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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 $^5D_2$, $^5D_1$, $^5D_0$ to ^7F_j levels of Sm^{2+}. Emission of $^5D_0$ 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 absented 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.

Keywords: rare-earth ions, divalent samarium, LaF3, absorption, emission, unempirical calculations, conductivity

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^{2+} 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.

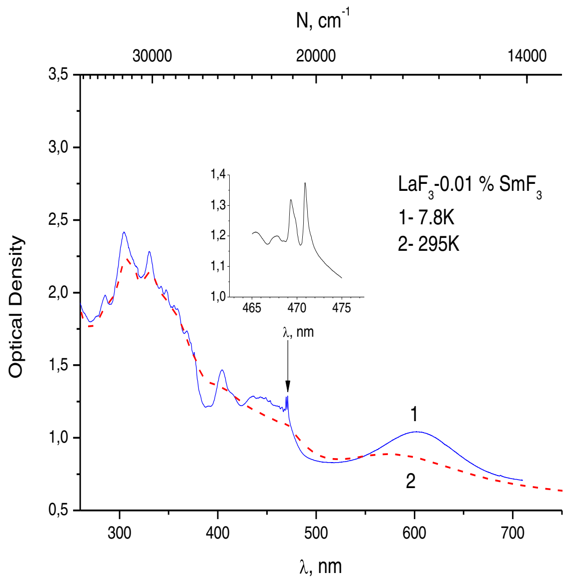

Fig.1. Absorption spectra of LaF_3- 0.01 % Sm^{2+} (thickness 2.5mm) at temperature 7 K (curve 1) and 295 K (curve 2). The inset in the graph displays the fine structure of spectrum. No absorption bands were observed in LaF_3-0.01% Sm^{3+} samples.

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 (Schlyter 1953). Cluster contains central fluorine ion and nearest lanthanum and fluorine shells – La_4F_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 $4f^6$-$4f^55d$ 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.

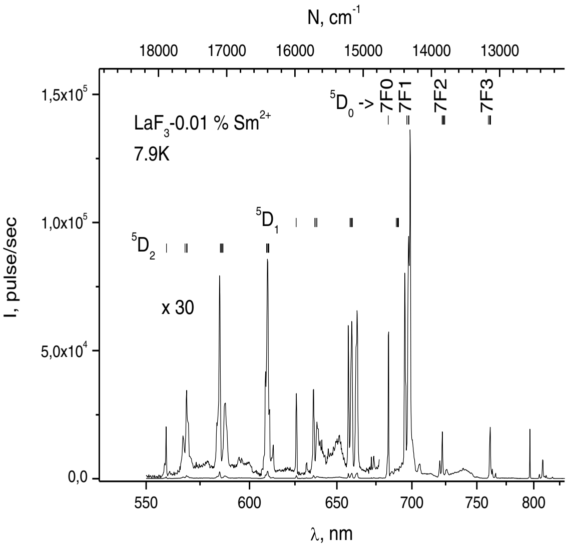

Fig.2. Emission spectra of LaF_3-0.01 % Sm^{2+} crystal at temperature 7.9 K. Left part of spectrum are increased by 30 times. Transitions from ^5D_j to ^7F_j are shown at the top of graph

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 ^7F_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 $^5D_2$, $^5D_1$, $^5D_0$ to ^7F_j of Sm^{2+} (see Fig.2). Emission of $^5D_0$ has decay time 8.9 ms at 7.5 K and quenching at temperatures 70-160 K.

The scheme of $4f^6$ levels of Sm^{2+} is similar to level scheme of isoelectronic Eu^{3+}, which levels are known in many hosts. The ground state is $^7F_0$, lowest excited states are $^7F_1$ - $^7F_6$. Next excited states $^5D_0$-$^5D_4$ are in the visible region. Positions of Sm^{2+} ^5D_j in LaF_3 are close to known positions in $LaCl_3$, BaFCl and near 20% less than Eu^{3+} positions in $LaCl_3$ (Fig.3).

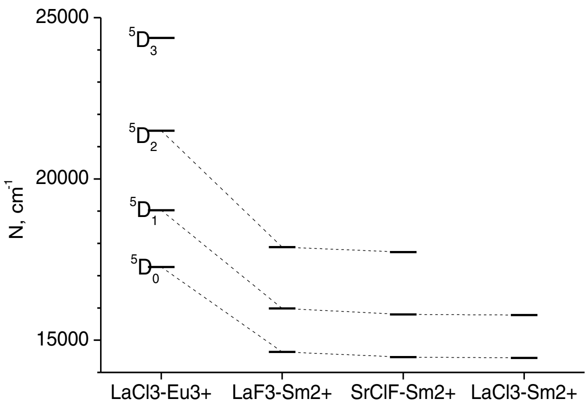

Fig.3. Scheme of ^5D_j energy levels of isoelectronic Eu^{3+} in $LaCl_3$ (Kumar et al. 1977), Sm^{2+} in SrClF (Grenet et al.1980), Sm^{2+} in $LaCl_3$ (Dieke et al.1962) and Sm^{2+} in LaF_3. In Sm^{2+} ion the energies of levels reduced by near 20% against that in Eu^{3+}.

Excitation spectrum at 77 K contains three bands at 485, 415 and 330 nm. No emission of Sm^{2+} 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 $4f^6$-$4f^55d$ transitions in Sm^{2+} 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 $LaCl_3$-Sm^{2+} may take place by interstitial positive ions near each Sm^{2+} ion or by an electron being transferred from a neighbouring Cl^- ion to a Sm^{2+} ion with a possible rearrangement of the equilibrium positions in this vicinity (Dieke 1968) .

Later the investigations of LaF_3 doped by divalent alkaline-earth ions Ca^{2+}, Sr^{2+}, Ba^{2+} were proved that the charge compensators are fluorine vacancies (Roos et al. 1985, Privalov et al. 1994). Introduction of divalent ions into LaF_3 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 ^{19}F (Privalov et al. 1994). With increasing the Ba^{2+} 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} $ohm^{-1}cm^{-1}$ (Sher et al. 1966). The conductivity of our undoped LaF_3 samples was $(0.4\text{-}1.2)\cdot 10^{-6}$ $ohm^{-1}cm^{-1}$ depending from purity of raw material. Conductivity was not increased with increasing of Sm^{3+} doping. With increasing of Sm^{2+} 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 LaF_3 conductivity with increasing Sm^{2+} 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 thermodepolarisation (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.

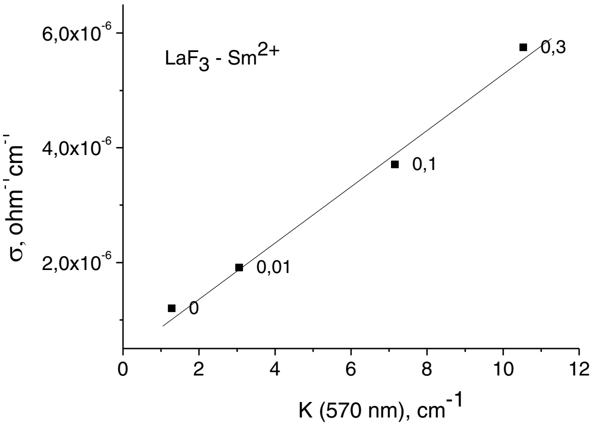

Fig.4. Conductivity of LaF_3-Sm^{2+}samples against of absorption coefficient of absorption band at 570 nm at room temperature. Concentrations of doped SmF_3 are shown near experimental points.

3.3. Calculations

To verify the applicability of La_4F_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_4F_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+} и Yb^{2+} ions also.

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