

XVI INTERNATIONAL
FEOFILOV SYMPOSIUM

Radiolysis of LaF₃ Crystals with Rare-Earth Impurities

E. A. Radzhabov^{a, b*}

^a Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia

^b Irkutsk State University, Irkutsk, 664003 Russia

*e-mail: eradz@igc.irk.ru

Received April 28, 2016

Abstract—The absorption spectra of LaF₃ crystals, both pure and doped with rare-earth fluorides (YF₃, CeF₃, NdF₃, PrF₃, SmF₃, EuF₃, GdF₃, TbF₃, DyF₃, HoF₃, ErF₃, TmF₃, YbF₃, and LuF₃) have been investigated. All these impurities can be separated into two groups with respect to the shape of the absorption spectra of irradiated crystals. The spectra of the crystals doped with Nd, Sm, Tm, and Yb exhibit, along with 200-nm hole band F_3^- , weak bands due to RE²⁺-anion vacancy centers. The spectra of LaF₃ crystals with Y, Ce, Pr, Gd, Tb, Dy, Ho, Er, and Lu impurities exhibit, along with the hole-center bands (F_3^- at 200 nm and V_{kA} at 320 nm), bands of comparable intensity, which can be attributed to RE³⁺-F centers. This conclusion is confirmed by preliminary quantum-chemical calculations and the estimation of the levels location in the energy-band diagram.

DOI: 10.1134/S0030400X16100210

INTRODUCTION

Lanthanum fluoride is characterized by high density (5.94 g/cm³) and the absence of hygroscopicity. The LaF₃ lattice is isomorphic for trivalent rare-earth ions. The spectroscopy of trivalent lanthanides in LaF₃ has been investigated in detail (see review [1]). At the same time, the spectra of divalent lanthanides in LaF₃ and related lattices have been studied rather poorly [2, 3]. The optical spectra of radiation-induced defects F and V_k [4, 5] and F_3^- [6] in LaF₃ crystal have been analyzed. LaF₃:RE³⁺ (RE are rare-earth ions) is a promising material for laser and scintillation applications. However, the radiolysis of LaF₃ crystals doped with rare-earth ions has been studied insufficiently [7].

EXPERIMENTAL

Fluoride crystals were grown by the Stockbarger method in a three-channel graphite crucible in vacuum.¹ A few percent of CdF₂ was added to the raw material to cleanse it from oxygen impurity. The concentrations of lanthanide fluoride impurities in the charge were 0.01, 0.1, and 0.3 mol %. The absorption spectra of some LaF₃ crystals exhibited bands in the vicinity of 192, 206, 217, and 228 nm and the strongest

band at 246 nm due to Ce³⁺ ions [8]. The trace cerium concentration in LaF₃ crystals was estimated (by comparing their absorption spectra with the spectrum of LaF₃-0.01% CeF₃) to be 0.001–0.005 mol %. The concentration of cerium impurity in the initial raw material synthesized in our laboratory and the LaF₃ crystals grown from it was much lower.

The absorption spectra in the range of 190–3000 nm were measured with a Perkin-Elmer Lambda-950 spectrophotometer.² The irradiation was performed using a BKHV-12 X-ray tube (voltage 40 kV, current 20 mA) for 40 min. The samples were placed directly on the output window of the X-ray tube and colored from two sides.

To estimate the influence of the neighboring anion vacancy on the optical transitions in Sm²⁺ ions, we performed nonempirical calculations of the optical transitions in a small cluster of LaF₃ crystal. An initial cluster consisted of central fluorine atom and the nearest spheres of surrounding ions: La₄F₈ with a charge of 4+. The wave functions of La and F were taken from the LANL2DZ basis, while the wave functions of samarium were taken from the SDD basis, in which the wave functions of f orbitals are presented more completely. Calculations were performed using the Gaussian 03 licensed package of quantum-chemi-

¹ The crystals were grown by V.A. Kozlovskii, and the LaF₃ raw material was synthesized by O.N. Solomein.

² Equipment of the Isotope Geochemistry Center of collective use, Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences.

cal programs [9] by the density functional theory (DFT) method. Mixed layers of La and F ions alternate with two fluorine layers in the LaF₃ lattice. The ion coordinates in the LaF₃ lattice were taken from [10]. The origin of coordinates was chosen to be at the fluorine ion, because the wave functions of the F center are diffuse, and several layers of the nearest environment must be applied to transfer them correctly.

EXPERIMENTAL RESULTS

Several absorption bands are induced in lanthanum fluoride crystals with rare-earth impurity ions under X-ray irradiation (Fig. 1). The strong band at about 200 nm is due to the absorption of molecular ions F_3^- [6]. A 330-nm band is also observed in the spectra. The wide band at 330 nm observed in the spectra of LaF₃ crystals irradiated at low temperatures that decayed at a temperature of 115 K was attributed to V_k centers [4]. The self-trapped holes in CaF₂ stabilized by rare-earth ions $F_2^-(Tm)$ with an absorption band at 320 nm are stable at room temperature and decay upon heating to 100°C [11]. The bands at about 330 nm in the LaF₃-RE spectra may be due to hole centers of the V_k type that are stable at room temperature (we will denote them as V_{kA}). The absorption bands in the range of 500–550 nm (Fig. 1) obviously belong to F -like centers [4]. The intensity of all induced absorption bands increased several times with an increase in the impurity concentration from 0.01 to 0.3 mol %.

The absorption spectra of all crystals exposed to X rays at room temperature can be separated into two groups. The first group includes the spectra of the crystals doped with Y, Ce, Gd, Tb, Ho, Er, and Lu (Fig. 1). The absorption spectra of these crystals contain bands at 520–550 (F centers), 330 (V_{kA}), and 200 nm (F_3^-). The intensity ratio for the absorption bands V_{kA} and F_3^- centers is different in different crystals. The crystals of this group are colored pink because of the absorption bands in the range of 520–550 nm. The intensities of the bands due to hole (V_{kA} , F_3^-) and electron centers are approximately the same (Fig. 1).

The second-group spectra (of the crystals doped with Nd, Sm, Yb, and Tm) are characterized by a strong absorption band at 200 nm (F_3^- centers), the absence of the 330-nm band, and weaker (by an order of magnitude) bands in the UV and visible spectral ranges (Figs. 2, 3). Under X-ray irradiation, a small fraction of related Ce^{3+} ions changed their valence, which manifested itself in the induced absorption spectra (Figs. 1, 2, the dip at 246 nm). The crystals are almost colorless because of the weak absorption in the visible region. Simultaneously with the formation of

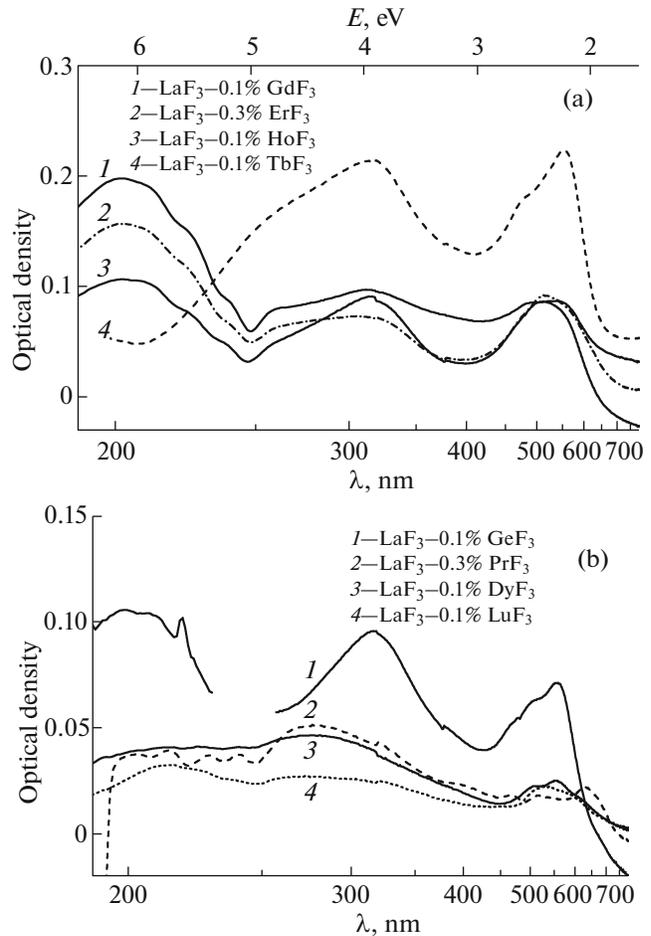


Fig. 1. X-ray-induced absorption spectra of the (a) first- and (b) second-group LaF₃ crystals with rare-earth impurities.

the UV band of F_3^- centers, weak bands in the range of 300–800 nm are also induced in LaF₃ crystals with YbF₃, TmF₃, SmF₃, and NdF₃ impurities, which will be referred to as “long-wavelength bands.” Each impurity forms its own characteristic long-wavelength absorption bands.

When growing LaF₃ crystals with SmF₃ impurity, we obtained both crystals containing only trivalent samarium ions and crystals with samarium partially transformed into the divalent state [3]. The absorption spectra of the grown LaF₃-Sm²⁺ and LaF₃-Sm³⁺ crystals after X-ray irradiation are identical, although the degree of transformation of Sm³⁺ into Sm²⁺ is low (Fig. 3). Irradiated LaF₃:Yb³⁺ crystals exhibited weak bands at 330 and 370 nm, which can be attributed to Yb²⁺ ions [12]. One can suggest that long-wavelength absorption bands are due to the formation of centers containing divalent rare-earth ions.

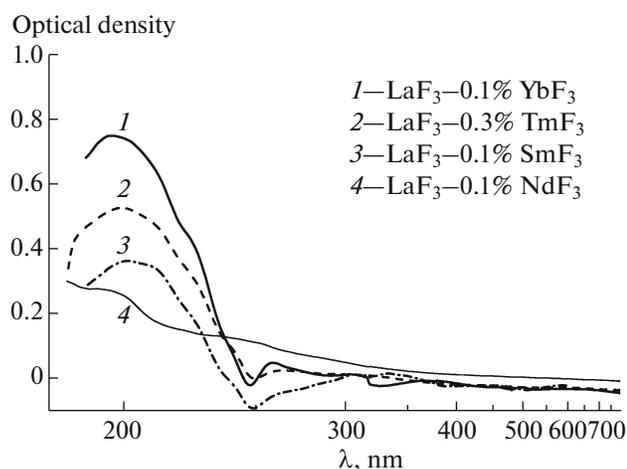


Fig. 2. X-ray-induced absorption spectra of the second-group LaF_3 crystals with rare-earth impurities.

CALCULATION RESULTS

To simulate the F center, the central fluorine atom was removed from the La_4F_8 cluster. A calculation of the F center showed that a local level occupied by one electron arises in the band gap. The orbital of this electron is localized in the vicinity of anion vacancy (Fig. 4). The optical transitions of the F center lie in the range of 350–620 nm (the oscillator strength is about 0.2), which is rather close to the experimental values for 460, 590, and 650 nm [4].

The main purpose of the preliminary simulation was to find the location of the F -center electron in the vicinity of which the trivalent rare-earth ion is placed. One of the lanthanum ions in the chosen cluster is replaced by a rare-earth ion. Since the total spin cluster must be specified in the calculation, the calculation was performed using two possible spin values, the model with the lowest total energy of cluster being chosen. It is of interest to compare the calculation results for ions with low and high second ionization potentials. The cerium ion belongs to the former ones. In the Ce^{3+} ion, the valence unpaired electron is located on the $4f$ atomic orbital; thus, with the F -center electron, we have two external electrons. The total spin can be either 1 or 0 (triplet or singlet states, respectively). The total energy of the cluster in the triplet state is 1.1 eV lower. In this case, the calculated orbital with the highest energy, occupied by one electron, resembles the orbital of the F center with a small contribution from the $4f$ atomic orbital of the cerium ion (Fig. 4). Similar results with an external electron localized mainly on vacancy were obtained for clusters with Y, Lu, and Pr ions.

The samarium ion is characterized by a relatively high second ionization potential. In the ground state of the Sm^{3+} ion, five electrons are located on the atomic $4f$ orbitals with parallel spins. The highest

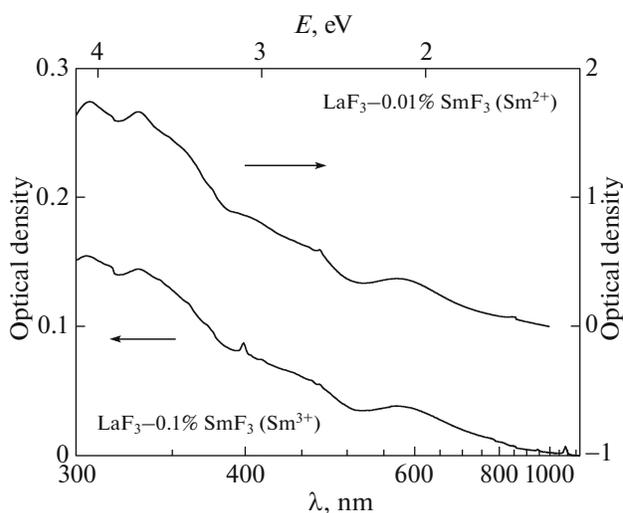


Fig. 3. Absorption spectra of divalent samarium in LaF_3 with SmF_3 impurity. Divalent samarium was obtained (upper curve) during crystal growth and (lower curve) under X-ray irradiation of a crystal containing only trivalent samarium.

energy orbital occupied by one electron in the SmLa_3F_7 cluster is the $4f$ orbital of the samarium atom (Fig. 4). Similar results with localization of external electron on the $4f$ level of lanthanide were also obtained for Eu, Tm, and Yb ions. For heavy Tm and Yb lanthanides, a lower total energy is possessed by a cluster with a lower multiplicity; under these conditions, an additional electron is captured by the impurity ion to reduce the total spin of the latter.

DISCUSSION

A room-temperature X-ray irradiation of lanthanum fluoride crystals containing rare-earth trivalent ions leads to the formation of electron centers with bands of 350–800 nm and hole centers with bands of about 200 nm (F_3^-) and about 330 nm (of the V_k type).

We separated rare-earth impurities with respect to the shape of induced absorption bands (see above). In the first group, the absorption bands located in the range of the F bands of pure lanthanum fluoride can be attributed to the absorption of the F centers perturbed by trivalent rare-earth ions. Based on the band intensity ratio for the hole and electron centers, the oscillator strength of the transitions in Sm (in the vicinity of 550 nm) was estimated to be 0.3–0.5; these values are close to the oscillator strength of F centers in alkali halides [13].

In the second group of impurities, the electron centers are divalent rare-earth ions. When analyzing the absorption spectra of LaF_3 –Sm crystals (Fig. 2), one can clearly see that the divalent samarium ions formed both during growth of LaF_3 – SmF_3 in a reduc-

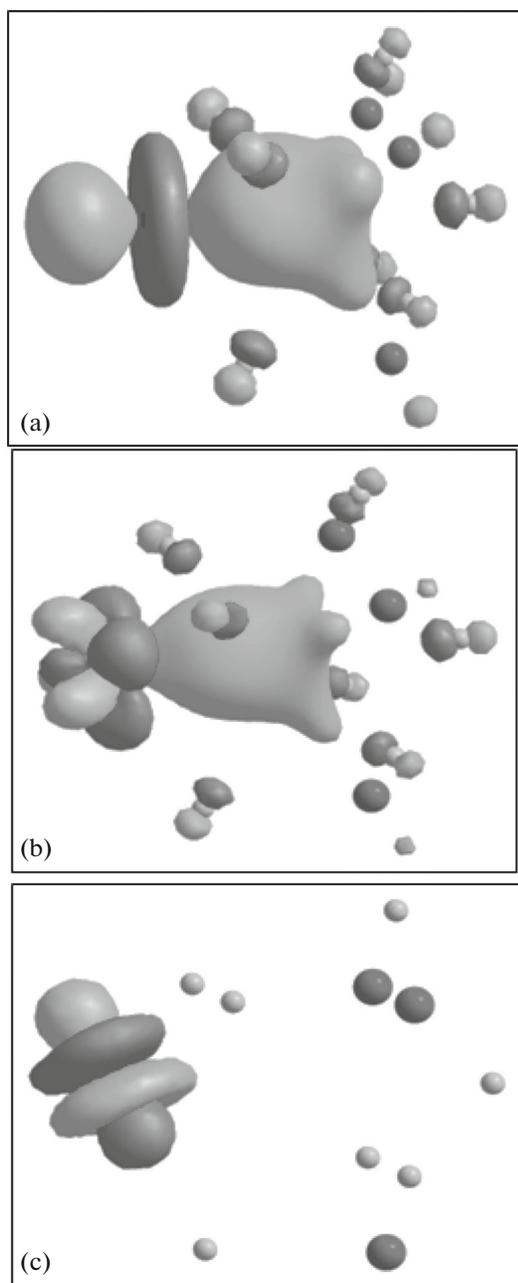


Fig. 4. Highest occupied single-electron orbitals for a La₄F₈ cluster containing (a) *F* center, (b) Ce³⁺–*F* centers, and (c) Sm²⁺ vacancy. Small and large circles indicate fluorine and lanthanum ions, respectively.

ing atmosphere and under X-ray irradiation of crystals containing trivalent samarium have identical spectra. Based on a comparison of the results of measuring conductivity and optical spectra and nonempirical quantum-chemical calculations, a conclusion about the formation of Sm²⁺–anion vacancy centers was drawn in [3]. An X-ray irradiation of LaF₃–Sm³⁺ gives rise to an absorption spectrum identical to the spectrum of Sm²⁺–anion vacancy centers (Fig. 3). This

important result indicates that the *F* centers formed under lanthanum fluoride irradiation are captured by trivalent samarium with the formation of Sm²⁺–vacancy centers. Even at a samarium concentration of 0.1 SmF₃ mol %, all newly formed *F* centers are spent to produce divalent samarium centers.

The formation of Eu²⁺–vacancy centers in LaF₃ was recently demonstrated in [12]. We could not grow LaF₃–EuF₃ crystals with a measurable content of trivalent europium; only spectra of Eu²⁺ ions were observed [12]. The difficulties of growing LaF₃ crystals with trivalent europium were also indicated in review [1].

Based on the similarity of X-ray-induced absorption spectra with Yb, Tm, and Nd impurities and the well-identified Sm²⁺–vacancy spectrum (Figs. 2, 3), one can suggest that X-ray irradiation of LaF₃ crystals with these impurities also results in the generation of divalent lanthanide–fluorine vacancy centers.

Generalizing what has been said above, one can conclude that centers composed of identical initial parts (Ln³⁺ ion, anion vacancy, and electron) are formed in lanthanum fluoride crystals with rare-earth ions under ionizing irradiation at room temperature. In the case of rare-earth ions from the first group, the electron is mostly localized on the anion vacancy, which results in the absorption spectra of *F*-like centers. For other rare-earth ions, the electron is mainly localized on the rare-earth ion (Figs. 2, 3).

One can suggest that the formation of centers of two types (RE²⁺–vacancy or RE³⁺–*F*) is due to the difference in the energy levels of RE²⁺ ions and the *F* center in the energy band diagram. Depending on which defect has a lower ground level, the electron prefers to be localized either on rare-earth ion or on an anion vacancy. The energy gaps between the level of RE²⁺ ion and conduction band in LaF₃ were estimated within the empirical model in [14] (table). The type of the electron center formed under X-ray irradiation is indicated in the third row of the table. Thulium and dysprosium are lanthanides with the closest energies of ground levels forming different electron centers. The lanthanides with a ground state located lower than in thulium (2.05 eV) form RE²⁺–vacancy centers, while the lanthanides with the ground level lower than in dysprosium (>1.51 eV) form RE³⁺–*F* centers (table). Therefore, the *F*-center level in LaF₃ lies 1.51–2.05 eV below the bottom of the conduction band. The only exception is the Nd²⁺ ion (table).

The ionization potential of the *F* center in LaF₃ can be estimated as follows. The experimental energies of the *F* bands split by the crystal field of the LaF₃ lattice are 1.9, 2.2, and 2.7 eV [4]. On the assumption that the first excited level of the *F* center is close to the bottom of conduction band, we find the gap to be about 1.9 eV,

Electron transfer energy from the RE^{2+} level to the LaF_3 conduction band [14]. The type of the electron centers formed under X-ray irradiation at room temperature ($F(RE^{3+}-F)$ or $V(RE^{2+}-vacancy)$) is indicated in the third row

RE^{2+}	Y	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
I, eV		-0.36	0.89	1.33	2.49	3.74	-0.77	0.58	1.51	1.35	1.15	2.05	3.33	
Center type	F	F	F	$V?$	V	V	F	F	F	F	F	V	V	F

a value falling in the experimental range of values (1.51–2.05 eV) (table).

The results of the preliminary quantum-chemical calculations are in good qualitative agreement with the experimental results and the estimates listed in the table.

CONCLUSIONS

Radiolysis of lanthanum fluoride crystals at room temperature leads to the formation of hole centers (V_{kA} and/or F_3^-) and electron F centers, which are captured by RE^{3+} impurity ions. The type of the X-ray-induced electron color centers in a doped LaF_3 crystal depends on the ratio of the ionization potentials of RE^{2+} ion and F center. Rare-earth (Sm, Eu, Tm, Yb) RE^{2+} ions with an ionization potential exceeding that of the F center (deep traps) form RE^{2+} -anion vacancy centers. The other rare-earth ions (Y, Pr, Gd, Tb, Dy, Ho, Er, Lu), which have a lower ionization potential, form $RE^{3+}-F$ centers; their optical spectra allow one to consider them as F centers perturbed by neighboring RE^{3+} ions.

REFERENCES

1. W. T. Carnall, G. L. Goodman, K. Rajnak, and R. S. Rana, *J. Chem. Phys.* **90**, 3443 (1989).
2. G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals* (Interscience, 1968).
3. E. A. Radzhabov and V. A. Kozlovskii, *Bull. Russ. Acad. Sci.: Phys.* **79**, 251 (2015).
4. E. A. Radzhabov and A. I. Nepomnyashikh, in *Proceedings of the International Conference on Inorganic Scintillators and Their Applications SCINT 95, Delft, The Netherlands, August 28–September 1, 1995*, p. 189; arxiv:1510.07781.
5. E. D. Thoma, H. Shields, Y. Zhang, B. C. McCollum, and R. T. Williams, *J. Lumin.* **71**, 93 (1997).
6. E. A. Radzhabov, *Opt. Spectrosc.* **120**, 294 (2016).
7. V. G. Vasil'chenko, Yu. A. Krechko, Yu. D. Motin, and B. P. Sobolev, *Nucl. Instrum. Methods Phys. Res. B* **122**, 63 (1997).
8. L. R. Elias, W. S. Heaps, and W. M. Yen, *Phys. Rev. B* **8**, 4989 (1973).
9. M. J. Frisch, G. W. Trucks, and H. B. Schlegel, *Gaussian 03, Revision E.1* (Gaussian Inc., Pittsburgh, PA, 2007).
10. K. Schlyter, *ARKIV FOR KEMI* **5**, 73 (1953).
11. P. V. Figura, A. I. Nepomnyashikh, and E. A. Radzhabov, *Opt. Spectrosc.* **67**, 1304 (1989).
12. E. A. Radzhabov and R. Shendrik, *Rad. Meas.* **90**, 80 (2016). doi 10.1016/j.radmeas.2016.02.012
13. *Physics of Color Centers*, Ed. by W. B. Fowler (Academic, New York, 1968).
14. P. Dorenbos, *J. Lumin.* **135**, 93 (2013).

Translated by Yu. Sin'kov