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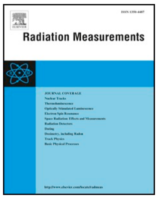

Optical absorption spectra of X-ray irradiated alkaline earth fluoride crystals doped with divalent rare-earth ions studied by thermal bleaching

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ABSTRACT

The absorption spectra of X-ray irradiated alkaline earth fluoride (CaF_2, SrF_2, BaF_2) crystals doped with Sm, Ho, Er, Tm ions are investigated by thermal bleaching of the sample in the 300–700 K temperature range. X-ray irradiation creates absorption bands of inter-configuration $4f^n$-$4f^{n-1}$-$5\,d^1$ transitions of divalent impurity ions and F_3^- and $(F_2^-)_{ii}$ hole centers. The thermal oxidation of the divalent RE ions have been observed. Two possible mechanism of thermal oxidation of divalent lanthanide ions in alkaline-earth fluorides are discussed.

1. Introduction

The optical properties of crystalline materials doped with rare - earth (RE) ions are due to the valence of impurity ions. Crystals of alkaline earth fluorides (CaF_2, SrF_2) proved to be a very special host for studying rare-earth ions, as it was found that ionizing or additive coloration could convert those trivalent rare-earth ions into the divalent state (Feofilov and Kaplyansky, 1962; McClure and Kiss, 1963; Shendrik et al., 2014, 2015; Shendrik et al., 2015). Divalent rare earth ions that are formed in alkaline-earth fluorides as a result of the absorption of ionizing radiation participate in energy transfer processes in crystals MeF_2-Pr^{3+} (Me = Ca, Sr, Ba) (R. Shendrik and E. Radzhabov et al., 2012; Shendrik et al., 2010). Divalent rare earth ions can also be observed upon formation of ionized photochromic centers. Such crystals demonstrate the photochromic behavior under x-ray or gamma irradiation and additive coloration and can be used in holography. The photochromic centers consist of one (PC^+) or two (PC) electrons bound at the anion adjacent to the trivalent rare earth ion RE in crystals CaF_2 (RE = La, Ce, Gd, Tb, and Lu) (Sizova and Radzhabov, 2012; Egranov and Sizova, 2013; Shendrik et al., 2016, Egranov at al, 2016). Crystals of alkaline earth fluorides doped with divalent neodymium can be used as Q-switches and passive mode-locking in lasers of the near IR wavelength range (1.3–1.6 μm) (Tokarev et al., 1991; Nepomnyachikh et al., 1991).

The study of changes in the valence states of rare - earth impurity ions in crystals of alkaline earth fluoride crystals was studied in research of electron thermal transfer from RE^{2+} ions (RE-Nd, Dy, Ho, Er) to Sm^{3+} ions in MeF_2-Sm^{3+} (Me = Ca, Sr) crystals (Arkhangel'skaya et al., 1969), also in irradiated MeF_2-RE^{2+} crystals (Me = Ca, Sr, Ba), doped with Nd, Ho, Er, Tu, exposed to ionizing irradiation (Arkhangel'skaya 1965, Merz and Pershan, 1967).

It was found that hole centers participate in the process of thermal bleaching of the irradiated crystals. In works (Figura et al., 1989, Radzhabov, 2016) it was shown that in X-ray irradiation of alkaline earth fluoride crystals doped with Tm^{3+} and Yb^{3+} creates.

RE^{2+} and $(F_2^-)_{ii}$ and F_3^- hole centers at room temperature.

Thus, the study of the processes of changing the valence of rare-earth ions in irradiated alkaline earth crystals is an urgent problem today. In (Bugaenko et al., 2008; Sizova and Radzhabov, 2012; Sizova et al., 2016), we studied the optical properties and thermal destruction of the induced centers of CaF_2, SrF_2, and BaF_2 crystals doped with YF_3, LaF_3, CeF_3, GdF_3, TbF_3, LuF_3 and NdF_3. The main topic of the present paper is to study the processes of changing the valence of RE^{3+} ions by radiation coloration crystals of alkaline earth fluorides (CaF_2, SrF_2, BaF_2) doped with SmF_3, HoF_3, TmF_3, ErF_3 within temperature range 300–700 K.

2. Experimental methodology

The CaF_2, SrF_2 and BaF_2 crystals doped with SmF_3, HoF_3, TmF_3, ErF_3 (from 0.1 to few mol. percent) were grown by the Stockbarger method in graphite crucibles in vacuum. At the first stage, pure crystals were grown with addition of some amount of CdF_2 to the raw material in order to remove oxygen. Then the crystals with an impurity of rare earth fluorides (REF_3) were grown from the crystalline raw material. The absence of oxygen in the final crystals was controlled by the absence of oxygen luminescence under sample illumination by a DDS-30 UV deuterium discharge lamp. The crystals CaF_2, SrF_2, BaF_2 were

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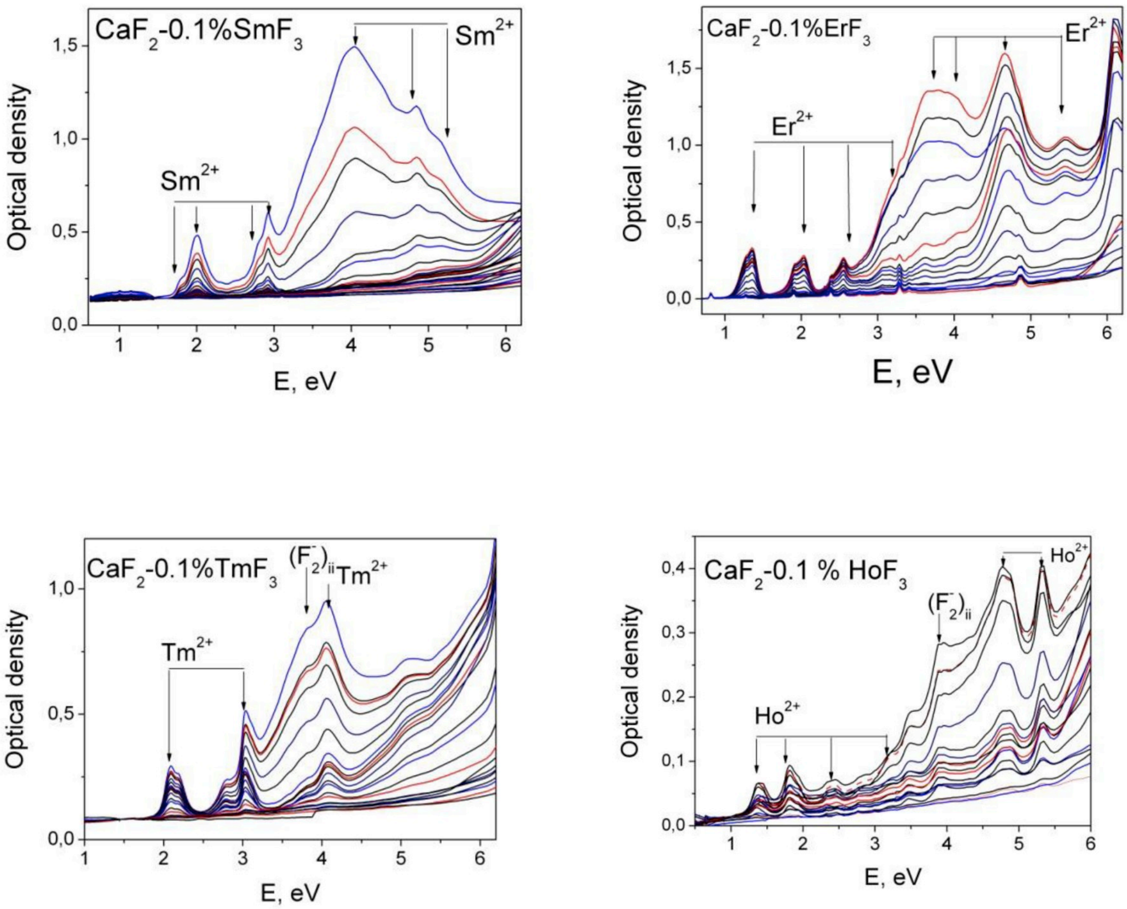

Fig. 1. Absorption spectra of CaF_2 doped with SmF_3 (a), ErF_3 (b), TmF_3 (c), HoF_3 (d) after X-ray irradiation at 300 K and annealed at temperatures in interval 300–700 K. Absorption spectra were measured at 300 K.

irradiated 300 K under X-ray tube with Pd anode operating at 35 kV and 20 mA for not more than 30 min.

The thermal decay of the radiation defects was investigated with absorption spectra in the temperature range 300–700 K.

The study of thermal decay of divalent RE bands was carried out as follows: the irradiated crystals were heated to a certain temperature, kept for 3 min and cooled down to room temperature, at which the absorption spectrum was measured. The temperature of the subsequent heating increased by 20 °C. Therefore an effective heating rate can be estimated as 0.11 K/s.

The optical absorption spectra were measured 300 K with a PerkinElmer Lambda 950 UV/VIS/NIR spectrophotometer.

3. Results and discussion

The absorption spectra CaF_2 doped with SmF_3, ErF_3, TmF_3, HoF_3 after X-ray irradiation at 300 K and annealed at temperatures in the interval between 300 and 700 K are shown in Fig. 1. The assignment of the absorption bands in the figure to the divalent rare earths is based on results of previous papers (Wood and Kaiser, 1962, Weakliem and Kiss, 1967; Figura et al., 1989; Merz, J., Pershan, P., 1967).

Fig. 2 shows the absorption spectra for CaF_2, SrF_2, BaF_2 doped with TmF_3, HoF_3, ErF_3 and SmF_3. All bands in absorption spectra are shifted to the higher energies in the row from CaF_2 to BaF_2. Similar shift is observed for CaF_2, SrF_2, BaF_2 doped with SmF_3 and ErF_3. This is caused by decrease of the crystal field splitting of 5d state of divalent lanthanides in row CaF_2- SrF_2- BaF_2 (Radzhabov and Nepomnyashchikh, 2008).

Also under X-ray irradiation at room temperature absorption bands related to the hole F_3^- and $(F_2^-)_{ii}$ centers were found in these crystals. The $(F_2^-)_{ii}$ -centers in alkaline-earth fluorides crystals are holes localized on interstitial F ions oriented along axis [110] (Radzhabov, 2016). The F_3^- centers are a chain of three F ions (two of them are found in anion positions, and one is interstitial) oriented along axis [111] (Radzhabov, 2016). The absorption band caused by F_3^- centers peaked at about 6.2 eV. The band peaked at 3.9 eV corresponds to $((F_2^-)_{ii}$ centers (Figura et al., 1989). These bands can be covered with strong bands of divalent RE^{2+} ions. The positions of the absorption bands of the hole centers in the CaF_2, SrF_2, BaF_2 crystals were determined by subtracting the absorption spectra of radiation- and additive colored crystals (Radzhabov, 2016, Figura et al., 1989). Additive coloration results in the formation of only electron centers, while radiation coloring leads to the formation of electron and hole centers.

The $(F_2^-)_{ii}$ centers can be quenched by heating of the crystals to 370–390 K, which is reflected by the most rapid decrease in absorption in the region of 4 eV in the spectra of CaF_2 crystals doped with all the investigated impurities (Fig. 1 a, b, c, d). The absorption band of the F_3^- centers (the maximum of absorption band near 6 eV) is more thermally stable and it is decreased along with absorption bands of Sm^{2+}, Ho^{2+}, Er^{2+}, Tm^{2+} (Fig. 1). The similar behavior was observed for crystals CaF_2, SrF_2, BaF_2 doped with Yb (Radzhabov, 2016) and Nd (Sizova et al., 2016).

Fig. 3 displays thermal decay of Tm^{2+}, Sm^{2+}, Ho^{2+} and Er^{2+} ions in CaF_2. As can be seen in Fig. 3, the course of the thermal-bleaching curves for Ho^{2+}, Er^{2+} and Tm^{2+} has a stair case character. After heating to 650 K (Ho), 630 K (Er), 690 (Tm), 750 K (Sm) the intensity of RE^{2+} bands has completely disappeared.

Decrease of absorbance related to RE^{2+} ions during thermal

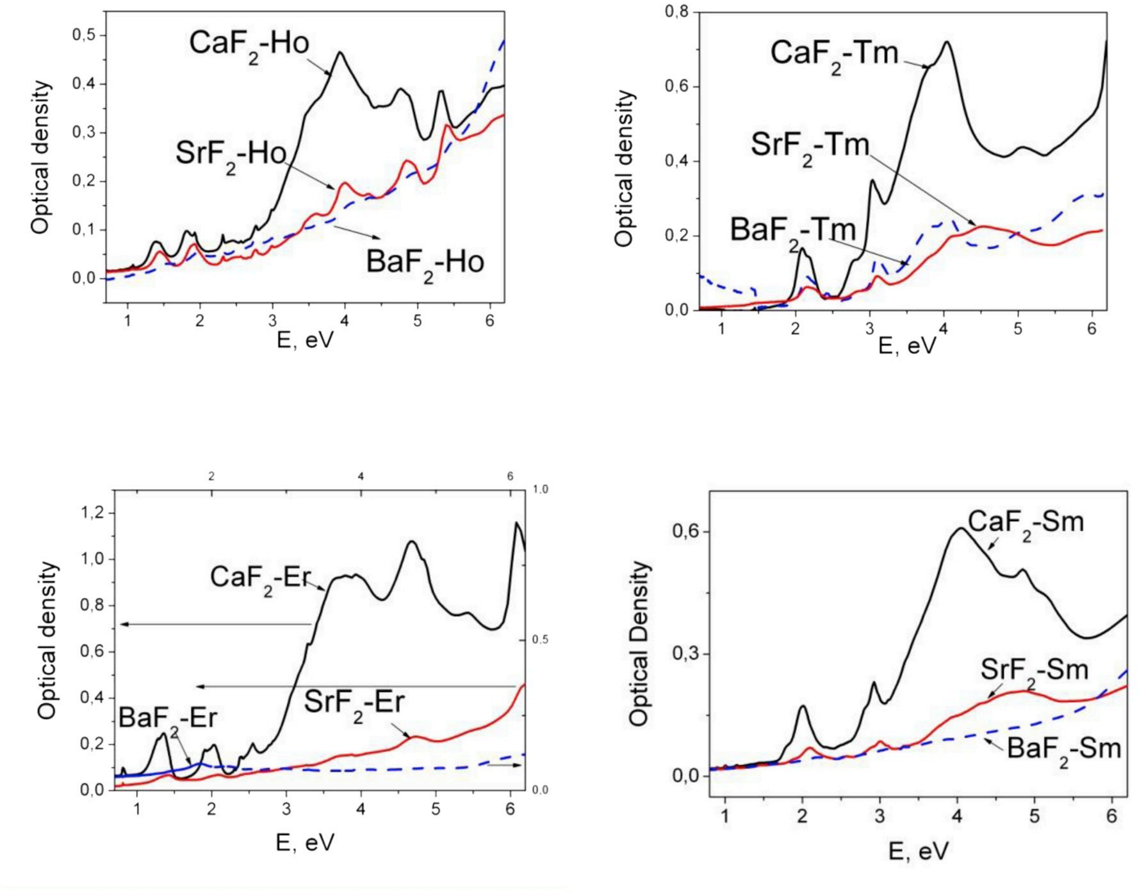

Fig. 2. Absorption spectra of CaF_2, SrF_2, BaF_2 doped with Ho (a), Tm (b), Er (c) and Sm (d) after X-ray irradiation at 300 K. Absorption spectra were measured at 300 K.

bleaching is caused by thermally stimulated electron escape from ground 4f state of divalent lanthanide ion to conduction band. RE^{2+} centers are electron traps and trap depth *E* can be estimated using Urbach equation (Urbach, 1948) and (Bos, 2017):

$$E = C_u k_B T_m \tag{1}$$

where is k_B is Boltzman constant, C_u – dimensionless Urbach constant (Bos, 2017) and T_m is the temperature of the thermally simulated luminescence peak associated with the energy needed to release an electron from the RE^{2+} trap. Since the temperature, where half of RE^{2+} ions are quenched ($T_{1/2}$), is only few degrees lower than T_m, the Urbach formula can also be used for thermal bleaching. For BaF_2 Urbach constant C_u was estimated equal to 29.0 by (Radzhabov and Kozlovsky, 2019). Using (Arkhangel'skaya, 1965) data for CaF_2 C_u is about 35.0.

Gaps between ground 4f state of divalent ion and bottom of conduction band estimated with Eq. (1) are about 1.5 eV for Ho^{2+} and 1.2 eV for Er^{2+} ions, that is close to the ones estimated using the vacuum referred binding energies (VRBE) model (Dorenbos, 2003, 2004, 2013). Position of ground states of Tm^{2+} and Sm^{2+} ions estimated with Eq. (1) are about 1.6 and 1.1 eV, respectively. The comparison is given in Table 1. The disagreement with VRBE model reaches more than 1.0 eV. Let us consider the possible mechanisms of destruction of the

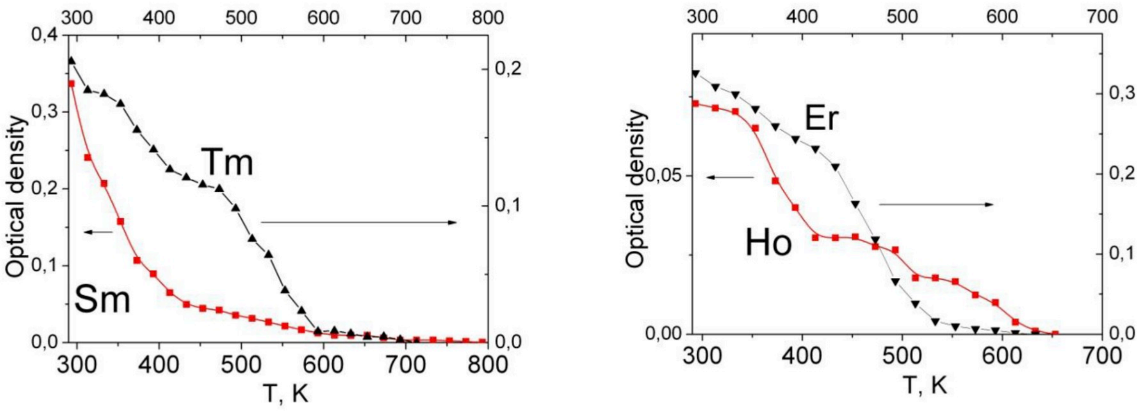

Fig. 3. Thermal decay of a) Tm^{2+} and Sm^{2+}, b) Ho^{2+} and Er^{2+} in CaF_2 doped with REF_3 crystals X-ray irradiated at room temperature. The optical density shown in the figures are taken from the maximum of the absorption bands at 2.1 eV for Tm^{2+}, 2.0 eV for Sm^{2+}, 1.8 eV for Ho^{2+}, 1.3 eV for Er^{2+}.

Table 1
Comparison of the trap depth according to the VRBE model and measured once with thermal bleaching and derived with Eq. 1

RE^{2+}	E, eV	
	VRBE	Eq. 1
Ho^{2+}	1.5	1.5
Er^{2+}	1.3	1.2
Tm^{2+}	2.2	1.6
Sm^{2+}	2.7	1.1

radiation induced centers of RE^{2+}, in order to explain the discrepancy between the estimates of the position of the level of RE^{2+} by Dorenbos model and thermal bleaching.

As pointed above an electron from RE^{2+} (Tm^{2+}, Sm^{2+}) can be released to conduction band in thermally stimulated process. In this case Eq. (1) gives a correct estimation of position of ground state of divalent lanthanide ion in band gap. However, in bleaching curves several parts can be distinguished. This is probably evidence of presence the second mechanism of RE^{2+} oxidation.

The second mechanism should be attributed to recombination of high temperature hole centers with divalent rare earth ions. According to VRBE model and Eq. (1) $T_{1/2}$ for Tm^{2+} and Sm^{2+} is higher than 850 K. However, these centers are bleached at much lower temperatures. This fact means, that only second oxidation hole assisted mechanism takes place for Tm^{2+} and Sm^{2+} ions.

It is known that hole in the $(F_2^-)_{ii}$ centers become mobile at about 350–400 K (Figura et al., 1989) and F_3^- are mobile at higher temperatures. Therefore, we can assume that first and second stages in Ho, Er bleaching curves in range 300–400 K and 400–500 K can be assigned to the second oxidation process, where mobile hole centers recombine with RE^{2+}. Thus, the third stage in Ho^{2+} curve can be attributed to the first oxidation mechanism, where an electron is thermally released from RE^{2+} ion to conduction band. $T_{1/2}$ for this process for Ho^{2+} is about 590 K for Ho^{2+} that corresponds to $E = 1.5$ eV between Ho^{2+} ground state and bottom of conduction band estimated with Eq. (1). This value is similar to energy calculated from VRBE model.

Thereby, the shallow electron traps such as Ho^{2+} and Er^{2+} can be oxidized by the two ways. There are thermally stimulated electron escape to conduction band and hole assisted oxidizing process. However, oxidation deeper electron traps such as Tm^{2+} and Sm^{2+} ions, is due to only hole assisted process.

4. Conclusion

The radiation coloring of CaF$_2$, SrF$_2$, and BaF$_2$ crystals doped with trivalent ions of RE elements (Tm, Er, Ho, Sm) results in the formation of divalent rare - earth ions. After heating the oxidation of RE^{2+} ions to trivalent state is observed.

The oxidation of divalent electron traps is assisted by recombination of a higher temperature hole centre with an electron in RE^{2+} ions without thermal release of an electron to conduction band. For shallow electron traps such as Ho^{2+} and Er^{2+} ions the thermal release of an electron from RE^{2+} takes also place.

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