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Radiation damage caused by swift heavy ions in CaF_2 single crystals

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HIGHLIGHTS

- The RIOA and TSL were studied in CaF_2 single crystals irradiated with SHIs.
- VUV absorption bands are connected with EEs localized near complex defects.
- There is some specificity of radiation damage under irradiation with Bi^{209} ions.

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ABSTRACT

The radiation-induced optical absorption in a wide spectral region of 1.5–10 eV have been investigated in nominally pure CaF_2 single crystals irradiated at 295 K with 0.23 GeV Xe^{132} or 2.38 GeV Bi^{209} ions (fluences of 10^{11}–10^{14} ions/cm^2) providing an extremely high density of electronic excitations. The stepwise annealing of the radiation-induced optical absorption have been analysed at the heating of irradiated crystals up to 1023 K and accompanying thermally stimulated luminescence has been detected at 300–750 K. The origin of several absorption bands (incl. vacuum ultraviolet region), the possible creation mechanisms of the corresponding radiation defects as well as the difference in radiation damage caused by Xe^{132} or Bi^{209} ions have been considered.

1. Introduction

Calcium fluoride single crystals, pure and doped with different cation impurities (Me^{3+}, Me^{2+}, Me^{+}), are widely used for many technical applications as optical materials (incl. lens and windows in ultraviolet laser lithography), laser media, radiation detectors and dosimeters, elements for navigation and orientation, etc. (see, e.g., Hayes, 1974: Sils et al., 2009). CaF_2 single crystal belongs to the materials with fluorite structure (space group $Fm\overline{3}m$), has 8 formula units per unit cell, where each eight-coordinated Ca^{2+} ion is located in the centre of a cube formed by eight equivalent F^- ions, while each F^- ion is surrounded by a tetrahedron of four equivalent Ca^{2+}.

The presence of extrinsic defects (impurities) and the rise of a number of structural intrinsic defects (point defects and aggregates) during a prolonged irradiation strongly affect the properties of CaF_2 useful for different applications. The oxygen contamination impedes the use of CaF_2 as an optical material for vacuum ultraviolet (VUV). A set of oxygen-related defects was investigated both experimentally and theoretically (Hayes, 1974; Rauch and Schwotzer, 1982; Radzhabov and Figura, 1994; Mysovsky et al., 2005). The systematic spectroscopic (incl. luminescence polarization) study of synthetic CaF_2 crystals doped with trivalent rare earth (RE^{3+}) impurities was started long ago by Feofilov and coworkers (Feofilov, 1959 and references therein) and continued by many authors (see, e.g., Radzhabov et al., 2007; Sils et al., 2009). Several absorption bands in a wide spectral region related to structural defects were detected in CaF_2 crystals irradiated with x- or γ-rays, electrons and fast neutrons (Hayes, 1974 and references therein; Radzhabov and Figura, 1994; Cooke and Bennett, 2003). Besides single F centres (an electron trapped by a fluorine vacancy), binary (M = F_2 centres) and more complex aggregates of F-type centres were identified and investigated in irradiated CaF_2 crystals by means of optical and EPR methods (Hayes, 1974 and references therein) as well as via theoretical calculations (see, e.g., Kotomin and Popov, 2007).

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The use of high-dense irradiation with swift heavy ions (SHIs) reveals several features in the mechanisms of radiation damage in wide-gap materials, the investigation of which is far from completion. The largest part of the energy (>95%, energy loss up to 40 keV/nm) of a SHI with $E > 1$ MeV/u is spent on ionization losses providing an extremely high density of electronic excitations (EEs) within cylindrical ion tracks (Schwartz et al., 1998; Itoh et al., 2009). Therefore, in addition to the universal knock-out (impact) mechanism, several other mechanisms of radiation damage connected with EEs are considered in wide-gap metal oxides and fluorides (see, e.g., Lushchik et al., 2006, 2007, 2013; 2016; Itoh et al., 2009 and references therein). There are few publications related to SHI-induced processes in CaF_2 (see, e.g., Boccanfuso et al., 2002; Davidson et al., 2002; Pandurangappa et al., 2011). The present paper is devoted to a comparative study of radiation damage caused by two types of SHIs: $_{54}Xe^{132}$ ions with zero nuclear spin and $_{83}Bi^{209}$ ions with an extremely high nuclear spin of 9/2 in CaF_2 single crystals with a relatively loose-packed lattice. Particular emphasis is laid on the analysis of induced optical absorption in VUV spectral region.

2. Experimental

Single crystals of CaF_2 as well as CaF_2 crystals doped with Tm^{3+} ions (about 1000 ppm) were grown from the melt by the Stockbarger method (oxygen-free version) at the State Optical Institute, Russia. The investigated nominally pure crystals contain about 100 ppm of Y^{3+} impurity ions (the main metal impurity in our samples). This rough estimate of impurity concentration was done by a shift of the fundamental absorption edge of CaF_2 doped with different concentration of YF_3 (Radzhabov et al., 2007). A specially treated (baked in a calcium vapour) CaF_2 crystal containing yttrium ions in a divalent state was considered as well. The platelets with typical size of $5 \times 5 \times 0.8$ mm^3 were cleaved from a crystal block along the (111) planes.

Samples have been irradiated at room temperature (RT) by SHIs perpendicular to the (111) crystal plane at the UNILAC linear accelerator of the GSI, Darmstadt (Bi^{209}, energy per nucleon 11.4 MeV/u, fluence of 3×10^{11}–10^{12} ions/cm^2) or DC-60 cyclotron in Astana (Xe^{132}, 1.75 MeV/u, 10^{11}–10^{14} ions/cm^2). The thickness of the samples for all irradiations was larger than the ion range R (~90 μm and ~18 μm for Bi^{209} or Xe^{132} ions, respectively) calculated using SRIM 2013 code (Ziegler et al., 1985). The average density of energy introduced into irradiated layer by a certain fluence of 2.38 GeV Bi^{209} is just twice as high as for the same fluence of 0.23 GeV Xe^{132} ions and for the highest used fluences it equals 2.65×10^{23} eV/cm^3 (10^{12} Bi/cm^2) and 1.28×10^{25} eV/cm^3 (10^{14} Xe/cm^2), respectively. Irradiation of the samples with x-rays was carried out for 1 h by using tungsten target operated at 50 kV and 15 mA.

The spectra of optical absorption were measured in the spectral region of 1.5–6.5 eV using a high-absorbance spectrometer JASCO V-660 and in the region of 4.5–10.0 eV using a vacuum monochromator VMR-2. The difference between two spectra measured at RT before and after irradiation is considered as radiation induced optical absorption (RIOA). The thermal annealing of RIOA was registered in a step-by-step regime: an irradiated crystal was heated with a constant rate $\beta = 2$ K/s from RT to a certain temperature T_i and rapidly cooled down to RT, while all the absorption spectra in the region from 1.5 to 10 eV were measured at RT. A set of RIOA spectra measured after preheating of the irradiated sample to different T_i (up to 773 K) allowed to analyse the dependence of optical density, measured for a certain spectral region, on the preheating temperature.

A high-temperature thermally stimulated luminescence (TSL, 300–800 K) of the irradiated samples was measured with a heating rate $\beta = 2$ K/s in the atmosphere of flowing nitrogen, using a Harshaw Model 3500 TLD Reader. It was possible to register a spectrally integrated (1.9–4.1 eV) signal or the TSL selected by an optical filter.

3. Experimental results and discussion

Fig. 1 shows the spectra of RIOA measured in a spectral region of 1.5–6.5 eV for CaF_2 irradiated at RT with two types of SHIs: 2.38 GeV Bi^{209} or 0.23 GeV Xe^{132} ions. The absorption spectrum of a specially prepared (baked in a calcium vapour) unirradiated CaF_2 single crystal containing Y^{2+} impurity ions is shown in Fig. 1 as well. Well-pronounced absorption bands peaked at about 5.45 eV; 3.65; 3.1; and 2.15 eV and related to complex photochromic centres containing Y^{2+} ions (Staebler and Schnatterly, 1971; Hayes, 1974) are also observed as peculiarities in the spectra of RIOA measured for SHI-irradiated samples. These absorption bands are absent in our virgin nominally pure CaF_2 with some amount of trivalent yttrium impurities.

Fig. 2 shows the spectra of RIOA measured in a wide region of 1.5–10 eV for a SHI-irradiated CaF_2 crystal (5×10^{13} Xe/cm^2, RT) directly after irradiation or after preheating to certain temperatures (from 440 K to 1023 K). All spectra were measured at RT. There are several RIOA bands in visible as well as in UV–VUV regions with dominant complex bands at ~2.2 eV, ~6.5 and ~9.7 eV. It is worth noting that a preheating of the SHI-irradiated crystal from 773 to 1023 K causes the enhancement of RIOA in the region above 6.8 eV (see curve 9, inset in Fig. 2), which is partly connected with the presence of some amount of oxygen-vacancy defects in our CaF_2 samples (see Radzhabov and Figura, 1994). Our nominally pure unirradiated CaF_2 sample contains rather small amount of oxygen impurity and there is no pronounced absorption band at ~9.7 eV (curve 10 in Fig. 2).

For comparison, the RIOA spectrum of a similar CaF_2 crystal irradiated at RT with x-rays is shown in Fig. 2 as well. The spectrum contains clearly visible Y^{2+}-related bands appearing due to $Y^{3+} \rightarrow Y^{2+}$ recharging under x-irradiation, while there are no RIOA bands above 8 eV. In our opinion, the intense band at 9.7–9.8 eV with slightly resolved doublet structure in SHI-irradiated CaF_2 is certainly related to the creation of structural defects via mechanisms typical of SHI irradiation. A significant displacement of host nuclei from their regular lattice sites takes place due to the elastic

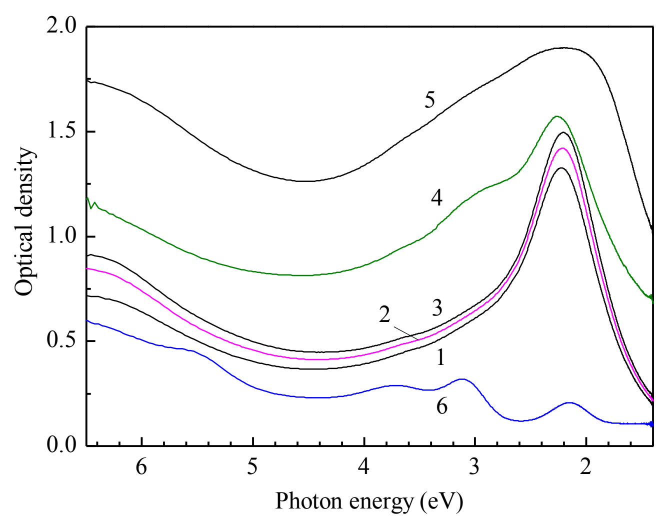

Fig. 1. Spectra of RIOA measured at RT for SHI-irradiated CaF_2 single crystals: 1×10^{13} Xe/cm^2 (1), 3.3×10^{13} Xe/cm^2 (2), 1×10^{14} Xe/cm^2 (3), 3×10^{11} Bi/cm^2 (4), 1×10^{12} Bi/cm^2 (5) and the spectrum of optical absorption for CaF_2:Y^{2+} (6) measured at 295 K.