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Sm$^{2+}$ spectra in lanthanum fluoride

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Abstract

Optical spectra and conductivity of LaF$_3$, containing Sm$^{2+}$, were studied. Three groups of emission lines near 560-620 nm, 650-690 nm and 680-770 nm at 7.9 K were attributed to the transitions from $^5$D$_2$, $^5$D$_1$, $^5$D$_0$ to $^7$F$_j$ levels of Sm$^{2+}$. Emission of $^5$D$_0$ has decay time 8.9 ms and quenching at temperatures 70-160 K. The linear dependence between conductivity and absorption coefficient of Sm$^{2+}$ bands was observed. The dependence associated with presence of anion vacancy, which compensates insufficient charge of Sm$^{2+}$ ions. Longest wavelength absorption band at 600 nm was absent in the excitation spectrum. The band was attributed to transitions from 4f$^6$ of Sm$^{2+}$ to vacancy level. Lesser wavelength absorption bands belong to 4f-5d transitions of Sm$^{2+}$ ions.

1. Introduction

In the past much research has been done on the spectroscopy of Sm$^{2+}$ in alkaline-earth fluorides (Wood and Kaizer 1962, A.A. Kaplyanskii and Feofilov 1962) and alkali-halide crystals. The investigations were mainly focused on understanding the energy level scheme and crystal field splitting as well as fluorescence for lasing application.

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At low temperatures divalent samarium ions show intensive luminescence in near infrared (~700 nm) due to $^5D_0-^7F_1$ transitions. In Ba- and Sr- fluorides Sm$^{2+}$ emission are quenched above 200 K while in CaF$_2$ the emission partially remains even at room temperature, which allows considering this material as red scintillator for x-ray detection (Dixie et al. 2014).

Apart to detailed studies of LaF$_3$-Sm$^{3+}$ (Carnall et al. 1989, Dieke 1968) the spectroscopy of Sm$^{2+}$ in this host remains uninvestigated. Weak green colour of some LaF$_3$-SmF$_3$ crystals was attributed partial conversion of initial Sm$^{3+}$ to divalent state during growth of crystal (Weller et al. 1964), but no spectroscopic investigations were performed. At the same time the emission spectra (not absorption spectra) of Sm$^{2+}$ in relative materials LaCl$_3$, LaBr$_3$ were carefully investigated (Dieke 1968). In the trihalide hosts the Sm$^{3+}$ substitute the La$^{3+}$ ion and needs to be accompanied by additional positive charged compensator, the nature of which is unknown (Dieke 1968).

The aim of this paper is to investigation of absorption and emission spectra of divalent samarium in lanthanum fluoride crystal and clarification the nature of charge compensator as well as its influence on optical transitions.

2. Experimental

The crystals were grown by Stockbarger method in graphite crucible in vacuum. A few percent of CdF$_2$ was added into raw materials for purification from oxygen impurity during growth. Impurity SmF$_3$ was added into LaF$_3$ powder in concentration of 0.01, 0.1 and 0.3 mol. %. Crucible allows to growth three crystal cylinders with 8 mm in diameter and 60 mm long at once. Three groups of the crystals containing only Sm$^{3+}$, mostly Sm$^{2+}$ and both ions were grown. The crystals containing Sm$^{2+}$ were green. Samples Ø8 x 2 mm were sawed and polished.

Absorption spectra in the range 190-3000 nm were taken with spectrophotometer Perkin-Elmer Lambda-950, emission spectra and spectra in vacuum ultraviolet region were measured using grating monochromator MDR2 (LOMO) and vacuum monochromator VMR2 (LOMO). Deuterium lamp L7292 (Hamamatsu) was used as source of vacuum ultraviolet. X-irradiation was performed using Pd-tube with 40 kV 20 mA.

Electrical conductivity of LaF$_3$ samples was measured at room temperature with 1 kHz AC current frequency. Silver paint (“Kontaktol”) was used as electrodes. AC voltage was applied to successively connected sample and $10^6$ ohm resistor, which was the input resistor of oscilloscope Rigol 1202. Lowest measurable conductivity of this circuit
was about $10^{-9}$ ohm$^{-1}$ cm$^{-1}$, this was enough to measurement of LaF$_3$ samples conductivity (typically above $10^{-6}$ ohm$^{-1}$ cm$^{-1}$).

To evaluation the influence of nearest anion vacancy on transitions of divalent samarium the unempirical calculations of small cluster of LaF$_3$ lattice were performed. Positions of ions of LaF$_3$ lattice were taken from paper (Schlyer 1953). Cluster contains central fluorine ion and nearest lanthanum and fluorine shells – La$_4$F$_7$ with total charge +4. Wavefunction of La taken from basis LANL2DZ, wavefunction of Sm taken from basis SDD, in which function of f-core are more complete. Calculations were made using “Gaussian 03” (Frisch et al. 2007) by methods of density functional (DFT) using B3LYP hybrid exchange energy functional. Optical transitions were calculated by method of TDDFT.

3. Results

3.1. Optical spectra

Broad unstructured absorption band at near 570 nm and several bands at shorter wavelength of LaF$_3$–Sm$^{2+}$ crystals were observed at room temperature (Fig.1). With decreasing temperature the structure of absorption at 500-300 nm region are appeared and maximum of long-wavelength band are shifted to 600 nm (see Fig.1). Double lines near 470 nm well coincides with estimation of edge of 4f$^5$-4f$^5$5d transitions of divalent samarium in LaF$_3$ (Dorenbos 2013). All absorption bands at 300-800 nm grew parallel with the increasing Sm$^{2+}$ concentration. Similar but much weaker absorption spectrum was appeared in LaF$_3$-Sm$^{3+}$ samples by x-irradiation at room temperature.

![Emission spectra of LaF$_3$-0.01 % Sm$^{2+}$ crystal at temperature 7.9 K. Left part of spectrum are increased by 30 times. Transitions from $^5$D$_j$ to $^1$F$_j$ are shown at the top of graph](image)

Emission of Sm$^{2+}$ ions appeared at temperatures lower than 200 K. Under excitation with a Xe discharge lamp at 300-500 nm region we observed the strong emission lines (Fig.2), which could be attributes to Sm$^{2+}$ emission. All observed lines could be divided into three groups. The distances between lines in each group are equal to distances between $^7$F$_j$ levels of Sm$^{2+}$ in LaCl$_3$ (Carnall et al. 1989, Dieke 1968). Therefore these three groups of lines could be definitely assigned to transitions from $^5$D$_2$, $^5$D$_1$, $^5$D$_0$ to $^1$F$_j$ of Sm$^{2+}$ (see Fig.2). Emission of $^5$D$_0$ has decay time 8.9 ms at 7.5 K and quenching at temperatures 70-160 K.
The scheme of 4f⁶ levels of Sm²⁺ is similar to level scheme of isoelectronic Eu³⁺, which levels are known in many hosts. The ground state is ⁷F₀, lowest excited states are ⁷F₁ - ⁷F₆. Next excited states ⁵D₀-⁵D₄ are in the visible region. Positions of Sm²⁺ ⁵Dₘ in LaF₃ are close to known positions in LaCl₃, BaFCl and near 20% less than Eu³⁺ positions in LaCl₃ (Fig. 3).

![Scheme of ⁵Dₘ energy levels of isoelectronic Eu³⁺ in LaCl₃ (Kumar et al. 1977), Sm²⁺ in SrClF (Grenet et al. 1980), Sm²⁺ in LaCl₃ (Dieke et al. 1962) and Sm²⁺ in LaF₃. In Sm²⁺ ion the energies of levels reduced by near 20% against that in Eu³⁺.](image)

Excitation spectrum at 77 K contains three bands at 485, 415 and 330 nm. No emission of Sm²⁺ was observed using 532 nm laser excitation. Excitation bands generally coincide with that of absorption with exception of band near 600 nm. Excitation and absorption bands at wavelength less than 500 nm undoubtedly belong to 4f⁶-4f⁷5d transitions in Sm²⁺ ions.

### 3.2. Electrical conductivity

Divalent samarium ion has charge less than the charge of lanthanum, therefore for the electrical neutrality of the crystal it is needed the additional positive charge for each divalent ion. Earlier was assumed that charge compensation in LaCl₃-Sm²⁺ may take place by interstitial positive ions near each Sm²⁺ ion or by an electron being transferred from a neighbouring Cl⁻ ion to a Sm²⁺ ion with a possible rearrangement of the equilibrium positions in this vicinity (Dieke 1968).

Later the investigations of LaF₃ doped by divalent alkaline-earth ions Ca²⁺, Sr²⁺, Ba²⁺ were proved that the charge compensators are fluorine vacancies (Roos et al. 1985, Privalov et al. 1994). Introduction of divalent ions into LaF₃ led to increasing of ionic conductivity (Roos et al. 1985), appearing the peaks of thermostimulated depolarisation (Roos et al. 1985) and changing the peaks of nuclear magnetic resonance of ¹⁹F (Privalov et al. 1994). With increasing the Ba²⁺ concentration up to 8 % the conductivity monotonically increased (Roos et al. 1984). All these phenomena caused by migration of fluorine vacancies. Based on these results one could assume that charge compensator of divalent samarium is fluorine vacancy, concentration of which can be evaluated by conductivity measurements. The lanthanum fluoride exhibits an unusually large polarization effect (Sher et al. 1966), therefore the electrical conductivity are measured with alternating current.

Undoped lanthanum fluoride crystals show relatively high electrical conductivity near 10⁻⁶ ohm⁻¹cm⁻¹ (Sher et al. 1966). The conductivity of our undoped LaF₃ samples was (0.4-1.2)·10⁻⁶ ohm⁻¹cm⁻¹ depending from purity of raw material. Conductivity was not increased with increasing of Sm³⁺ doping. With increasing of Sm²⁺ concentration (absorption bands) the conductivity of the samples was monotonically increased. Both absorption and conductivity followed the logarithmic-type growth with increasing samarium doping. Finally, we obtained linear increase of LaF₃ conductivity with increasing Sm²⁺ absorption (Fig. 4).
The linear dependence on Fig.4 are plotted using absorption at 570 nm, straight lines can be obtained for any absorptions within 300-700 nm range, also. These results are proved that anion vacancy accompanied each divalent samarium ion. Based on ionic thermodipolarisation (Roos et al. 1985) and dielectric relaxation investigations of Me$^{2+}$ doped LaF$_3$ (Roos et al. 1985, Roos et al. 1984) one could infer that anion vacancy should be in close vicinity of divalent samarium.

3.3. Calculations

To verify the applicability of La$_4$F$_8$ cluster we calculate sequentially the optical spectra of unperturbed cluster, F-center and Sm$^{2+}$-vacancy center.

One-electron molecular orbital diagram of initial La$_4$F$_8$ cluster shows band gap around 6 eV between filled fluorine levels and unoccupied lanthanum levels, while the optical transitions (by TDDFT method) begin above 5.5 eV. The experimental value of LaF$_3$ band gap is 10.5 eV (Krupa et al. 1997).

For calculation of F center we remove fluorine F$^0$ from center of cluster. Molecular orbital diagram shows that in the band gap appears a level occupied by an electron. Sufficient part of electron density of this level is around vacancy position. Three first optical transitions are 2.1, 2.5 and 3.1 eV, which are somewhat higher than the experimental position of F-center bands at 1.9, 2.1, 2.7 eV (Radzhabov et al. 1995).

Changing nearest lanthanum by samarium leads to optical spectrum consisting of groups of bands 0.9-1.2 eV (1400-900 nm) and 2.6-4.1 eV (480-300 nm). Long wavelength bands belong to transitions from 4f$^6$ states of samarium to the 1s-level of vacancy. In shorter wavelength bands the addition of 4f$^6$ - 4f$^5$5d$^1$ transitions become sufficient. The calculated Sm-to-vacancy transitions are at longer wavelength than experimental band at 600 nm, but the next group of calculated transitions are close to experimental Sm$^{2+}$ f-d transitions.

While the calculations were performed without geometry optimization, but the main conclusions are reliable: the long-wavelength bands are due to Sm-to-vacancy transitions and short-wavelength bands are due to Sm$^{2+}$ f-d transitions.

4. Discussion

First excitation band of Sm$^{2+}$ in LaF$_3$ are observed at 485 nm (see Fig.3), this is correlate with estimation (Dorenbos 2013) of long wavelength 4f$^6$ - 4f$^5$5d$^1$ transitions at 490 nm. But the origin of absorption band at 600 nm, which intensity is proportional to that of other Sm$^{2+}$ bands, is still unclear.
It is known that anion vacancy create a level in forbidden band of crystal, on which the electron could transfers or traps. Such transitions from impurity levels to levels of anion vacancy were observed in oxygen-vacancy centres in alkali halides and alkaline-earth fluorides earlier (Radzhabov et al. 1986, Mysovsky et al. 2011). Similar types of transitions are possible in the case of Sm$^{2+}$-vacancy centre also.

Let’s consider possible scheme of molecular orbitals of Sm$^{2+}$- fluorine vacancy centre. In ground state all 6 outer electrons occupied the 4f atomic orbitals of samarium. Long-wavelength absorption band belongs to allowed transitions to vacancy level, and the shorter -wavelength bands are due to transitions to 5d Sm$^{2+}$ ion. Our preliminary calculations of quantum cluster of LaF$_3$-Sm$^{2+}$ are in agreement with this scheme of molecular orbitals.

Positions of all rare-earth divalent and trivalent ions within zone bands of LaF$_3$ were evaluated recently (Dorenbos 2013). Most deeply in the forbidden band of the crystal LaF$_3$ are the ground state of Sm$^{2+}$ (2.5 eV from bottom of conductivity band), Eu$^{2+}$ (3.7 eV) and Yb$^{2+}$ (3.3 eV) (Dorenbos 2013). Therefore the creation of Me$^{2+}$-vacancy centres in lanthanum fluoride with similar types of electron transitions could be assumed for Eu$^{2+}$ and Yb$^{2+}$ ions also.

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