



Structural defects caused by swift ions in fluorite single crystals



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ABSTRACT

A comparative study of radiation damage caused by the irradiation of oxygen-free calcium fluoride single crystals with \sim GeV ^{132}Xe or ^{209}Bi heavy ions, 100-keV light hydrogen ions (protons) or X-rays at room temperature has been performed. Optical absorption in a wide spectral region from NIR to VUV (1.5–10.5 eV), its dependence on stepwise preheating of the irradiated CaF_2 crystals to a certain temperature as well as thermally stimulated luminescence accompanying the main annealing stages have been analyzed. It is shown that in addition to different F-type aggregates, Ca colloids and trifluorine quasi-molecules, complex and temperature stable structural defects responsible for VUV absorption (in particular, the 9.8 eV band) are induced in CaF_2 only after irradiation with swift heavy ions. The origin and tentative creation mechanisms of such defects as well as the features of the used irradiation types are considered.

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1. Introduction

Calcium fluoride, CaF_2 is a wide-gap crystal ($E_g = 12.2$ eV), which belongs to the materials with the fluorite structure – a cubic lattice, space group $Fm\bar{3}m$. The fluorite structure with eight-coordinated Ca^{2+} and four-coordinated F^- can also be described as a three-dimensional chessboard, where the first half of fluorine cubes is occupied by calcium ions and the second half is cation-free.

Nowadays, CaF_2 single crystals, both nominally pure and doped with various cation impurities, mainly trivalent rare-earth ions, RE^{3+} , are widely used for many applications as optical materials, laser media, detectors of radiation, elements for navigation and holography systems (see, e.g., [1–3]). The oxygen contamination strongly affects the functionality of fluorite thus impeding its use as an optical material for vacuum ultraviolet (VUV) spectral region. A set of oxygen-related defects manifesting themselves, for instance, via a number of optical absorption bands was thoroughly investigated and calculated [4–6]. At present, VUV grade CaF_2 single crystals with very low concentration of oxygen impurities (oxygen-

free) are elaborated for the use as lens and window materials in microlithography.

The spectroscopic study of synthetic $\text{CaF}_2:\text{RE}^{3+}$ single crystals started by Feofilov's group [7] was continued by many authors (see Refs. [1,2,8] and references therein). The prevalent lattice defects in CaF_2 are anion Frenkel defects – fluorine interstitials and vacancies. The calculated and experimentally determined values of the formation energy of an anion Frenkel pair lie in the range 2.5–3 eV that is several times lower than the formation energy of an anion exciton (\sim 11 eV) and the energy gap [1,9]. Similar to alkali halide crystals, different color centers are formed in synthetic fluorite single crystals under thermochemical (additive) coloration or irradiation with γ - and X-rays, electrons and fast neutrons (see Refs. [1,5,10–12] and references therein). The numerous optical absorption bands at 1.5–3.5 eV were ascribed to an electron F center (an electron trapped in a fluorine vacancy) and its aggregates: F_2 (M), F_3 (R), F_4 (N) centers consisting of two to four vacancies/electrons. In addition to “simple” color centers, even more complex aggregates of F-type centers and metallic (calcium) colloids were investigated by electron microscopy, magnetic resonance and optical methods or studied theoretically (see, e.g., [13–17]). It is worth noting that a free calcium metal lattice almost perfectly matches a cation sublattice of a CaF_2 crystal.

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Therefore, the processes of calcium colloid formation/annealing in CaF₂ could be rather different from those for intrinsic metal colloids in LiF, where the cation sublattice constant is significantly smaller than for free Li metal (see, e.g. Refs. [17,18]).

It has been recently demonstrated that the radiation defect creation under high-dense irradiation of wide-gap materials with swift heavy ions (SHIs) cannot be confined to the universal knock-out (impact) mechanism connected with elastic collisions of energetic incident particles (especially neutrons) with the crystal nuclei resulting in the formation of Frenkel pairs [18–24]. Note that a SHI with the energy exceeding 1 MeV per nucleon spends about 95% of its energy on ionization losses causing extremely high density of electronic excitations within a cylindrical ion track (energy loss up to 40 keV/nm) [19,25]. There are already several publications devoted to SHI-induced processes in CaF₂ [26–29].

The present study is a logical extension and development of our recent paper [30] that reported the first detection of SHI-induced optical absorption in the VUV region. In the present work, the particular emphasis is laid on the comparative study of radiation damage caused by the irradiation of oxygen-free CaF₂ single crystals at room temperature with 100-keV protons, 0.23-GeV Xe and 2.38-GeV Bi heavy ions or X-rays. The annealing of radiation-induced optical absorption (RIOA) in a wide spectral region of 1.5–10 eV, accompanied thermally stimulated luminescence (TSL) as well as the nature and creation mechanisms of the related radiation defects are analyzed.

2. Experimental

VUV grade CaF₂ single crystals were grown from the melt by the Stockbarger-Bridgeman technique in a graphite crucible at the State Optical Institute, Sankt-Petersburg, Russia. The investigated nominally pure crystals contained 30–100 ppm of trivalent yttrium ions. The concentration of Y³⁺ (the main impurity ion) in our samples was roughly estimated via the onset shift of intrinsic absorption of fluorite matrix (see Ref. [8]). According to the absorption spectra in VUV region, our samples contained very small amount of oxygen impurity ions, and the corresponding peaks at 6–10 eV were practically absent (see Section 3 for details). The samples were cleaved from the crystal block along the (111) planes and had typical dimensions of 5 × 5 × 0.8 mm³.

The samples were irradiated at room temperature (RT) by SHIs perpendicular to the (111) crystal plane at the UNILAC linear accelerator of the GSI, Darmstadt by 2.38-GeV ²⁰⁹Bi ions (11.4 MeV/u, fluence of 3 × 10¹¹ ions/cm²) and at the DC-60 cyclotron in Astana by 0.23-GeV ¹³²Xe ions (1.75 MeV/u, 10¹⁴ ions/cm²). According to SRIM 2013 code [31], ion range approximately equals 90 (Bi) and 18 μm (Xe) that is significantly smaller than the sample thickness. For both cases, electronic losses exceed 20 keV/nm, while nuclear losses are significantly lower, and Frenkel defect creation via the knock-out mechanism is especially efficient close to the ion tracks end. The proton irradiation was carried out using KIIA 500 kV ion implanter of Ion Beam Laboratory at the University of Helsinki. The samples were irradiated with the 200 keV hydrogen molecular beam corresponding to the 100-keV protons at the fluence of 10¹⁷ cm⁻² (for details see Ref. [32]). The penetration depth of such protons into CaF₂ was estimated as 0.8 μm with radiation damage level of about 0.2 dpa. Irradiation of the samples with X-rays was performed using a tungsten tube operated at 50 kV and 15 mA, approximate absorbed dose was 10 kGy.

The spectra of optical absorption were measured using a high-absorbance double-beam spectrometer JASCO V-660 with a double monochromator (1.5–6.5 eV) and a homemade setup based on a single grating vacuum monochromator VMR-2. In the latter case, the constant number of incident photons of different energies

(4.5–10.5 eV) from the hydrogen discharge in a flow capillary tube was maintained by varying the slit width of the monochromator and using the constant signal from sodium salicylate for normalization. During the experiment maintenance with the irradiated samples, we tried to avoid slight bleaching of RIOA by visible light.

The annealing of optical absorption was measured in a stepwise regime: a sample was heated up to a certain temperature T_i in a flowing nitrogen atmosphere with a constant rate $\beta = 2$ K/s, rapidly cooled down to RT, and then the absorption spectrum was measured. Such preheating was carried out up to ~750 K, while higher temperatures were reached in a high-temperature furnace: sample was placed into a porcelain boat and heated in a flowing argon atmosphere. Several “heating-cooling-measuring” cycles were executed for preliminary irradiated samples, while all spectra were measured at RT.

The TSL curves were registered for a spectrally integrated (1.9–4.1 eV) signal using a Harshaw Model 3500 TLD Reader under sample heating with $\beta = 2$ K/s in the atmosphere of flowing nitrogen. Another TSL setup allowed to analyze the emission within certain TSL peaks: the emission spectrum was repeatedly measured using an ARC SpectraPro 300i grating monochromator equipped with a cooled CCD detector with spectral sensitivity in the range of 190–1100 nm. Each emission spectrum was measured within a temperature interval of about 5 K ($\beta = 10$ K/s).

Cathodoluminescence (CL) spectra were measured at the sample excitation by an electron beam of 10 keV energy and 0.5 μA current. To avoid surface charging under electron excitation, the samples were covered by a 3-nm platinum film. According to the CASINO simulation [33], the penetration depth distribution for the 10-keV electrons in CaF₂ approximately coincides with the range of 100-keV protons estimated via SRIM code. CL setup (see for details [32,34]) was equipped with a vacuum cryostat (5–400 K) and two monochromators covering a wide spectral range from 1.5 to 10 eV: ARC SpectraPro 2300i monochromator with various detectors and a homemade vacuum double monochromator with a Hamamatsu photomultiplier R6836. Electron gun (Kimball Physics ECG-3101) can be used in a steady-state or pulse (10 ns, 5 kHz) mode.

3. Experimental results

Fig. 1 shows the spectra of RIOA measured at RT in a wide spectral region of 1.5–10.5 eV for CaF₂ crystals irradiated with H (protons), Xe or Bi swift ions. Note that the difference between two spectra of optical absorption measured at RT before and after irradiation (i.e. for the virgin and the same sample after irradiation) is considered as RIOA within the framework of the present paper. The spectrum can be divided tentatively into three regions (maxima at about 2.2, 6.5 and 9.8 eV) related to different types of radiation defects.

The first, complex and wide RIOA band with the maximum at ~2.2 eV in the visible spectral region has been thoroughly studied and ascribed in the literature to electron F-type centers which can be detected in additively colored crystals as well. Single F centers and their aggregates are associated with a number of absorption bands in this spectral region (see Refs. [1,3,17] and references therein). Single F centers (absorption band peaked at 3.3 eV) can be formed by ionizing radiation at low temperature, while they become mobile around 250 K and unstable at RT [35]. The F₂ centers are responsible for two bands (2.38 and 3.39 eV) corresponding to the orientation of the nearest F centers along <100> (dominant center type) or <110> directions; thermal stability of these M centers is rather low. An F₃ center consists of three nearest-neighbor F centers aligned along <100> and is associated with the absorption band peaked at 1.83 eV. Therefore, mainly complex F center aggregates are responsible for the observed non-elemental

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