

CONDENSED-MATTER SPECTROSCOPY

F_3^- Molecular Ions in Fluoride Crystals

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Abstract—The UV absorption spectra of F_3^- molecular ions in LaF_3 , SrF_2 , CaF_2 , and BaF_2 crystals doped with rare-earth elements are studied. Comparison of radiation-colored and additively colored crystals reveals the absorption bands of F_3^- hole centers in the region near 6 eV. Nonempirical calculations of optical transitions agree well with experimental results.

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INTRODUCTION

The single-charge molecular ions X_3^- ($X = Cl, Br, I$) have been studied in the gas phase, solutions, and ionic crystals [1, 2]. Based on the similarity of the absorption spectra of irradiated alkali halide crystals and solutions, the absorption bands in the range of 5–6.2 eV are assigned to the absorption of Cl_3^-, Br_3^-, I_3^- ions [3, 4]. The X_3^- centers in alkali halide crystals are divided into three types, namely, $V_2, V_3,$ and V_4 . In potassium halides, the V_2 centers are formed by irradiation at 100 K, while the V_3 and V_4 centers are formed at temperatures of 200 and 300 K, respectively [5]. The low-temperature V_2 and V_4 have dichroic absorption. It is believed that the V_3 center corresponds to an isolated X_3^- ion, while the V_2 and V_4 centers include one or two vacancies near the molecular ion [5].

The F_3^- and Cl_3^- trihalide ions are obtained by codeposition of sodium and cesium halides with argon in a proportion of 1/400 at 15 K [6]. The Cl_3^- absorption band is observed near 4.9 eV, while absorption in the samples with F_3^- begins at about 6.2 eV and intensifies with decreasing wavelengths. The distance between fluorines in the F_3^- ion was estimated in [6] to be 1.55 Å, while nonempirical calculations performed in [1, 2] yield a higher distance of 1.74 Å. Relatively recently, F_3^- were observed in the gas phase by electron-capture mass-spectrometry [7]. The energy of dissociation of F_3^- into F^- and F_2 is 1.02 eV, which makes problematic the existence of F_3^- ions in aqueous solutions [8].

The absorption band of F_3^- in CaF_2 –Tm and CaF_2 –Dy lies at 6.0 eV [9]. The trihalide centers in these crystals are formed under the action of X-ray radiation at temperatures exceeding 100 K [9]. At the same time, the absorption band of trifluoride molecules in LiF is observed at a considerably larger photon energy of 11 eV [10, 11]. In $SrCl_2$ – K^+ crystals [12], the Cl_3^- centers easily reoriented along the principal axis of the crystal under irradiation by polarized light, which led to almost total dichroism in the absorption band of these centers at 4.7 eV.

The formation of stable hole centers is an important process needed for understanding the details of radiation-induced coloration of halide crystals. In the present work, we study the formation of temperature-stable (300–500°C) trifluoride molecular ions F_3^- in fluoride crystals ($LaF_3, CaF_2, SrF_2, BaF_2$).

EXPERIMENTAL TECHNIQUE

The fluoride crystals were grown by the Stockbarger method in a three-channel graphite crucible in vacuum.¹ Several percent of CdF_2 were added into the batch to purify it from oxygen impurities. The concentration of lanthanide fluorides in the batch was 0.01, 0.1, and 0.3 mol %. The absorption spectra in the range of 190–3000 nm were measured on a Perkin–Elmer Lambda-950 spectrophotometer,² and the spectra in the vacuum ultraviolet region were recorded using a laboratory setup equipped with a VMR2

¹ The crystals were grown by V.A. Kozlovskii.

² The equipment of the Baikal Analytical Center of Collective Use, Siberian Branch, Russian Academy of Sciences.

monochromator (115–300 nm). An L7292 deuterium lamp (Hamamatsu) was used as a source of vacuum ultraviolet radiation, and an FEU-142 photomultiplier was used as a detector.

X-ray irradiation was performed using a BKHV-12 X-ray tube at a voltage of 40 kV and a current of 20 mA for 40 min. The samples were placed directly at the exit window of the X-ray tube and colored from two sides.

The additive coloration of crystals was done in a stainless steel autoclave at temperatures of 700–850°C. The crystal samples and metal potassium pieces were placed in different containers. After evacuation to 10⁻² Torr, the autoclave was put down into a furnace. After heating to a required temperature, the autoclave with the samples was kept in the furnace for 1–3 h depending on the thickness of samples and the coloration temperature. As a result of coloration, the surface of SrF₂ and BaF₂ samples became opaque, and the samples were polished again. The lanthanum fluoride crystals, both pure (see [13]) and doped with rare earths, became grey after coloration. In a microscope, we observed the appearance of metal particles (obviously, La) over the entire volume of samples. Heating of additively colored lanthanum fluoride crystals to 700–900°C with subsequent quenching decreased the number of metal particles, but did not cause coloration.

Nonempirical calculations of crystalline clusters were performed using a Gaussian package [14] by the density functional theory (DFT) with the B3LYP hybrid potential and basis sets 6N311G(d, p) (for CaF₂) and LANL2DZ for LaF₃. The energies of optical transitions were calculated by the time-dependent density functional theory (TDDFT).

EXPERIMENTAL RESULTS

Lanthanum Fluoride

X-ray irradiation of LaF₃ crystals doped with rare-earth ions RE³⁺ (Yb, Tm, Sm, Ho) at room temperature leads to the formation of centers exhibiting an intense absorption band with a maximum at 6.2 eV (Fig. 1).

The absorption spectra of LaF₃ crystals show bands at 6.46, 6.02, 5.69, 5.30, and (most intense) 5.0 eV, which belong to Ce³⁺ ions [24]. The trace concentration of cerium in LaF₃ crystals was estimated to be 0.001–0.005 mol % by comparing their absorption spectrum with the spectrum of LaF₃–0.01% CeF₃. Under the effect of X-ray radiation, a small part of Ce³⁺ ions changed their valence, which manifested itself in induced absorption spectra (Fig. 1, dip at 5.0 eV).

The band at 6.2 eV is most pronounced in LaF₃–YbF₃ crystals. With increasing concentration of trivalent rare-earth ions, this band becomes more intense (at the same irradiation dose). Simultaneously

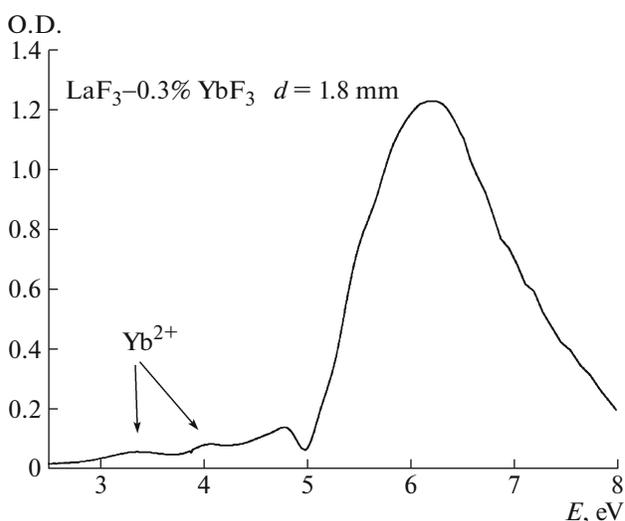


Fig. 1. X-ray-induced absorption spectrum of a LaF₃–0.3% YbF₃ crystal at room temperature. The suggested bands of F₃⁻ and Yb²⁺ centers are shown. The dip near 5 eV is caused by transformation of Ce³⁺ ions.

with the formation of the 6.2-eV UV band, the spectra of LaF₃ with YbF₃, TmF₃, SmF₃, and NdF₃ impurities also show weak induced bands in the range of 0.5–4 eV, which we will call “long-wavelength bands.” Each impurity forms its own typical long-wavelength absorption bands, while the position and width of the 6.2-eV band remain unchanged. The long-wavelength absorption bands in irradiated LaF₃–SmF₃ crystals are caused by the transitions in the divalent rare-earth ions created by ionizing radiation. The long-wavelength absorption bands in LaF₃ are at least an order of magnitude weaker than the 6.2-eV absorption band (Fig. 1).

Upon heating the irradiated LaF₃–0.3% YbF₃ crystal, the 6.2-eV band is destroyed at temperatures of 350–650°C. The irradiation of LaF₃–YbF₃ crystals by a DDC30 deuterium discharge lamp quenches the band of induced F₃⁻ centers simultaneously with the bands of Yb²⁺ centers at 4.0 and 3.35 eV. The 6.2-eV band dichroism, i.e., the difference between the absorption spectra measured through a polarizer oriented along and perpendicular to the principal axis of the crystal, was not observed.

Alkaline-Earth Fluorides

In alkaline-earth fluorides with trivalent rare-earth ions, X-ray radiation at room temperature induces electron (RE²⁺ ions) and hole (F₃⁻, V_{kA}) centers. The appearance of the F₃⁻ band is masked by the strong bands of divalent RE²⁺ ions in the region of 6.2 eV. In

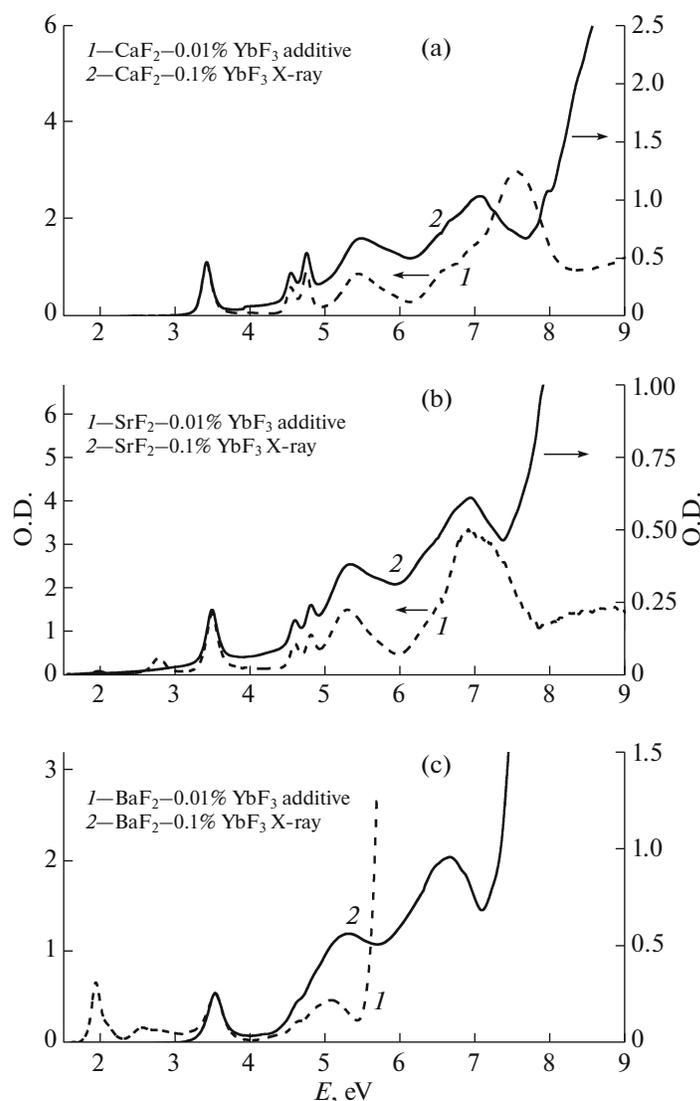


Fig. 2. Comparison of the absorption spectra of (a) CaF_2 - YbF_3 , (b) SrF_2 - YbF_3 , and (c) BaF_2 - YbF_3 crystals induced by (1) additive coloration and (2) X-ray radiation.

a previous work [9], the total absorption in the region of 5–8 eV was divided into the F_3^- and Tm^{2+} absorption by comparing the absorption spectra of X-ray-irradiated and additively colored crystals. In the region of 6.2 eV, Yb^{2+} makes a smaller contribution to the total absorption than Tm^{2+} . This allowed us to more reliably separate the absorption of F_3^- hole centers in CaF_2 – 0.1% YbF_3 crystals (maximum at 6.08 eV, halfwidth 2.03 eV) (Fig. 2a). In SrF_2 -0.1% YbF_3 crystals, the absorption band of F_3^- molecular ions lies at 6.0 eV and has a halfwidth of 1.7 eV (Fig. 2b). In addition to the main hole centers F_3^- , these crystals at room temperature contain hole centers $(\text{F}_2^-)_{ii}$ with the absorption band near 4.1 eV [23], which can be quenched by heat-

ing to 100–120°C (see also [9]). The absorption bands of divalent ions and F_3^- hole centers in crystals of alkaline-earth fluorides are approximately the same in intensity (Fig. 2).

In additively colored BaF_2 - Yb crystals in the region above 5.5 eV, one observes strong absorption of unknown nature (Fig. 2c). Similar strong absorption bands are also observed at 7.8 eV in CaF_2 (Fig. 2a) and 7.0 eV in SrF_2 (Fig. 2b). We observed similar absorption at photon energies exceeding 5.5 eV in additively colored BaF_2 crystals with different rare-earth ions (Sm, Nd, Ho, Tm, Er, Gd, Lu), as well as in pure crystals. Previously, a significant increase in the absorption above 5.5 eV was observed in additively colored BaF_2 -Nd crystals [15]. Heating of additively colored

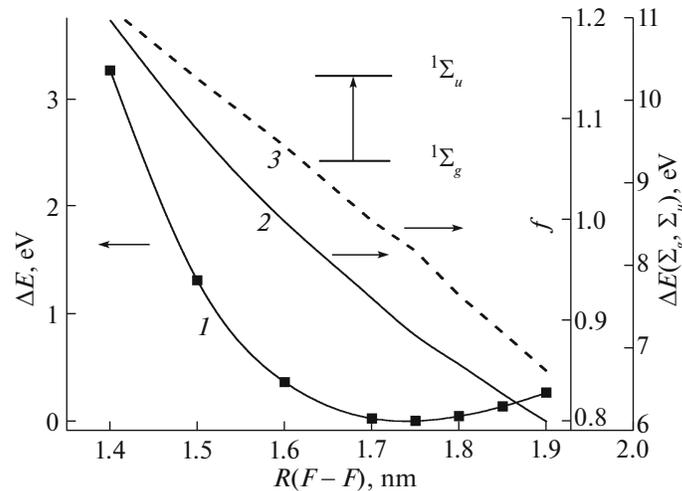


Fig. 3. (1) Total energy, (2) optical transition energy, and (3) oscillator strength of the linear F₃⁻ molecular ion.

BaF₂-Tm crystals to 800°C eliminated the UV absorption with simultaneous elimination of all the other bands. The UV absorption in BaF₂ is overlapped with the absorption of F₃⁻ centers, which does not allow one to separate the complete F₃⁻ band by comparing the spectra of radiation-colored and additively colored crystals (Fig. 3). At the same time, the similarity of the absorption spectra of BaF₂-Yb (Fig. 2c) with the spectra of CaF₂-Yb and SrF₂-Yb (Figs. 2a, 2b) in the range of 4–5.5 eV allows us to conclude that the F₃⁻ band in BaF₂ also lies near 6 eV.

CALCULATIONS

The scheme of molecular orbitals of trihalide single-charged ions in the form as it is today was proposed for the first time by Pimentel [16]. The electronic and vibrational levels of X₃⁻ trihalide ions were calculated in a number of works (see, for example, [1, 2, 17–20]). The *p_z* atomic orbitals of terminal fluorine atoms form the highest occupied σ_g orbital, while the *p_z* orbitals of three fluorine atoms form the lowest unoccupied σ_u orbital. The electronic configuration of the ground state is σ_g², which corresponds to the term ¹Σ_g; the excited-state configuration is σ_g¹σ_u¹, which corresponds to the term ¹Σ_u.

The nonempirical calculation of the linear F₃⁻ ion points to a small contribution of the *s* states of the central fluorine to the highest occupied σ_g orbital. The unoccupied σ_u orbital is formed by three differently directed *p_z* orbitals of fluorine. The ¹Σ_g–¹Σ_u transition is an allowed dipole transition with a high oscillator strength (1–2) and orientation along the axis of the

molecule. The equilibrium distance between neighboring fluorine ions is 1.75 Å, the charges of terminal fluorine ions are –0.45, the charge of the central fluorine is –0.1, and the optical transition energy is 7.16 eV. With decreasing equilibrium distance, the total energy strongly increases, as do as the energy and oscillator strength of the ¹Σ_g–¹Σ_u transition (Fig. 3).

Based on the photodissociation of F₃⁻ centers in CaF₂ into H and V_k centers, a model of the F₃⁻ center as a molecular ion formed by an interstitial fluorine atom and two on-site fluorine atoms with the molecular axis oriented along the main diagonal of the fluorine cube was proposed in [9]. The calculation of a (Ca₆F₉)⁵⁺ cluster appropriate for this model showed that the F–F distance in the F₃⁻ molecular ion decreases due to the formation of the F–F–F bond from the initial 2.37 to 1.73 Å (by 0.64 Å), which is close to the calculated distance in the free F₃⁻ ion. The energy of the ¹A_{1g}–¹A_{2u} transition (corresponding to the ¹Σ_g–¹Σ_u transition in the free ion) is 6.52 eV, which is close to the experimental value of 6.08 eV. The transition oscillator strength is 0.36.

At the same time, measurements of the absorption dichroism of Cl₃⁻ centers in SrCl₂ crystals, which have a fluorite structure, convincingly showed that these centers are oriented along the 100 axis [12]. Because of this, we also calculated the properties of the F₃⁻ center oriented along the fourth-order axis in CaF₂. The interstitial fluorine is located between two neighboring fluorine atoms with the initial distance between them being 1.37 Å. In the process of optimization of the Ca₆F₁₃ cluster geometry, the distance between neighboring fluorine atoms in the F₃⁻ center was increased to 1.88 Å, which corresponded to the shift of

terminal fluorine atoms by 0.52 Å with respect to their positions in the unperturbed lattice. The calculated maximum of the ${}^1\Sigma_g^- \rightarrow {}^1\Sigma_u$ absorption band lies at 5.7 eV and the transition oscillator strength is 0.8. At present, it is impossible to choose between two orientations of F_3^- centers in CaF_2 ; to do this, it is necessary to measure the dichroism.

There exist several possible orientations of molecular F_3^- ions in the LaF_3 lattice. Based on the assumption that the F_3^- center is oriented along the principal axis of the crystal, we chose the La_5F_{20} cluster, in which the interstitial fluorine lies between two on-site fluorine atoms directed along the Z axis. The largest lattice distortion is caused by the interstitial fluorine, which shifts two neighboring fluorine atoms and two next lanthanum ions from the center along the Z axis. The equilibrium distance between fluorine atoms in the F_3^- ion is 1.71 Å. To calculate the optical transition, we reduced the cluster to La_5F_{12} . The wavelength of the optical transition corresponding to ${}^1\Sigma_g^- \rightarrow {}^1\Sigma_u$ in the free ion is 6.36 eV, which is close to the experimental value 6.2 eV. The transition oscillator strength is 1.3.

DISCUSSION

The 6.2-eV band formed under X-ray irradiation at room temperature is identical in LaF_3 crystals doped with different trivalent lanthanides (Yb, Tm, Sm, Ho). Therefore, this band corresponds to the absorption of intrinsic centers, i.e., F_3^- molecular ions. The F_3^- absorption bands in different fluorides are similar in position and half-width. This is explained by a strong molecular bond in the trifluoride ion. The ${}^1\Sigma_g^- \rightarrow {}^1\Sigma_u$ transition energy is to a large extent determined by the distance between fluorine atoms and, in the first approximation, can be described by the results shown in Fig. 3. In lithium fluoride crystals, the considered absorption band of F_3^- is significantly shifted to shorter wavelengths (to 11.3 eV) [8, 9]. For this transition, the distance between fluorine atoms must decrease to 1.42 Å, which requires a considerable energy of 2.8 eV (Fig. 3). It is obvious, that the F_3^- centers in LiF require additional investigations.

Let us consider the radiation-induced formation of defects in LaF_3-SmF_3 crystals. X-ray irradiation of these crystals leads to the appearance of the absorption bands of the Sm^{2+} -anion vacancy centers, which we studied previously in [21], as well as to the formation of centers with the absorption band at 6.2 eV. The Sm^{2+} -anion vacancy center is formed at the expense of an electron and an anion vacancy. Therefore, the remained interstitial fluorine atom can combine with the hole and thus form an F_3^- center, in the same way

as this occurs in alkali- [22] and alkaline-earth [9, 12] halide crystals.

The intensity ratio of the absorption band of the F_3^- center and the absorption bands of Yb^{2+} (and other Re^{2+} ions) is considerably higher in lanthanum fluoride crystal (Fig. 1) than in alkaline-earth fluoride crystals (Fig. 2). This can be caused by the relation between the oscillator strengths of F_3^- and Yb^{2+} in these crystals. The quantum-chemical calculations yield similar oscillator strengths of F_3^- centers in LaF_3 and CaF_2 . The difference in the absorption intensities is likely caused by a lower oscillator strength of the $4f-5d$ transitions of divalent rare-earth ions in LaF_3 with respect to the corresponding transitions in alkaline-earth fluorides. In lanthanum fluoride crystals, the anion vacancy playing the role of a charge compensator lies close to divalent Sm^{2+} . The excited $5d$ states of divalent ions in LaF_3 will also involve the anion vacancy, which, of course, will lead to a decrease in the overlap of the $4f$ and $5d$ states and to a decrease in the oscillator strength of the $4f-5d$ transition.

CONCLUSIONS

The absorption bands of F_3^- hole centers stable at room temperature are separated by comparing the absorption spectra of X-ray irradiated and additively colored fluoride crystals with rare-earth ions. The F_3^- molecular ions in alkaline-earth fluoride crystals (CaF_2 , SrF_2 , BaF_2) and LaF_3 are characterized by a broad absorption band near 6 eV.

The nonempirical calculations of clusters of CaF_2 and LaF_3 lattices reveal the formation of the F_3^- molecular ion with the energy of the optical transition corresponding to the ${}^1\Sigma_g^- \rightarrow {}^1\Sigma_u$ transition in the free ion close to the experimental value.

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