

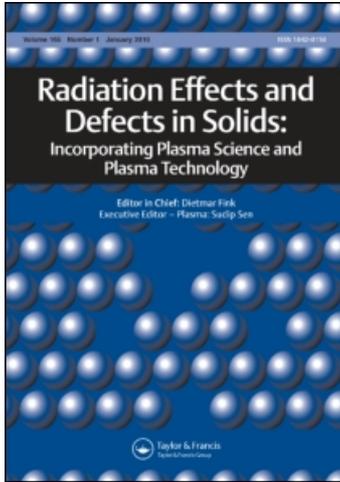
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F-AGGREGATE CENTERS FORMATION IN BaLiF₃ CRYSTALS

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The kinetics of F-aggregate centers formation is investigated in the inverted fluoroperovskite of BaLiF₃ submitted to electron-irradiation. By studies of the changes in the absorption spectra during storage of samples in the dark, at room temperature, it was possible to verify a surprising and interesting dependence on defect formation with the crystal growth direction. In spite of its cubic structure, crystals grown in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions and submitted to the same conditions of irradiation, showed in each case different species of F-aggregate centers. It was possible, in particular, to enhance the production of a defect absorbing at 630 nm in $\langle 100 \rangle$ crystals which we believe to correspond to F₂⁺-centers in BaLiF₃.

Keywords: F-aggregate centers; Color centers; BaLiF₃ crystals

1 INTRODUCTION

Fluoroperovskites are potentially hosts for laser active media. Among them, Pb⁺(1)-centers in BaLiF₃:Pb²⁺ have shown good optical properties as a candidate for laser medium [1–3]. Therefore a controlled radiation defect formation was undertaken in both pure and doped BaLiF₃ crystals in order to optimize the formation of Pb⁺(1)-centers. Four parameters were investigated: temperature and dose of electron irradiation, crystal growth direction and impurity concentration [3].

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In this work we present the results obtained for the study of the dependence on defect formation with the crystal growth direction in BaLiF₃ crystals.

2 EXPERIMENTAL RESULTS AND DISCUSSION

Pure BaLiF₃ crystals of good optical quality were grown in the $\langle 100 \rangle$ and $\langle 111 \rangle$ directions by using the Czochralski growth method. The samples were exposed to high energy electrons (1.5 MeV and current of 0.3 mA) at 173 K and at room temperature. The applied dose was 1 MGy. Thermal aggregations at room temperature in the dark, after irradiation, were monitored by absorption spectra measured at 300 K, using a double beam Cary 17 D spectrophotometer.

The results obtained for crystals grown in the $\langle 100 \rangle$ direction can be seen in Fig. 1. Figure 1(a) shows the results concerning the thermal decay of samples irradiated at 173 K; Fig. 1(b) shows the same for irradiation at 300 K.

We can distinguish different behaviors for samples irradiated at different temperatures. For crystals irradiated at 173 K we can observe a pronounced decay of the primary irradiation defects absorbing in the UV region at 260 nm (F-center), 305 and 420 nm (F₂-center) [4], already during the first 48 h of storage. In this case the thermal decay is not followed of significant aggregate-defects formation. For crystals irradiated at 300 K, however, the UV band decay causes simultaneous formation of major aggregate-defects which absorb in the visible region, mainly a kind of defect absorbing at 630 nm which we believe to be F₂⁺-centers [4].

Figure 2 shows the results concerning crystals grown in the $\langle 111 \rangle$ direction. Comparing these curves with those of Fig. 1 we can observe a completely different behavior. For $\langle 111 \rangle$ crystals the primary irradiation defects are comparatively more stable. After 30 days of storage we still have high concentrations of defects absorbing in 260, 305 and 420 nm, for both 173 and 300 K electron-irradiations. In the last case we can clearly see an enhancement of a 725 nm absorbing defect, at least on a first stage of 30 days of aggregation, but in much lower concentrations than the observed one for 630 nm absorbing defects in $\langle 100 \rangle$ crystals.

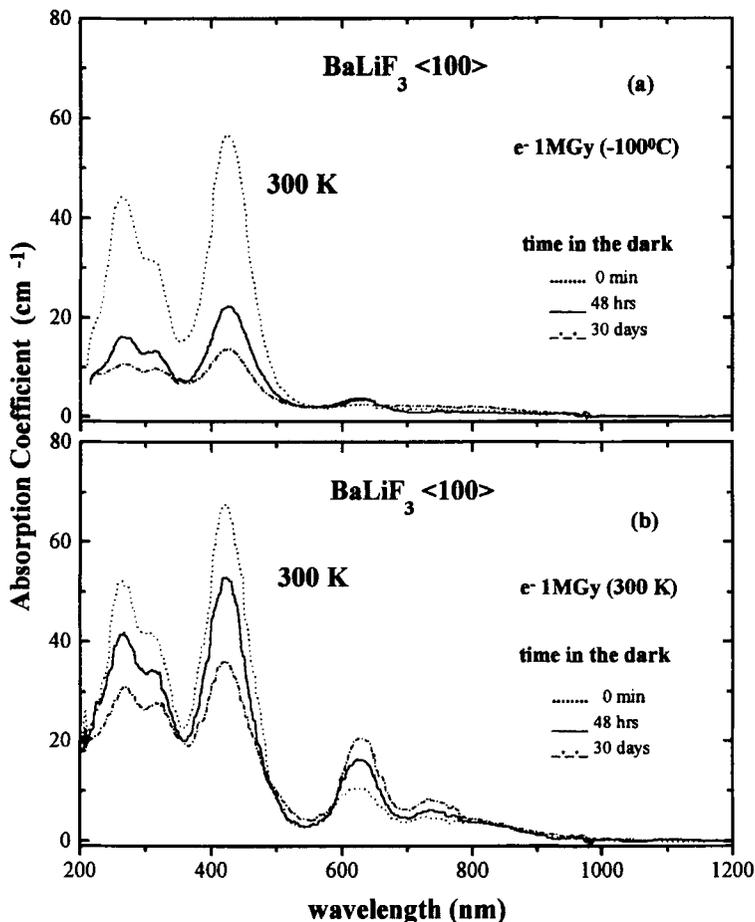


FIGURE 1 Absorption spectra (300 K) of $\langle 100 \rangle$ BaLiF₃ crystals electron irradiated at 173 K (a) and 300 K (b) recorded for different conditions: immediately after removal of samples from liquid nitrogen dewar (.....), after 48 h (—) and 30 days (----) keeping the crystals in the dark.

The growth and decay curves of the prominent absorption peaks situated at 260, 305, 420, 630 and 725 nm, monitored for a total period of 6 months, are illustrated in Fig. 3 for crystals irradiated at room temperature. It is interesting to remark a continuous enhancement of the 630 nm absorption defect for $\langle 100 \rangle$ crystals for such long period of time (final absorption coefficient value of 28 cm⁻¹). For $\langle 111 \rangle$ crystals

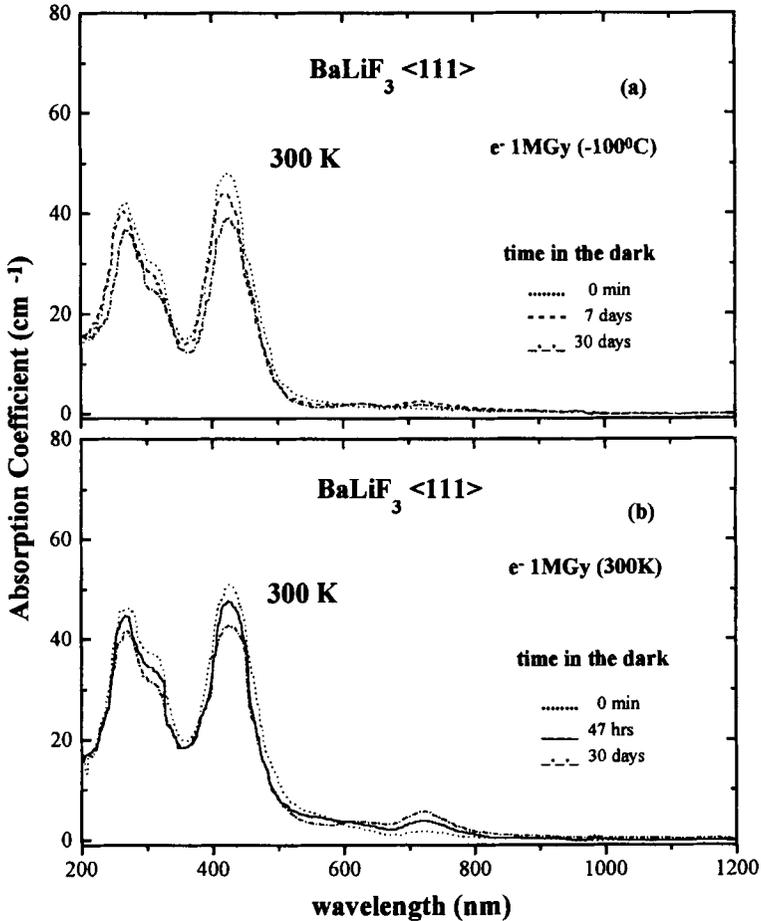


FIGURE 2 Absorption spectra (300 K) of $\langle 111 \rangle$ BaLiF_3 crystals electron irradiated at 173 K (a) and 300 K (b) recorded for different conditions: immediately after removal of samples from liquid nitrogen dewar (\cdots); after 47 h (—), 7 days (--) and 30 days ($\text{-}\cdot\text{-}$) keeping the crystals in the dark.

after 30 days the 725 nm band saturates (absorption coefficient equal to 5.5 cm^{-1}) and begins to slowly decay while the 630 nm band continues to increase (absorption coefficient of 4.7 cm^{-1} after 6 months of monitoring). These results indicate that aggregation of defects is more probable in $\langle 100 \rangle$ crystals.

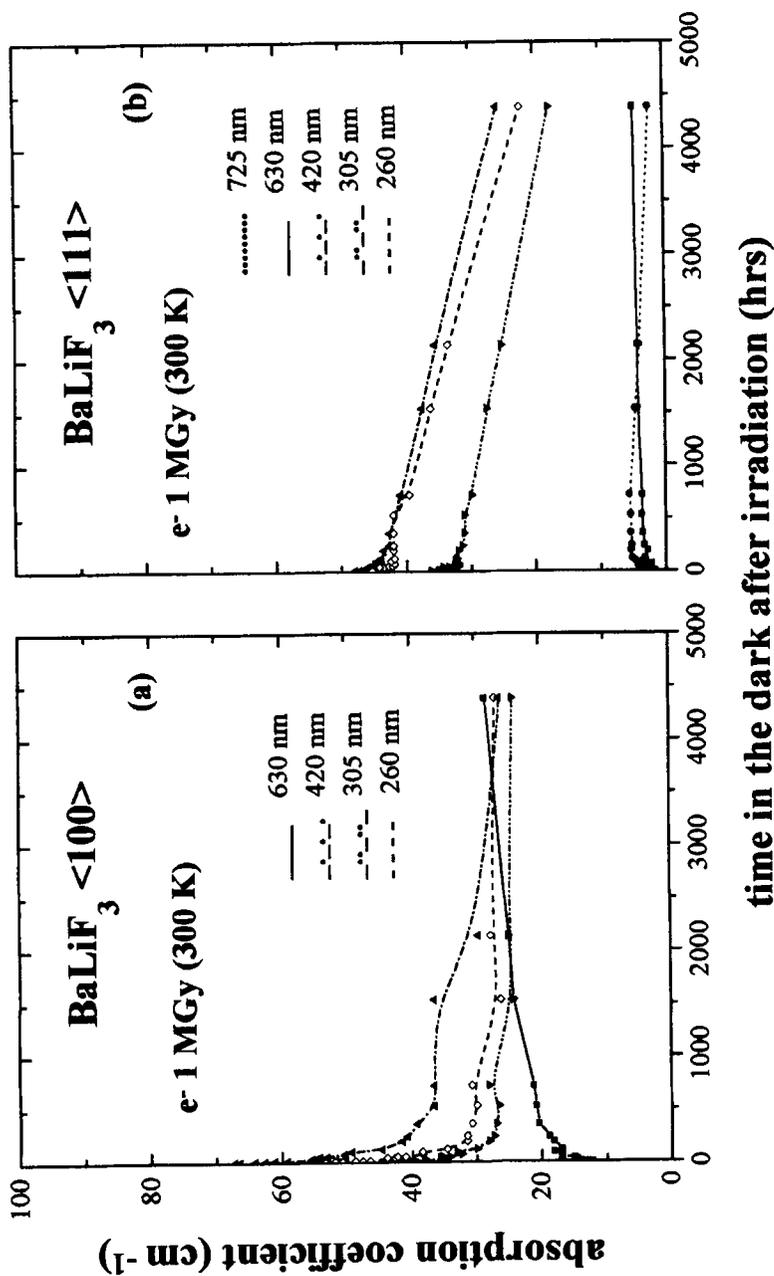


FIGURE 3 Growth and decay curves of absorption peaks versus time of storage in the dark at room temperature. Graphic (a) corresponds to <100> crystals; graphic (b) to <111> crystals. Measurements and electron-irradiation made at room temperature.

Although the BaLiF_3 crystal has a cubic structure and thus corresponds to an isotropic medium it was surprising for us to verify a distinct behavior for crystals grown in different directions. F-aggregate centers formation depends on the mobility of defects in the crystal, mainly by vacancy migration. Recombination processes also compete and can inhibit the defect aggregation processes. These recombination effects can be minimized when fluorine ions can easily migrate through the crystal to form clusters. Concerning these last two points there are two works in the literature. In the first one, Baldochi *et al.* [5] showed, by neutron diffraction techniques, that both $\langle 111 \rangle$ and $\langle 100 \rangle$ BaLiF_3 crystals presented a good crystalline quality. Besides, the last one was better. The crystalline quality depends on the number of crystalline domains formed during the growth process, as well as on their angular width and angular dispersion between them. In the second work, by Jackson *et al.* [6], they concluded that, concerning migration processes at low temperatures in BaLiF_3 crystals, the dominant process would be fluorine migration by the vacancy mechanism. At higher temperatures the existence of lithium and fluorine interstitial ions could also provide another source of migration.

Taking the above considerations in mind we can suggest the following explanation for the differences observed between $\langle 111 \rangle$ and $\langle 100 \rangle$ BaLiF_3 crystals. During the irradiation with high energy electrons both fluorine and lithium ions at interstitial positions can be produced. For irradiation at low temperatures interstitial ions are near the corresponding vacancies, when compared to room temperature irradiation. Thus, the probability of recombination in this case is higher. The domain boundaries, are natural traps of interstitial ions. The vacancy migration in the neighborhood of these boundaries can then lead to recombination among the vacancies with the interstitial ions, located in the boundaries. Therefore, it is easier in this case, to regenerate the original lattice. For room temperature irradiated crystals, the higher crystalline (smaller number of crystalline domains) order favors the formation of interstitial-fluorine ions clusters, thus diminishing the recombination processes. These clusters are usually very stable leading to the higher stability of the F-aggregate centers seen in the $\langle 100 \rangle$ crystals. This could explain why the F-aggregates are better formed in the $\langle 100 \rangle$ than in the $\langle 111 \rangle$ grown crystals.

3 CONCLUSIONS

In the present work evidence has been presented to show that the mechanisms of production of F-aggregate defects are distinct for BaLiF₃ crystals of good crystalline quality grown in the $\langle 111 \rangle$ and $\langle 100 \rangle$ directions. Radiation induced defects in $\langle 111 \rangle$ crystals are comparatively more stable at least in the first three months of storage. On the other hand, for $\langle 100 \rangle$ BaLiF₃ crystals, storage of crystals at room temperature in the dark enables a production of high concentrations of a 630 nm defect which we believe to correspond to the absorption of the F₂⁺-centers.

Acknowledgments

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References

- [1] L. Prado, N.D. Vieira, Jr., S.L. Baldochi, S.P. Morato and J.Y. Gesland, *Solid State Commun.* **87**, 41 (1993).
- [2] L. Prado, N.D. Vieira, Jr., S.L. Baldochi, S.P. Morato, J.P. Denis, N. Tercier and B. Blanzat, *J. Phys. Chem. Solids* **57**, 413 (1996).
- [3] L. Prado, Tese de Doutorado, IPEN, S.P. (1997).
- [4] L. Prado, L. Gomes, S.L. Baldochi, S.P. Morato and N.D. Vieira, Jr., *J. Phys.: Cond. Matter* **10**, 8247 (1998).
- [5] S.L. Baldochi, V.L. Mazzochi, C.B. Parente, and S.P. Morato, *Mat. Res. Bull.* **29**, 1321 (1994).
- [6] R.A. Jackson, M.E.G. Valerio and J.F. de Lima, *J. Phys.: Cond. Matter* **8**, 10931 (1996).