

Spectra of Divalent Samarium in LaF₃ Crystals

E. A. Radzhabov^{a, b} and V. A. Kozlovskiy^a

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

^bIrkutsk State University, Irkutsk, 664003 Russia

e-mail: eradzh@igc.irk.ru

Abstract—The optical spectra and electrical conductivity of LaF₃ crystals containing Sm²⁺ ions are studied. Groups of emission lines at 560–620, 650–690, and 680–770 nm at 7.9 K are produced by transitions from states ⁵D₂, ⁵D₁, and ⁵D₀ to states ⁷F_{*j*} of Sm²⁺ ions. Radiative transitions from state ⁵D₀ are characterized by a decay time of 8.9 ms and temperature quenching in the range of 70–160 K. A linear dependence of the crystals' electrical conductivity on the magnitude of absorption bands of Sm²⁺ ions is observed, due the presence of anionic vacancies that compensate for the low charge of Sm²⁺ ions. The long-wavelength absorption band at 600 nm that is not observed in the excitation spectra is produced by the transition from 4*f*Sm²⁺ to the 1*s* level of anion vacancies. Absorption bands with wavelengths below 520 nm are due to 4*f*–5*d* transitions in the Sm²⁺ ions.

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INTRODUCTION

The spectroscopy of Sm²⁺ ions in crystals of alkaline earth fluorides [1, 2] and alkali halides was studied in detail in the 1960s. These studies were aimed mainly at understanding the scheme of energy levels and the effects of the crystals' fields, along with their fluorescence for laser applications. At low temperatures, Sm²⁺ ions have effective luminescence in the near infrared (~700 nm) range (transitions ⁵D₀–⁷F₁). In the crystals of Ba and Sr fluorides, fluorescence is quenched above 200 K, while luminescence is partially maintained in CaF₂ at room temperature. This allowed CaF₂–Sm²⁺ material to be proposed as a red scintillator for X-radiation [5].

Even though the optical spectra of LaF₃–Sm³⁺ were studied in detail in [3], the spectroscopy of divalent samarium in LaF₃ has yet to be examined. The slight greenish color of some crystals of LaF₃–SmF₃ was associated with the conversion of small fractions of Sm³⁺ ions into Sm²⁺ ions [4]. At the same time, the *f*–*f* spectra of Sm²⁺ in related crystals of LaCl₃, LaBr₃, and other compounds were studied in detail in [6]. Since Sm²⁺ displaces La³⁺ ions, a charge compensator (the nature of which remains unknown) is required [6].

The aim of this work was to study the spectroscopy of optical transitions (absorption and emission) associated with ions of divalent samarium, and to determine the nature of the charge compensator for Sm²⁺ ions in LaF₃.

EXPERIMENTAL

Stockbarger LaF₃ crystals were grown in a three-barreled graphite crucible in vacuum. Several percent of CdF₂ was added to the raw materials to eliminate oxygen impurities. The concentrations of SmF₃ impurities in the mixtures were 0.01, 0.1 and 0.3 mol %. Crystals were grown that contained only Sm³⁺, along with crystals in which a substantial fraction of the trivalent samarium ions was converted into bivalent form (denoted below as LaF₃–Sm³⁺ and LaF₃–Sm²⁺, respectively). The color of the LaF₃–Sm²⁺ crystals varied from light to dark green as the concentration of samarium rose; the crystals of LaF₃–Sm³⁺ were colorless.

The absorption spectra in the region of 190–3000 nm were measured on a PerkinElmer Lambda-950 spectrophotometer; emission spectra and spectra in the vacuum ultraviolet region up to 120 nm were measured on a laboratory setup that included VMR2 (115–300 nm) and MDR2 monochromators. The vacuum ultraviolet source was a Hamamatsu L7292 deuterium discharge lamp; the radiation detector was an FEU142 unit.

Electrical conductivity was measured using alternating current at a frequency of 1 kHz and a voltage of 4 V at room temperature. Contacts were glued onto silver using the conductive adhesive Kontaktol. Alternating voltage was applied to the cell containing the crystal (connected in series with a load resistance of 1 Mohm, the input resistance of our Rigol 1202 oscilloscope). The lowest conductivity measured by the apparatus was ~10^{–9} Ohm^{–1} cm^{–1}, allowing us to accu-

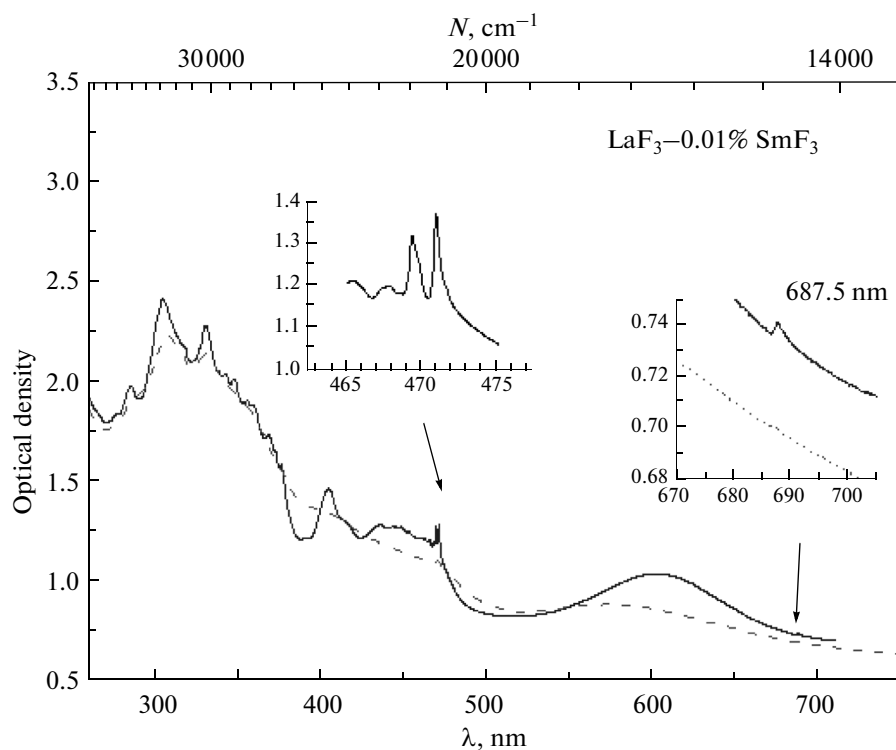


Fig. 1. Adsorption spectra of Sm^{2+} ions in crystals of $\text{LaF}_3\text{-}0.01\% \text{SmF}_3$ at temperatures 7.8 K (solid line) and 295 K (dashed line). The inserts show the fine structure of the absorption lines. In the spectra of LaF_3 containing only Sm^{3+} , no absorption bands were observed in this region.

rately measure the conductivity of LaF_3 at levels of $10^{-6} \text{ Ohm cm}^{-1}$ and higher.

RESULTS AND DISCUSSION

Optical Spectra

A broad structureless band with a maximum around 600 nm and a series of bands at wavelengths of less than 480 nm with weakly expressed structure at low temperatures was observed in the absorption spectrum of $\text{LaF}_3\text{-}\text{Sm}^{2+}$ (Fig. 1). There was a double line around 470 nm and a single line around 690 nm (Fig. 1). All bands grew in proportion to the rising concentration of Sm^{2+} . The same shape, but with an absorption spectrum much lower in optical density, was observed after the $\text{LaF}_3\text{-}\text{Sm}^{3+}$ crystals were irradiated with X-radiation.

A series of narrow lines in the 500–900 nm range of wavelengths was observed in the emission spectra upon excitation with laser light of 405 nm at 7.9 K; the line of maximum intensity lay at 698.5 nm (Fig. 2). The emission spectrum of Sm^{2+} samarium ions can be divided into three groups of lines; the distances between the lines in the group correspond to the known distances between the levels of 7F_j of Sm^{2+} ion in other crystals [6]. The groups of lines can be ascribed with certainty to transitions from levels 5D_2 ,

5D_1 , 5D_0 to the 7F_j levels of Sm^{2+} ions (Fig. 2). The glow from the 5D_0 level is characterized by a decay time of 8.9 ms at 7.5 K.

The position the of $4f$ levels of Sm^{2+} ion can be compared to the system of levels of isoelectronic Eu^{3+} ions, the levels of which are known for many crystals (Fig. 3): ground state 7F_0 , first excited levels ${}^7F_1\text{--}{}^7F_6$, and excited states ${}^5D_0\text{--}{}^5D_4$ in the visible region. The positions of Eu^{3+} levels ${}^5D_0\text{--}{}^5D_3$ are known for crystals of LaCl_3 [6]. The energies of Sm^{2+} levels in crystals of LaF_3 and LaCl_3 are close and $\sim 20\%$ lower than the energy of Eu^{3+} levels in LaCl_3 (Fig. 3).

The temperature dependence of line quenching (5D_2 , 5D_1 , ${}^5D_0 \rightarrow {}^7F_0$) at a constant heating rate of 10 K/min has at least three stages: 20–30, 50–70, and 115–160 K. The stages of quenching are due to the interaction between levels and nonradiative transitions to the ground state.

Bands at 485, 415, and 330 nm are observed in the excitation spectra of Sm^{2+} luminescence at 80 K. The efficiency of excitation falls rapidly at wavelengths greater than 500 nm, and no Sm^{2+} emissions were detected upon excitation with laser light at 532 nm. The excitation and absorption bands in the region below 500 nm are undoubtedly related to $4f\text{--}5d$ transitions in the Sm^{2+} ions.

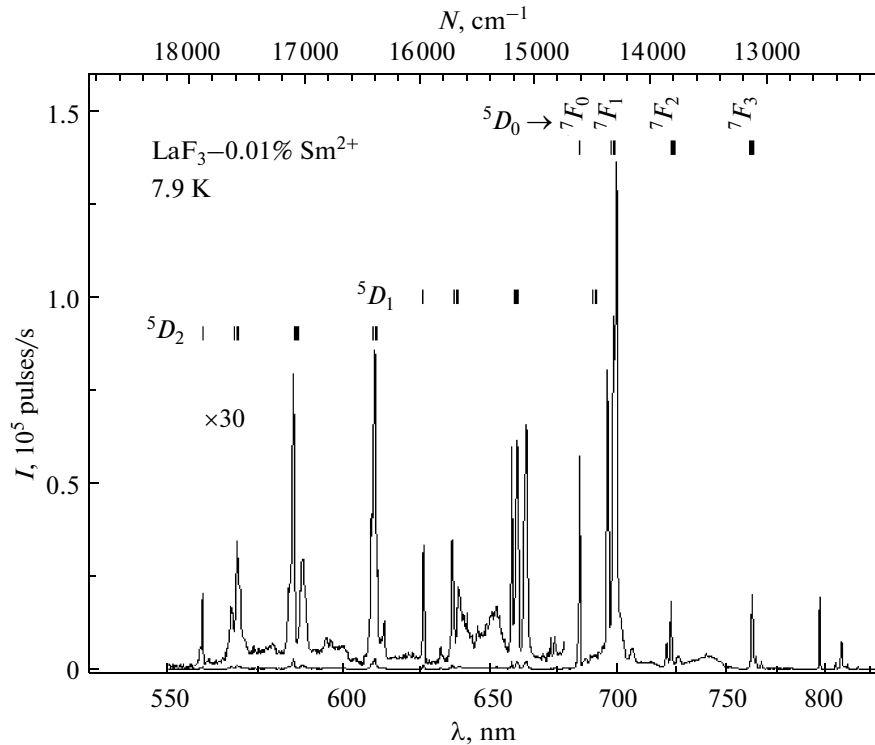


Fig. 2. Luminescence spectra of Sm^{2+} ions in crystals of $\text{LaF}_3\text{-}0.01\text{ SmF}_3$ at 7.9 K. The left part of the spectrum is magnified 30 times. Group transitions ${}^5D_j\text{-}{}^7F_j$ are shown above the lines while maintaining the upper and lower symbols.

Electroconductivity

Since divalent samarium ions have charges lower than that of lanthanum, excessive positive charge is needed to maintain electrical neutrality. It was initially assumed that the charge in the crystals of $\text{LaCl}_3\text{-Sm}^{2+}$ can be compensated for by interstitial positive ions or the transfer of electrons from the nearest halogens to Sm^{2+} [6]. In studying LaF_3 crystals with impurities of divalent alkaline earth metals Ca^{2+} , Sr^{2+} , and Ba^{2+} , it was found that fluorine vacancies can act as charge compensators [8, 9]. Adding divalent impurities increases ionic conductivity [8], produces peaks on the curve of the thermally stimulated depolarization, and results in dielectric losses [8] and the splitting of peaks in the spectra of ${}^{19}\text{F}$ nuclear magnetic resonance [9]. These phenomena are caused by the migration of anion vacancies. We may therefore assume that anion vacancies likely compensate for the charge of divalent samarium in crystals of lanthanum fluoride.

A feature of LaF_3 is the high electrical conductivity of its undoped crystals at room temperature, $\sim 10^{-6}\text{ Ohm}^{-1}\text{ cm}^{-1}$ [10]. The conductivity of lanthanum fluoride is several orders of magnitude higher than that of alkaline earth fluorides. It was established in a number of studies that the conductivity of LaF_3 is due to the migration of fluorine vacancies [8–10]. The conductivity of LaF_3 grew significantly with the introduction of bivalent ions of Ba, Sr, and Ca, due to the

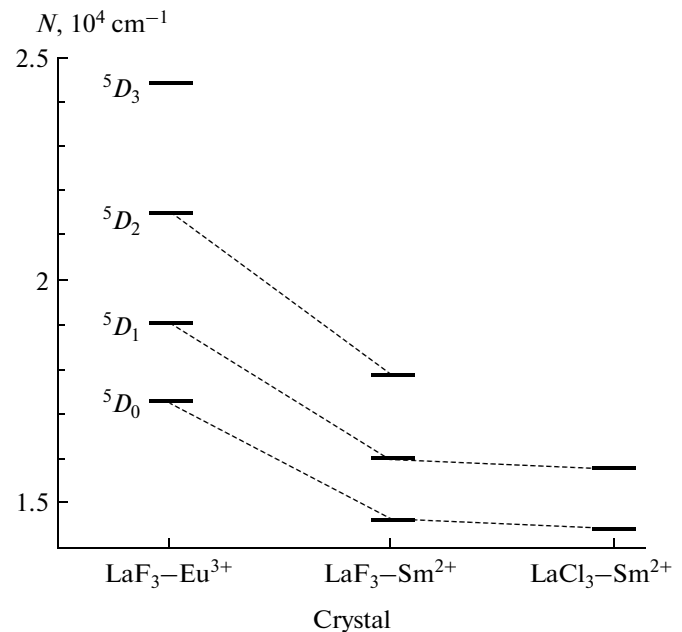


Fig. 3. Diagram of the energy levels of Eu^{3+} ions in LaCl_3 [6] and Sm^{2+} in crystals of LaCl_3 [12], LaF_3 . In Sm^{2+} ions, the energy of the terms is reduced by 18–20%, relative to that of the terms for Eu^{3+} .

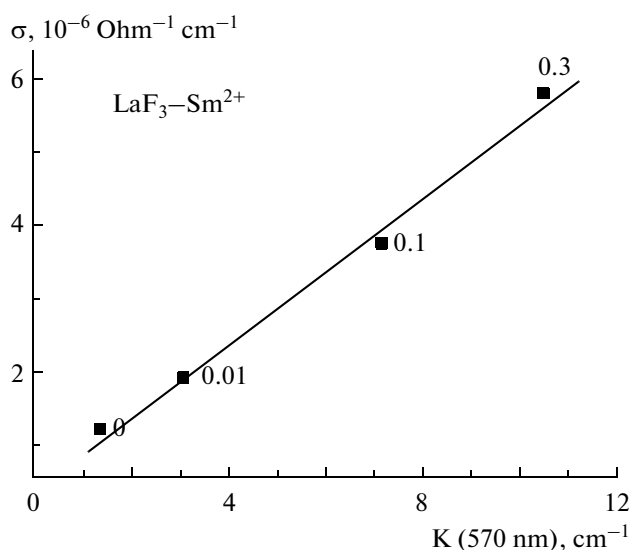


Fig. 4. Dependence of the electrical conductivity of $\text{LaF}_3\text{-Sm}^{2+}$ crystals on the optical density in the absorption band at 570 nm for samples 3 mm thick. Concentrations of SmF_3 impurities added to each batch are given next to the experimental points.

formation of charge-compensated anionic vacancies during crystal growth. As the concentration of Ba^{2+} rose, the isothermal conductivity of LaF_3 grew and reached saturation level at a concentration of $\sim 8\%$ barium [11]. The concentration of anionic vacancies can thus be judged from the level of electric conductivity. Due to the strong contact polarization of LaF_3 crystals [11], their electrical conductivity is measured with alternating current.

The conductivity of our undoped LaF_3 crystals was $(0.4\text{--}1.2) \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$, depending on the feedstock. The conductivity depended weakly on the concentration of Sm^{3+} ions. As the concentration of divalent samarium rose, the conductivity of crystals grew monotonically. A linear dependence was found between the conductivity of the crystals and the optical absorption of Sm^{2+} ions (Fig. 4), strong evidence that fluorine vacancies compensate for the charge of Sm^{2+} . Due to the considerable Coulomb attraction of the opposite charges, we may assume that most of the positively charged fluorine vacancies are located in the immediate vicinity of the negatively charged Sm^{2+} ions.

Calculations

Ab initio calculations of the optical transitions of a small cluster of LaF_3 crystals were performed to estimate the effect the levels of neighboring anionic vacancies have on optical transitions in Sm^{2+} . Our undisturbed cluster consisted of a central fluorine ion and nearby areas of La_4F_8 ions with a charge of $4+$. The wave functions of La and F were taken from the LANL2DZ basis; those of samarium were taken from

the SDD basis, in which the wave functions of f -orbitals were presented more fully. Calculations were performed using the Gaussian03 package of quantum chemical programs [16] and the density functional technique (DFT). Optical transitions were calculated according to TDDFT. In the crystal lattice of LaF_3 , mixed layers of La and F ions were interspersed with two layers of fluorine. A fluorine ion was selected as the origin of the coordinates, since the wave functions of the F-centers were diffuse and several layers of the inner circle were needed for their proper transmission. The coordinates of the LaF_3 lattice ions were taken from [17]. Calculations for the F-centers showed that a local level occupied by one electron emerges in the band gap. Optical transitions of the F-centers are located in the area of 2–3.5 eV (oscillator strength, ~ 0.2), which is quite close to the experimental values of 1.9, 2.1, 2.7 eV in [18]. Replacing the lanthanum ion nearest the vacancy on samarium produces an optical spectrum consisting of bands around 1400 and 1300 nm, and a maximum at 900 nm, along with a group of bands in the range of 480–300 nm. The long-wavelength bands are due to transitions from the $4f^6$ states of samarium at the level of anionic vacancies. The contributions from the $4f^6\text{--}4f^55d^1$ transitions in Sm^{2+} ions are considerable in the short-wavelength bands.

RESULTS AND DISCUSSION

We observed the long-wavelength excitation band of Sm^{2+} luminescence at 485 nm; this corresponds to the estimates in [7], according to which long-wave $4f^6\text{--}4f^55d^1$ transitions in the Sm^{2+} ions in LaF_3 should be observed around 490 nm. The nature of the absorption band around 600 nm, the value of which is proportional to those of other samarium bands, remains obscure.

As is well known, anion vacancies create levels in the band gap of a crystal in which electrons can move or capture. Such transitions from the impurity state to the state of a neighboring anion vacancy were observed earlier for oxygen-vacancy centers in the crystals of alkali and alkaline earth halides [14, 15]. Since the level of F-centers (anion vacancies that capture electrons) and the basic level of Sm^{2+} lie deep in the band gap, the answer to the question “Which configuration is more important: $\text{Sm}^{3+}\text{-F-center}$ or $\text{Sm}^{2+}\text{-vacancy}$ ” is important. However, the observed emission lines of Sm^{2+} and increased conductivity undoubtedly prove that the ground state is the $\text{Sm}^{2+}\text{-vacancy}$ configuration. The level of anionic vacancies is then the one closest in terms of excitation energy.

Let us consider one possible scheme for the orbitals of Sm^{2+} center–fluorine vacancies. In the ground state of the center, all six of the outer electrons are located on the $4f$ atomic orbitals of the Sm^{2+} ion, since the $4f$ levels of Sm^{2+} are lower in energy in the band gap than the level of the anion vacancy. The first absorp-

tion band is due to electron transfer at the level of vacancies, and the subsequent bands are due to transfers to the $5d$ state of the Sm²⁺ ion. The absence of Sm²⁺ luminescence lines when excited to the long-wavelength absorption band is obviously due to the considerable relaxation of the first excited state. Preliminary calculations for quantum clusters of LaF₃–Sm²⁺ confirm the qualitative scheme for the molecular orbitals of Sm²⁺ center–anionic vacancies.

The ground states lying deepest in the band gap of the LaF₃ crystal are those of Sm²⁺ (2.5 eV from the conduction band), Eu²⁺ (3.7 eV), and Yb²⁺ (3.3 eV) divalent ions [7], so the formation of divalent ion–anionic vacancy centers with a similar scheme of levels should also be expected for Eu²⁺ and Yb²⁺ ions.

CONCLUSIONS

—The low-temperature luminescence line spectra of LaF₃–Sm²⁺ crystals are caused by groups of transitions from levels 5^5D_2 , 5^5D_1 , 5^5D_0 to the levels of 7^7F_j in Sm²⁺ ions.

—Anionic vacancies in the immediate vicinity of impurity ions compensate for the charge of Sm²⁺ ions.

—The allowed optical transitions of electrons from the $4f$ shells of samarium ions to the $1s$ level of vacancies produce long-wavelength absorption bands at 600 nm, while transitions to the $5d$ levels of samarium shells produce absorption bands with wavelengths less than 500 nm.

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