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Study of heavy-ion induced modifications in BaF_2 and LaF_3 single crystals

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Abstract

BaF_2 and LaF_3 single crystals were irradiated with different ions from Ne to U having energies between 1.4 and 13.3 MeV/u and were subsequently analyzed with scanning force microscopy (SFM), optical spectroscopy and surface profilometry. Similar to numerous other ionic crystals, ion-induced hillocks were observed by SFM, the mean size on the nanometer scale depending on the electronic energy loss. BaF_2 shows optical color-center absorption spectra, which consist of broad bands ascribed to F-center aggregates, whereas LaF_3 does not exhibit any specific absorption bands. Depending on the beam parameters (energy, fluence, etc.), the irradiation of both crystals leads to more or less pronounced out-of-plane swelling. In order to study the thermal behaviour of ion-induced modifications, isochronal annealing has been performed. Both crystals show a decrease of the relative step height and the areal density of the hillocks with increasing temperature.

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1. Introduction

In order to further improve the understanding of the peculiarities of damage induced by energetic heavy ions in ionic fluoride crystals, investigations of various species with different crystal and electronic structures are highly needed. In the recent past, ion damage was analyzed in different alkali and alkaline earth fluoride single crystals such as LiF [1–4], MgF_2 [5] and CaF_2 [4,6] and additionally also in LaF_3 [7]. We now extended our studies to BaF_2 and also enlarged an already existing data set for LaF_3, using scanning force microscopy (SFM), optical spectroscopy and surface profilometry, the techniques being addressed elsewhere [5–9].

2. Ion-irradiation

BaF_2 and LaF_3 single crystals from Korth Kristalle, Germany, were irradiated at room

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temperature, under normal incidence with ^{238}U (1.7, 2.9, 5.4 MeV/u), ^{209}Bi (11.1 MeV/u), ^{132}Xe (4.1 MeV/u), ^{70}Zn (1.9 MeV/u), ^{58}Ni (9.1 MeV/u) and ^{22}Ne (1.4 MeV/u) ions at GSI, Darmstadt, with ^{129}Xe (2.3 MeV/u) and ^{208}Pb (4.5 MeV/u) ions at GANIL, Caen and with ^{181}Ta (13.3 MeV/u) ions at RIKEN, Wako. In the case of Ta, the primary energy of 20.8 MeV/u was reduced to 13.3 MeV/u via an Al degrader. The energy losses and ranges were calculated with the TRIM program [10]. The thickness of the samples was always larger than the ion ranges.

3. Measurements and results

3.1. Scanning force microscopy

Subsequent to ion irradiation, the crystals were inspected by SFM (microscope model P47-P47H, NT-MDT Co., Russia) in ambient air, applying contact mode at a constant loading force of about 10 nN. Except Ne, whose electronic energy loss, dE/dx, was below the threshold for hillock creation, all ion species produced tiny hillocks on the surface exposed to the projectiles (see Fig. 1). Approximating the hillock shape by a section of a sphere, mean hillock diameters and heights were extracted from the micrographs.

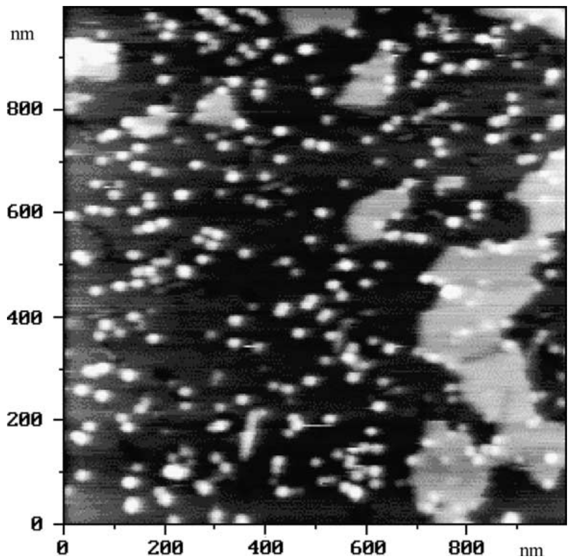

Fig. 1. Topographic SFM image of a BaF_2 single crystal irradiated with Ta (13.3 MeV/u, fluence 4×10^{10} ions/cm^2). The direction of fast scanning was from top to bottom. Light (dark) gray values indicate large (small) height values. The extended gray regions represent terraces left over from crystal cleavage.

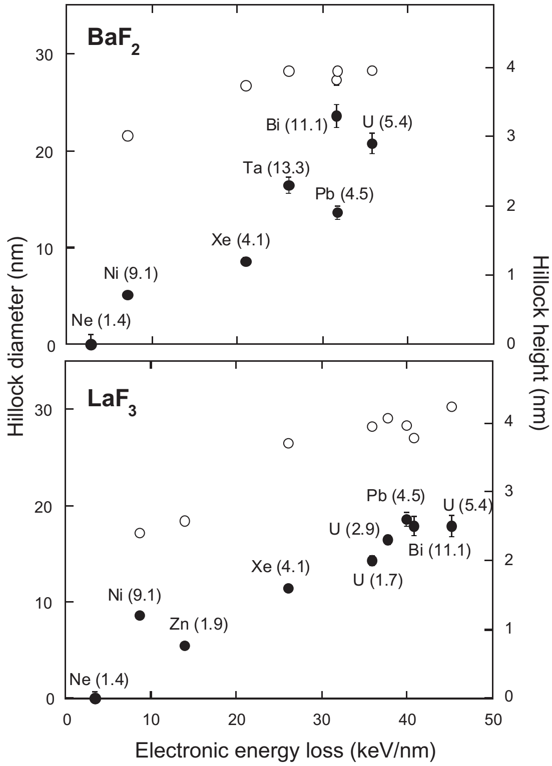

Fig. 2. Mean hillock diameters (○) and heights (●) as a function of electronic energy loss for BaF_2 and LaF_3 single irradiated with several ion species. The element symbols and specific energies (in MeV/u) assigned to the heights refer also to the diameters at the same energy loss. The error bars representing 1σ of the mean values are shown only when being larger than the data point symbols.

Similar to the findings for other fluorides [4,7,11], the diameters enlarge only very moderately, whereas the heights grow considerably with increasing dE/dx (Fig. 2).

3.2. Optical spectroscopy

All irradiated crystals were inspected at room temperature also with a double-beam UV–Vis spectrometer (ATI Unicam UV4, UK). The absorption spectrum of BaF_2 is dominated by a broad band around 750 nm, comparable with the

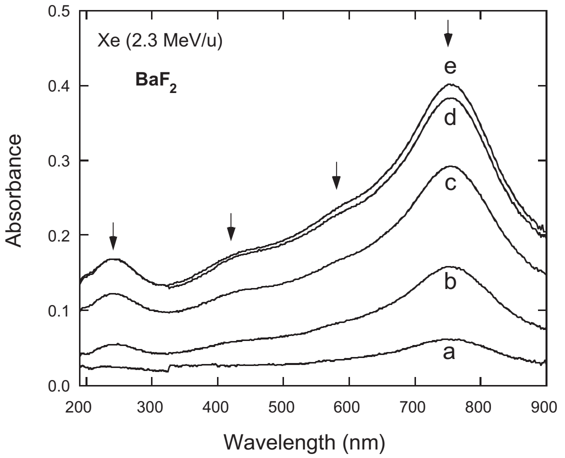

Fig. 3. Optical absorption spectra of BaF_2 irradiated with Xe (2.3 MeV/u) ions of different fluences: (a) 8.3×10^{10}, (b) 2.6×10^{11}, (c) 5×10^{11}, (d) 8×10^{11} and (e) 1×10^{12} ions/cm^2.

broad 550-nm band of ion-irradiated CaF_2 [13]. With increasing fluence, a second band appears at about 240 nm and, in addition, two shoulders arise at ≈420 and 580 nm, respectively (see Fig. 3). The integral absorption increases as a function of ion fluence approaching saturation at high fluences. We also observed that irradiation with different ion species at different fluences does not change significantly the general spectral shape, indicating the creation of the same kinds of defect. No spectral features unambiguously attributable to F- and F_2-centers could be identified in BaF_2. According to den Hartog, the F- and F_2-bands in BaF_2 should be located at ~606 and 765 nm, respectively [12]. The 750-nm band in BaF_2 and the 550-nm band in CaF_2 were already observed by Smakula after irradiation with X-rays [14]. At that time, no reasonable explanation was available. We assume that the bands can be attributed to small aggregates (including also F_2-centers), because they bleach relatively readily when illuminated with intense light of similar wavelength, a behaviour that is not typical of metallic colloids. The 240 nm band in BaF_2 may have the same origin as a new band generated by high energy Ni ions that was recently observed in CaF_2 near 185 nm and was assigned to a V-center arising from interstitial fluorine atoms displaced during irradiation [15]. In BaF_2, its maximum is shifted to larger wavelength due to the bigger BaF_2 lattice constant. For the sake of completeness, we also mention that the presence of oxygen impurities in BaF_2 may contribute to the absorption in the UV region around 220, 280 and 335 nm [16].

In contrast to BaF_2, the LaF_3 crystal does not show any distinct absorption bands, even at larger energy losses (U ions). There is only a moderate increase of the absorbance over the spectral range from 200–700 nm. This absence of color centers in LaF_3 at room temperature can be probably explained by their thermal instability above 140 K [17]. We remark that electron paramagnetic resonance (EPR) spectra of LaF_3 irradiated with X-rays at 25 K showed a triplet pattern that was attributed to a hole trapped on two adjacent fluorine ions, i.e. a V_k-center [18].

3.3. Ion-induced swelling

Out-of-plane swelling was measured with a profilometer (DEKTAK 8000) where a high-precision stage moves the sample beneath a diamond-tipped stylus over the border line between the nonirradiated and the irradiated surface area. Similar to earlier results on LiF [2] and CaF_2 [6], the swelling of BaF_2 and LaF_3 crystals also increases linearly at low fluences and approaches saturation at high fluences (Fig. 4). The volume increase of LaF_3 is less pronounced than in the case of LiF [9], however significantly stronger than for MgF_2, CaF_2 and BaF_2.

The nature of the defects responsible for ion-induced swelling is not yet identified. However, it is known that for the creation of a permanent defect, a given H-center must be well-separated from a neighboring F-center, in order to prevent recombination. Due to structural differences of the fluorides, the recombination and aggregation processes of the various centers may differ significantly. In crystals with the fluorite structure, such as CaF_2 and BaF_2, strong recombination may be responsible for the low yield of stable F–H pairs [19].

3.4. Thermal annealing

To examine the temperature dependence of hillocks and swelling, we performed isochronal annealing by applying a sequence of heating periods up to about $T = 800$ K, each period of 15 min

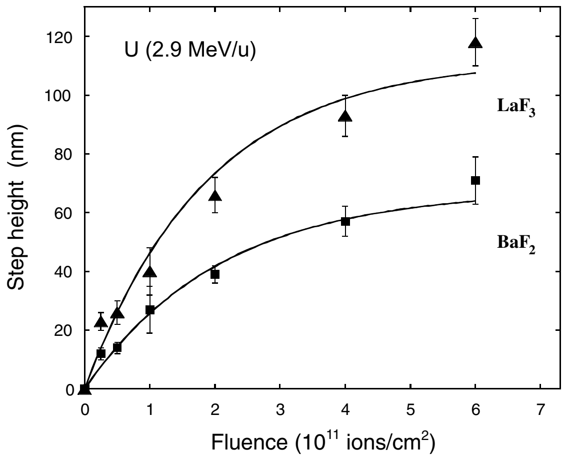

Fig. 4. Mean step height versus ion fluence for LaF_3 and BaF_2 irradiated with U (2.9 MeV/u) ions. The error bars represent 1σ of the single measurements (each data point resulting from about ten profilometer scans). Saturation curves of the type $1 - \exp(-A \times \Phi)$, were fit to the data, where Φ denotes the ion fluence and A is the track cross section contributing to swelling.

length and with constant temperature. Starting from room temperature with hillock density N_0 and step height l_0 the decreasing values N and l were measured for each annealing temperature, each time cooling the sample down to room temperature for this purpose.

SFM imaging visualizes that the number of hillocks on both crystals decreases as a function of temperature. At about 670 K, the hillocks disappear completely and bigger defect clusters are formed (Fig. 5). It should be mentioned that SFM images of CaF_2 single crystals irradiated at relatively high temperature with electrons show Ca aggregates on the surface [20]. These aggregates are mainly caused by thermally stimulated surface diffusion. Probably, the same effect exists both in BaF_2 and LaF_3 single crystals.

The thermal data were analyzed according to the isochronal annealing model of [21] by plotting $\ln(-\ln(N/N_0))$ and $\ln(-\ln(l/l_0))$ versus $1/T$. The Arrhenius plots illustrating the annealing of hillocks and swelling are presented in Fig. 6. By fitting a straight line of slope $-E_a/k$, we deduced the

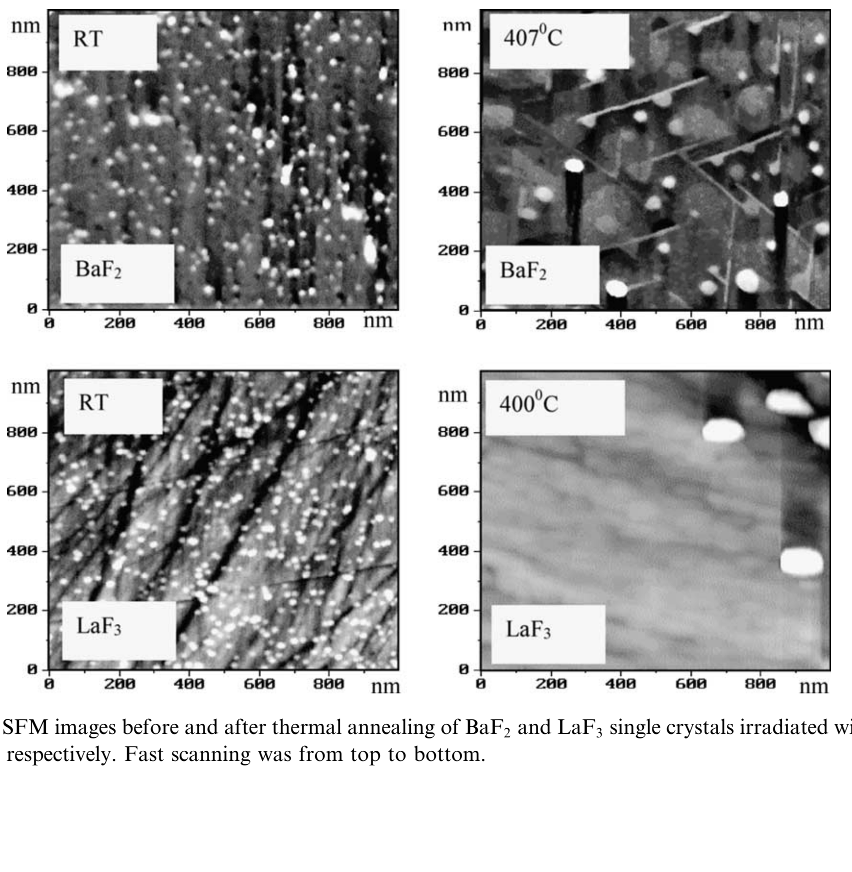

Fig. 5. Topographic SFM images before and after thermal annealing of BaF_2 and LaF_3 single crystals irradiated with U (11.1 MeV/u) and U (5.4 MeV/U), respectively. Fast scanning was from top to bottom.

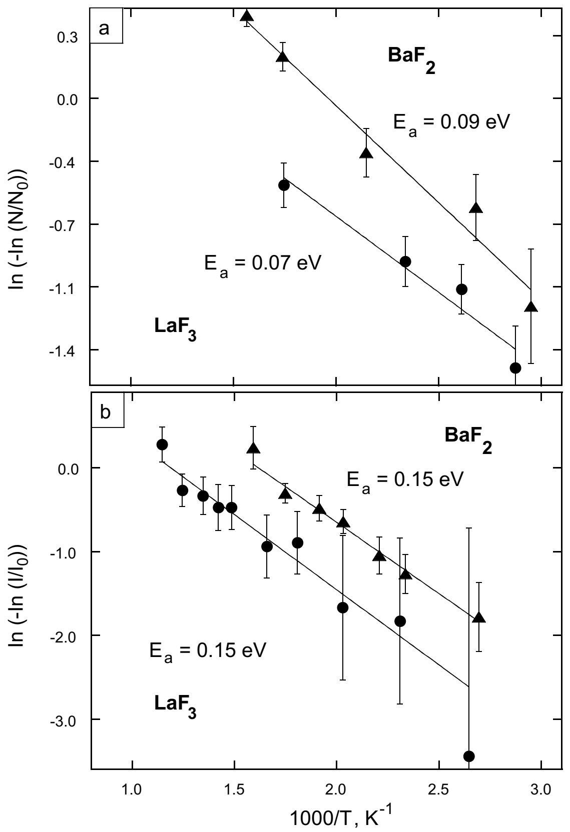

Fig. 6. Arrhenius plots for isochronal annealing. (a) Hillocks of irradiated LaF_3 (U ions, 5.4 MeV/u) and of BaF_2 (U ions, 11.1 MeV/u). (b) Out-of-plane swelling of irradiated LaF_3 (Sn ions, 4.3 MeV/u) and BaF_2 (Xe ions 5.5 MeV/u). The error bars are derived from 1σ of the mean values of the variables under study, using Gauss's law of error propagation. The straight lines represent weighted least-square fits to the data points.

activation energy E_a (k is the Boltzmann constant). The resulting activation energies for the annealing processes of hillocks and swelling are 0.09(1) and 0.15(2) eV for BaF_2 and 0.07(1) and 0.15(3) eV for LaF_3, respectively.

In this context, it is worth mentioning that BaF_2 and LaF_3 are well-known superionic conductors in which the fluorine anions transport the electric charges [22,23]. In the case of BaF_2, the superionic behaviour starts to be observable at a temperature of about 1000 K [24]. The anionic conductivity of LaF_3 is already high at room temperature and becomes even much larger above about 500 K. Possibly, these lower activation energies, which facilitate the annealing process of ion induced hillocks and swelling, correspond with the high anion mobility in this kind of ionic crystal.

4. Conclusions

Similar to LiF, MgF_2 and CaF_2, also BaF_2 and LaF_3 exhibit ion-induced hillocks and out-of-plane swelling, respectively resulting from relaxation of surface stress created by single tracks, and of stress caused by bulk expansion. Although both crystals show about the same hillock size, a higher swelling effect was observed for LaF_3. The activation energies for thermal annealing of hillocks and of swelling are rather low and point to the activation of hole centers, which are in general much more mobile than electron centers. The optical absorption spectra of BaF_2 indicate that the ion-induced damage is dominated by defect aggregates rather than by single F- and F_2-centers.

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