) for $BaLiF_3$ crystals and an effective internuclear distance of 2.80 Å (the real value is 2.83 Å). The results obtained give support to the previous tentative identification of colour centres in $BaLiF_3$.

From a qualitative point of view it is interesting to point out that the measured ultraviolet spectra of irradiated $BaLiF_3$ presented a complex structure depending on the applied conditions of temperature and dose of electron irradiation. It was not possible to produce isolated F centres in the same way as was done for $KMgF_3$ crystals (in this case a preferential production of F centres was obtained even for room temperature irradiation). In $BaLiF_3$ crystals, F (260 nm) and F_2 (420 nm) centres always appear together, in nearly the same concentrations. The 305 nm absorption band was not observed for $KMgF_3$ crystals.

Kristianpoller and Trieman [12] had already reported the observation of absorption bands at 280 and 410 nm in x-irradiated $BaLiF_3$ crystals at 80 K. They attributed the 280 nm absorption to F-centre defects. The difference in the F-centre wavelength position between our results and theirs could be explained by a possible overlap of the two defects absorbing at 305 and 260 nm produced, unintentionally, in the same concentrations. Our ultraviolet spectrum was similar to that obtained by Tale *et al* [4]. These authors observed an optically detected EPR (ODEPR) signal by monitoring at 450 nm. They concluded, unlike us, that the 420 nm band corresponds to hole centres. From figure 1, we can note that the 420 nm band is asymmetrical on the longer-wavelength side. This could suggest the presence of another defect, whose absorption band would not be well resolved. Moreover, our luminescence experiments shown that the 420 nm band corresponds to absorptions of several distinct defects. We can also recall that F_2 centres do not show EPR signals and that V_K centres absorb at nearly 340 nm in both LiF and $KMgF_3$ crystals. Also, we have observed in $BaLiF_3$:Pb irradiated crystals [1] a 420 nm absorption suppression. Pb^{2+} ions

are well known to be good electron [20] and hole [21] traps. In some systems, Pb^{2+} ions are employed to inhibit the F$_2$-centre production. In the light of these arguments, we maintain our view that F$_2$ centres in BaLiF$_3$ are responsible for the appearance of the 420 nm band.

As regards the visible spectrum of irradiated BaLiF$_3$ crystals, our results and those reported in the literature show that the production of F-aggregate centres depends strongly on the conditions of growth, purity and preparation of the crystals. We were surprised to observe a distinct behaviour for crystals grown in different directions but subjected to the same conditions of irradiation. This result would be unexpected for unpolarized-light measurements for cubic crystals, which do not present phase changes and can be considered as an isotropic medium for any temperature. The visible absorption bands correspond to more complex F-aggregate centres. Their formation depends on the migration of the primary defects of irradiation. So the experimental results might suggest, without entering into detail, that the mechanisms of defect aggregation in ⟨100⟩ and ⟨111⟩ crystals are different. This remains an unsolved problem and is now under investigation.

The absorption band at 632 nm is tentatively identified as due to F$_2^+$ centres and is produced in larger concentrations for crystals grown in the ⟨100⟩ direction. The corresponding emission was found at 702 nm. It is interesting to note that F$_2^+$-centre emission in alkali halides exhibits a large Stokes shift. Nevertheless, we cannot yet explain why it does not work in the same way on BaLiF$_3$ crystals. On the other hand, the 725 nm defect presents a large Stokes shift with the corresponding emission at 1062 nm. This could be due to F$_2^-$ centres, but sufficient evidence is not yet available to make a definitive assignment. Likewise, the stronger emissions at 433 and 565 nm could correspond to the interaction of impurities with colour centres (F and F$_2$ centres respectively). In fact, we have been able to observe, in some early experiments, a strong absorption band at 518 nm (10 K) in a ⟨100⟩ irradiated crystal more highly contaminated with Ca^{2+} ions. On the other hand, a strong 480 nm emission was observed in LiF crystals doped with Mg^{2+} ions when excited in the 375 nm region [22], which was attributed to F$_z$ centres.

5. Conclusions

The purpose of the present work was to provide some insight into a general view of the defect-centre formation in BaLiF$_3$ crystals. In this paper we report preliminary results relating to the production of colour centres in BaLiF$_3$ crystals subjected to electron irradiation. Our experimental results concerning absorption, emission and excitation spectra measurements show that defect formation depends strongly on the conditions of growth and preparation of the samples. By comparing BaLiF$_3$ with KMgF$_3$ and LiF crystals, we have identified the absorptions at 260, 420, 632, 386 and 480 nm as F, F$_2$, F$_2^+$, F$_3$ and F$_3^+$ centres respectively. These assignments were supported by evaluation of the absorption position energies for these defects by employing a model for predicting the transition energies of the hydrogen molecule (in its different electronic states) immersed in a dielectric medium. The experimental absorption spectra show qualitatively the same complex structure in the ultraviolet region for both room and low irradiation temperatures. Increase of the dose and temperature of the irradiation only increased the concentration of defects. Defects absorbing at 260, 305 and 420 nm were always produced in equivalent concentrations. Irradiation at room temperature of crystals grown in ⟨100⟩ and ⟨111⟩ directions favours the formation of different kinds of F-aggregate centre in each type of sample. For ⟨100⟩ crystals, in particular, we were able to observe the formation of F$_2^+$ centres identified by the 632 nm band absorption and by the 702 nm emission. Further experiments correlating magnetic properties and optical properties (ODMR) could confirm our results.

Acknowledgment

References

[1]   Prado L, Vieira N D Jr, Baldochi S L, Morato S P and Gesland J Y 1993 *Solid State Commun.* **87** 41
[2]   Prado L, Vieira N D Jr, Baldochi S L, Morato S P, Denis J P, Tercier N and Blanzat B 1996 *J. Phys. Chem. Solids* **57** 413
[3]   Prado L, Baldochi S L, Morato S P and Vieira N D Jr 1997 *Proc. Symp. on Lasers and Their Applications* (Campinas, SP, Brazil: UNICAMP) pp 288–91
[4]   Tale I, Kulis P, Rogulis U, Tale V, Trokss J, Veispals A, Barboza-Flores M and Fitting H J 1997 *J. Lumin.* **72–74** 722
[5]   Gektin A V, Shiran N V and Voronova V V 1997 *IEEE Trans. Nucl. Sci.* **44** 857
[6]   Baldochi S L and Gesland J Y 1992 *Mater. Res. Bull.* **27** 891
[7]   Riley C R and Sibley W A 1970 *Phys. Rev.* B **1** 2789
[8]   Hall T P P and Leggeat A 1969 *Solid State Commun.* **7** 1657
[9]   Riley C R, Yun S I and Sibley W A 1972 *Phys. Rev.* B **5** 3285
[10] Koumvakalis N and Sibley W A 1976 *Phys. Rev.* B **13** 4509
[11] Podinsh A and Sibley W A 1978 *Phys. Rev.* B **18** 5921
[12] Kristianpoller N and Trieman B 1983 *Radiat. Effects* **72** 201
[13] Kristianpoller N, Trieman B, Chen R and Kirsh Y 1988 *Phys. Status Solidi* b **149** 45
[14] Basiev T T, Mirov S B and Osiko V V 1988 *IEEE J. Quantum Electron.* **24** 1052
[15] Herman R, Wallis M C and Wallis R F 1956 *Phys. Rev.* **103** 87
[16] Mulliken R S 1932 *Rev. Mod. Phys.* **4** 1
[17] Slater J C 1963 *Quantum Theory of Molecules and Solids* vol 1 (New York: McGraw-Hill) p 67
[18] Hirschfelder J O 1938 *J. Chem. Phys.* **6** 795
[19] Aegerter M A and Luty F 1971 *Phys. Status Solidi* b **43** 245
[20] Tsuboi T 1980 *Phys. Rev.* B **21** 2635
[21] Schoemaker D and Kolopus J L 1970 *Solid State Commun.* **8** 435
[22] Courrol L C and Gomes L 1997 *J. Phys. Chem. Solids* **58** 281
[23] Fowler W B (ed) 1968 *Physics of Color Centers* (New York: Academic)