

# X-ray damage characterization in BaLiF<sub>3</sub>, KMgF<sub>3</sub> and LiCaAlF<sub>6</sub> complex fluorides

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## Abstract

Two-inch sized KMgF<sub>3</sub>, BaLiF<sub>3</sub> and LiCaAlF<sub>6</sub> (LiCAF) single crystals were grown by the Czochralski method under a CF<sub>4</sub> atmosphere. X-ray irradiation was used to carry out a comparative study of induced optical absorption phenomena and colour centre creation in the ultra-violet and visible spectral regions. The integral of the induced absorption spectra is significantly lower in LiCAF with respect to the other studied materials. It is found that the amplitude of the F-absorption band is suppressed more than a factor of 3 by Mg-doping. For Mg-doped crystals, the optimum doping concentration is about 0.2 mol% of Mg<sup>2+</sup>. © 2004 Elsevier Ltd. All rights reserved.

*Keywords:* Fluoride crystal; Window material; Induced absorption; Colour centre

## 1. Introduction

Fluoride single crystals present many advantages as optical materials. Their high potential as window materials in the ultra-violet (UV) and vacuum-ultra-violet (VUV) wavelength regions was also identified based on their short wavelength absorption edges (Shimamura et al., 2000a, b; Bensalah et al., 2001).

Recently, development of VUV wavelength technologies has increased. In particular, an interest in using 157 nm laser source in projection semiconductor lithography as a successor to 193-nm-based systems was announced (Harbison, 2000; Hooker and Landsberg, 1994; Whitfield et al., 2001). One of the most serious problems in realizing the 157-nm-based system is the development of suitable optical materials for lenses and other optical components. For an all-refractive design of the 157 nm laser source,

a second material other than CaF<sub>2</sub> is strongly required. Primary candidates for a second material were LiF and MgF<sub>2</sub>, however, they have several disadvantages such as a fragile and hygroscopic nature and large birefringence (Bloomstein et al., 1997). Complex fluoride single crystals, such as Colquiriite- and Perovskite-type fluorides, also present many advantages as optical materials, because of their unique properties, such as large band gap. Therefore, we can regard these materials as suitable candidates.

Window materials in the optical lithography systems must withstand intense UV/VUV laser irradiation without changing their transmission characteristics. In fluoride crystals, irradiation by X- or gamma- ray or UV light occasionally creates colour centres demonstrating themselves in the appearance of absorption bands in VUV, UV or visible wavelength regions.

In the present work, we describe X-ray-induced radiation damage in KMgF<sub>3</sub> (KMF), BaLiF<sub>3</sub> (BLF) and LiCaAlF<sub>6</sub> (LiCAF) single crystals by optical absorption in the UV/VIS spectral regions, and show how it can be reduced by doping with aliovalent ions in LiCAF single crystal.

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## 2. Experimental

### 2.1. Growth procedure

Crystal growth was performed in a vacuum-tight Czochralski (CZ) system equipped with an automatic diameter control system. The starting material was prepared from commercial fluoride powders of LiF, KF, MgF<sub>2</sub>, CaF<sub>2</sub>, BaF<sub>2</sub> and AlF<sub>3</sub> (> 99.99%). In the case of KMF and LiCAF crystal growth, the initial concentrations were 5 mol% KF enriched and 3 mol% LiF and AlF<sub>3</sub> enriched from the stoichiometric one, in order to compensate for the vapourization of KF, LiF and AlF<sub>3</sub> from the melt (Shimamura et al., 2000b, 2001). In the case of BLF crystal growth, the initial concentration was 43 mol% BaF<sub>2</sub>: 57 mol% LiF because BLF melts incongruently (Agulyanskii and Bessonova, 1982). The starting material was placed in a Pt crucible 100 mm in diameter. Both rotary and diffusion pumps were used to achieve  $\approx 10^{-3}$  Pa and effectively eliminate water and oxygen from the growth chamber and the starting material. Subsequently, high purity CF<sub>4</sub> gas (99.99%) was slowly introduced into the furnace. Thereafter, the starting material was melted. The pulling rate was 1.0 mm/h and the rotation rate was 15 rpm.

### 2.2. Experimental methods

Colour centre creation was studied by means of irradiation-induced absorption measurements at RT. The transmission spectra of the materials under study were measured using a Jasco V-530 UV/VIS (190–1000 nm) spectrometer, before (transmission  $T_0$ ) and immediately after (transmission  $T_{\text{irr}}$ ) an X-ray irradiation procedure. The induced absorption

$$\mu(\lambda) = \ln(T_0(\lambda)/T_{\text{irr}}(\lambda)) \quad (1)$$

was calculated. Due to the strongly inhomogeneous irradiation of the sample volume by the X-rays used, the sample thickness was not considered and all the samples prepared were of the same thickness of about 2 mm. (Complete absorption of X-rays generated by the source described below typically occurs, for example in LiCAF, for sample thickness below 1 mm using a standard attenuation calculation according to Evans (1968)). Irradiation was accomplished using an X-ray tube (25 kV, Rigaku spectrometer and Micrometer II. X-ray source). Prior to the measurement of  $T_0$  the samples were annealed at 400°C (KMF), 250°C (BLF) and 350°C (LiCAF) for 2 h to empty trapping levels in the material. Annealing temperatures were determined by thermally stimulated luminescence (TSL) measurements above RT. TSL was measured in the 20°C–480°C range either by the simple spectrally unresolved mode (using a EMI9636QB photomultiplier) or using a double stage microchannel plate followed by a diode array, which allows the detection of the TSL signal both as a function of temperature and emission wavelength. Irradiations were performed by an X-ray

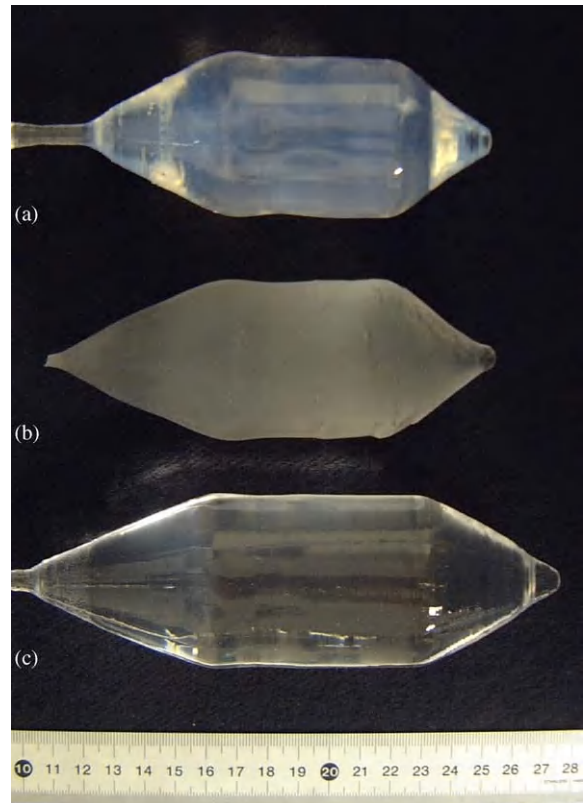


Fig. 1. As-grown (a) BaLiF<sub>3</sub>, (b) KMgF<sub>3</sub> and (c) LiCaAlF<sub>6</sub> single crystals 2-in in diameter without inclusions and cracks.

tube (Machlett OEG 50 operated at 30 kV), and doses from several hundred up to 1100 Gy were irradiated as noted for each case in the text (dose levels evaluated in air).

## 3. Results and discussion

Fig. 1 shows as-grown KMF, BLF and LiCAF single crystals with 2-in (50 mm) in diameter and 150 mm in length. No cracks, bubbles or inclusions were observed. Fig. 2 shows induced absorption after X-ray irradiation for BaLiF<sub>3</sub>, KMgF<sub>3</sub> and LiCaAlF<sub>6</sub> single crystals. All the three materials were grown by the same technology and from the raw material from the same source and of the same purity, so that a mutual comparison of their stability under X-ray irradiation is possible and reliable. Due to the technology used, extremely low contamination by oxygen ions, OH<sup>-</sup>, etc. can be guaranteed (Shimamura et al., 2000a, b, 2001; Bensalah et al., 2001), so that the observed induced absorption features should not be substantially distorted by the presence of oxygen related defects. F-centre governed induced absorption spectra were obtained in all three complex fluoride systems. F-aggregate centres are clearly present both in KMF and BLF materials, while in LiCAF no

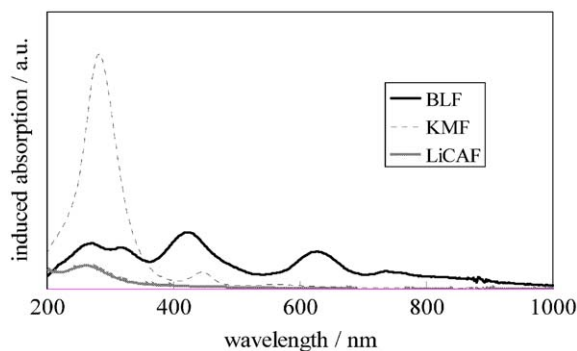


Fig. 2. Induced absorption after X-ray irradiation for BaLiF<sub>3</sub>, KMgF<sub>3</sub> and LiCaAlF<sub>6</sub> single crystals.

evidence was obtained under comparable experimental conditions. The tendency to create F-aggregate centres is apparently a drawback, if radiation resistance of a material is considered. Considering the achieved results, the most radiation resistant and stable material is apparently LiCAF and thus it is worth optimizing it further. We considered the possibility of decreasing the F-centre concentration in LiCAF crystal. This can be achieved by reducing the concentration of fluorine vacancies, which is considered as an intrinsic problem for undoped LiCAF crystal (the energy necessary for the removal of a fluorine ion from a regular site at the crystal surface). Furthermore, the vacancies could be brought by deviations in the crystal composition from the stoichiometry. A simple coulombic equilibrium-based approach consists in the increase of a positive charge in the crystal (e.g. by doping with substitutional ions with a higher positive valency), which would inhibit (or at least decrease) the formation of fluorine vacancies during the crystal growth. An important requirement is that such doping should not create any other trap level within the forbidden gap of the crystal. There are many possibilities in the LiCAF structure due to three available cationic sites. As the most feasible, doping with divalent ions at the Li site was considered. In order to limit the occupation of Ca<sup>2+</sup> sites by divalent dopants, one must choose an ion with a size similar to that of Li. The most stable divalent ions are those from the alkaline earth metal group and among them, the Mg<sup>2+</sup> ion satisfactorily fits to the Li size. Moreover, Mg<sup>2+</sup> is known not to create any trap levels within the CaF<sub>2</sub> forbidden gap (Denks et al., 1999; Bermudez, 2001), so that Mg doping is finally chosen. To test the importance of the ionic size, Ba<sup>2+</sup> doping was tried as well, since Ba<sup>2+</sup> ions are approximately twice as large as Li<sup>+</sup> ones, so the probability of their occurrence at the Li site in LiCAF is negligible.

Fig. 3(a) shows the induced absorption for the undoped, 0.2 mol% Mg-doped and 0.2 mol% Ba-doped-LiCAF crystals after a cumulative dose of 240 Gy. As can be seen the amplitude of the F-absorption band decrease compared to undoped one, while no significant change is obtained for

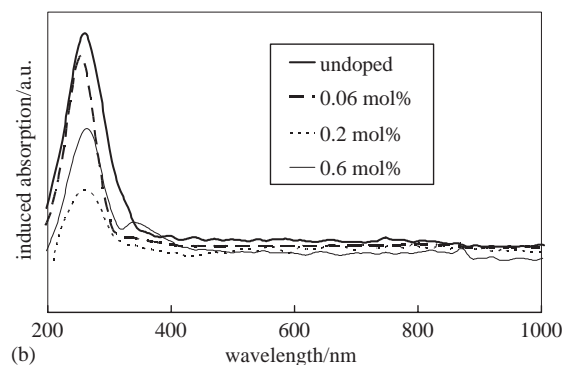
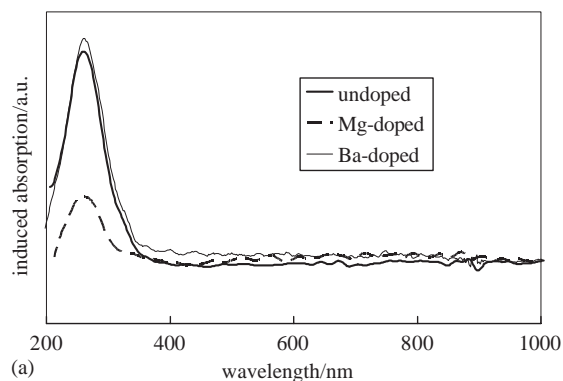


Fig. 3. Induced absorption after X-ray irradiation; (a) undoped, 0.2 mol% Mg and 0.2 mol% Ba doped LiCaAlF<sub>6</sub> crystals, (b) undoped, 0.06, 0.2 and 0.6 mol% Mg doped LiCaAlF<sub>6</sub> crystals.

the Ba-doped LiCAF. The amplitude of induced absorption at 262 nm for the undoped and Mg-doped (0.06, 0.2 and 0.6 mol% in melt) LiCAF are shown in Fig. 3(b). It can be noticed that the amplitude of the F-absorption band is lowered by more than a factor of 3 in the Mg-doped LiCAF (0.2 mol%) compared to the undoped crystal, from the data given in Fig. 3(b). It can be deduced that best MgF<sub>2</sub> doping concentration is about 0.2 mol% in the melt.

The total damage ( $M$ ) was defined and that value denotes the integral of the induced absorption:

$$M = \int_{\lambda_1}^{\lambda_2} \mu(\lambda) d\lambda. \quad (2)$$

The total damage was calculated from  $\lambda_1 = 200$  to  $\lambda_2 = 1000$  nm. Fig. 4 shows the total damage for the above fluoride crystals. While extensive damage appeared in the KMgF<sub>3</sub> and BaLiF<sub>3</sub> crystals after X-ray irradiation, Mg-doped LiCAF had almost the same resistance as high-quality CaF<sub>2</sub> crystals.

#### 4. Summary

X-ray irradiation was used for a comparative study of induced absorption phenomena within UV-VIS spectral re-

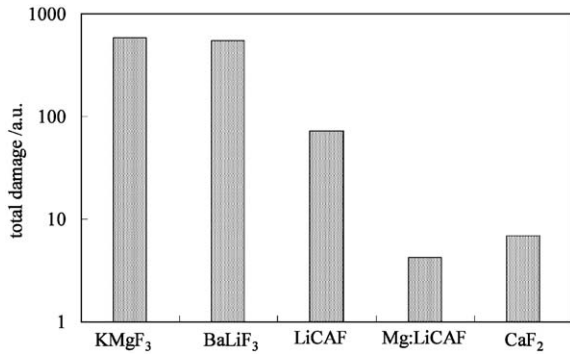


Fig. 4. The total damage (the integral of the induced absorption) for BaLiF<sub>3</sub>, KMgF<sub>3</sub>, LiCaAlF<sub>6</sub>, Mg:LiCaAlF<sub>6</sub> and CaF<sub>2</sub> single crystals by the X-ray irradiation.

gions in KMF, BLF and LiCAF single crystals prepared under equivalent conditions by the Czochralski method under CF<sub>4</sub> atmosphere. Induced absorption spectra are governed by the F-centre absorption in the UV region in all the three materials. The integral of the induced absorption spectra is several times lower in LiCAF with respect to other studied materials. Mg doping decreases the amplitude of the F-centre absorption band and the optimum doping concentration turns to be about 0.2 mol% of MgF<sub>2</sub> in the melt. It is proposed that Mg<sup>2+</sup> partly occupies Li sites. Thus, it introduces an excess positive charge in the cation sublattice, which can reduce the concentration of fluorine vacancies in the process of crystal growth and consequently the concentration of F centres after an X-ray irradiation. As a result, Mg-doped LiCAF had almost same resistance as high-quality CaF<sub>2</sub> crystals.

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