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 (CaF₂, SrF₂, BaF₂) 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 4fⁿ−1-5d¹ transitions of divalent impurity ions and F³⁻ and (F²⁻)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 (CaF₂, SrF₂) 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 MeF₂-Pr³⁺ (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 (PC¹⁻) or two (PC) electrons bound at the anion adjacent to the trivalent rare earth ion RE in crystals CaF₂ (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 the research of electron thermal transfer from RE⁺² ions (RE-Nd, Dy, Ho, Er) to Sm³⁻ ions in MeF₂-Sm³⁺ (Me = Ca, Sr) crystals (Arkhangelskaya et al., 1969), also in irradiated MeF₂-RE⁺² ions (Me = Ca, Sr, Ba), doped with Nd, Ho, Er, Tm, exposed to ionizing irradiation (Arkhangelskaya 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 Sm⁺³ and Yb³⁺ creates.

RE⁺²⁺ and (F²⁻)ii and F³⁻ 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 CaF₂, SrF₂, and BaF₂ crystals doped with YF₃, LaF₃, CeF₃, GdF₃, TbF₃, LuF₃ and NdF₃. The main topic of the present paper is to study the processes of changing the valence of RE³⁺ ions by radiation coloration crystals of alkaline earth fluorides (CaF₂, SrF₂, BaF₂) doped with SmF₃, HoF₃, TmF₃, ErF₃ within temperature range 300–700 K.

2. Experimental methodology

The CaF₂, SrF₂ and BaF₂ crystals doped with SmF₃, HoF₃, TmF₃, ErF₃ (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 CdF₂ to the raw material in order to remove oxygen. Then the crystals with an impurity of rare earth fluorides (REF₃) 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 CaF₂, SrF₂, BaF₂ were...
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 CaF2 doped with SmF3, ErF3, TmF3, HoF3 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 CaF2, SrF2, BaF2 doped with TmF3, HoF3, ErF3 and SmF3. All bands in absorption spectra are shifted to the higher energies in the row from CaF2 to BaF2. Similar shift is observed for CaF2, SrF2, BaF2 doped with SmF3 and ErF3. This is caused by decrease of the crystal field splitting of 5d state of divalent lanthanides in row CaF2- SrF2- BaF2 (Radzhabov and Nepomnyashchik, 2008).

Also under X-ray irradiation at room temperature absorption bands related to the hole F3− and (F2−)ii centers were found in these crystals. The (F2−)ii centers in alkaline-earth fluorides crystals are holes localized on interstitial F ions oriented along axis [110] (Radzhabov, 2016). The F3− 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 F3− centers peaked at about 6.2 eV. The band peaked at 3.9 eV corresponds to ((F2−)ii) centers (Figura et al., 1989). These bands can be covered with strong bands of divalent RE2+ ions. The positions of the absorption bands of the hole centers in the CaF2, SrF2, BaF2 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 (F2−)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 CaF2 crystals doped with all the investigated impurities (Fig. 1 a, b, c, d). The absorption band of the F3− centers (the maximum of absorption band near 6 eV) is more thermally stable and it is decreased along with absorption bands of Sm2+, Ho2+, Er2+, Tm2+ (Fig. 1). The similar behavior was observed for crystals CaF2, SrF2, BaF2 doped with Yb (Radzhabov, 2016) and Nd (Sizova et al., 2016).

Fig. 3 displays thermal decay of Tm2+, Sm2+, Ho2+ and Er2+ ions in CaF2. As can be seen in Fig. 3, the course of the thermal-bleaching curves for Ho2+, Er2+ and Tm2+ has a stair case character. After heating to 650 K (Ho), 630 K (Er), 690 (Tm), 750 K (Sm) the intensity of RE2+ bands has completely disappeared.

Decrease of absorbance related to RE2+ ions during thermal
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):

\[
E = C_\text{u}k_BT_m
\]  

(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 (Arkhangelskaya, 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

![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.](image1)

![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\(^{2+}\).](image2)
radiation induced centers of $\text{RE}^{2+}$, in order to explain the discrepancy between the estimates of the position of the level of $\text{RE}^{2+}$ by Dorenbos model and thermal bleaching.

As pointed above an electron from $\text{RE}^{2+}$ $(\text{TM}^{2+}, \text{Sm}^{2+})$ 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 rare earth ions. After heating the oxidation of $\text{RE}^{2+}$ ion to trivalent ions of RE elements (Tm, Er, Ho, Sm) results in the formation of a higher temperature hole centre with an electron in $\text{RE}^{2+}$ ions. According to VRBE model and Eq. (1) $T_{1/2}$ for $\text{TM}^{2+}$ and $\text{Sm}^{2+}$ 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 $\text{TM}^{2+}$ and $\text{Sm}^{2+}$ ions.

It is known that hole in the $\text{F}^{-}, \text{F}^{-}$ centers become mobile at about 350–400 K (Figura et al., 1989) and $\text{F}^{-}$ 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 $\text{RE}^{2+}$. Thus, the third stage in $\text{Ho}^{2+}$ curve can be attributed to the first oxidation mechanism, where an electron is thermally released from $\text{RE}^{2+}$ ion to conduction band. $T_{1/2}$ for this process for $\text{Ho}^{2+}$ is about 590 K for $\text{Ho}^{2+}$ that corresponds to $E=1.5$ eV between $\text{Ho}^{2+}$ 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 $\text{Ho}^{2+}$ and $\text{Er}^{2+}$ 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 $\text{Tm}^{2+}$ and $\text{Sm}^{2+}$ ions, is due to only hole assisted process.

4. Conclusion

The radiation coloring of $\text{CaF}_2$, $\text{SrF}_2$, and $\text{BaF}_2$ 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 $\text{RE}^{2+}$ 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 $\text{RE}^{2+}$ ions without thermal release of an electron to conduction band. For shallow electron traps such as $\text{Ho}^{2+}$ and $\text{Er}^{2+}$ ions the thermal release of an electron from $\text{RE}^{2+}$ takes also place.

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Table 1

<table>
<thead>
<tr>
<th>$\text{RE}^{2+}$</th>
<th>$E$, eV</th>
<th>VRBE</th>
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<td>$\text{Ho}^{2+}$</td>
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<td>1.5</td>
<td></td>
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<tr>
<td>$\text{Er}^{2+}$</td>
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<td>1.2</td>
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<tr>
<td>$\text{Tm}^{2+}$</td>
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<td>1.6</td>
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<tr>
<td>$\text{Sm}^{2+}$</td>
<td>2.7</td>
<td>1.1</td>
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Comparison of the trap depth according to the VRBE model and measured once with thermal bleaching and derived with Eq. 1.