

## Optical transitions in pairs of trivalent ion–interstitial fluorine in alkaline-earth fluorides

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### 1 Introduction

Trivalent ions incorporated into lattice of alkaline-earth fluorides are accompanied with charge-compensating interstitial fluorines. Nearest-neighbour position (NN) of interstitial fluorine is favourable in CaF<sub>2</sub>, giving tetragonal symmetry to centre. The next nearest-neighbour position (NNN) of interstitial fluorine is favourable in BaF<sub>2</sub> lattice, giving trigonal symmetry to centre. There are only few paper on optical spectra of alkaline-earth fluorides doped by La or Y in vacuum ultraviolet region. The La or Y ions not introduced new absorption bands, but only slightly shifts vacuum ultraviolet absorption edge to low energy side of CaF<sub>2</sub>–Y [1], BaF<sub>2</sub>–La [2] crystals.

If trivalent ion has no own optical bands a new type of transitions can be observed – the transitions between impurity metal and interstitial fluorine. Such absorption in vacuum ultraviolet region and luminescence in ultraviolet region we identified in CaF<sub>2</sub>, SrF<sub>2</sub> and BaF<sub>2</sub> crystals doped with LaF<sub>3</sub> or YF<sub>3</sub> impurity.

Density functional theory (DFT) has by now become a reliable standard tool for calculating ground-state properties such as energies, geometries, and vibrational frequencies. The time-dependent extension of DFT (TDDFT) provides an attractive framework for calculating excitation energies, transition moments. The Becke, Lee, Yang and Parr exchange-correlation functional B3LYP is widely used in quantum chemical DFT calculations. However sometimes the obtained states of defects in crystal lattice calculations become too delocalised [3] and using the exchange-correlation functional with increasing part of the amount of the exact exchange in the density functional (e.g. BHHLYP) leads to better results.

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## 2 Experimental

LaF<sub>3</sub> or YF<sub>3</sub> impurity was added into raw materials in amount from 0.01 to few molar%. The crystals were grown in vacuum in graphite crucible. All crystals were grown in the Institute of Geochemistry, Russian Academy of Science, Irkutsk, Russia.

The excitation spectra in 4–12 eV region were measured with grating vacuum monochromator VMR2. Emission spectra were measured with two grating monochromators having flat sensitivity curves at 4–7 eV region and at 2.5–4 eV region. For some measurements the emission was excited by xenon and krypton resonance discharge lamps, having most intensive lines at 10.0 eV and 8.4 eV respectively.

Another emission and excitation measurements were carried out using a low temperature luminescence set-up for VUV spectral region connected to the undulator beam-line BW3 of HASYLAB at DESY [5]. Photons generated by two interchangeable undulators are tunable in the energy range of 30–2000 eV by means of Zeiss SX700 monochromator. Luminescence was detected with a 0.4 m monochromator in Seya–Namioka. The optical slit width of the secondary monochromator was typically 2 nm. Excitation and emission spectra were measured in time integrated mode.

Unempirical Hartree–Fock (HF) and density functional (DFT) calculations of absorption and triplet-singlet luminescence of crystal cluster, containing the impurity ion-interstitial fluorine pair were performed using PCGamess code [6]. Crystal cluster was surrounded by few tens of effective core potentials of cations and then up to 10 thousands of point charges [2]. LANL2DZ (Los Alamos National Laboratory effective core potential with a double-zeta basis set for valence electrons) basis set was used in both types of calculations. Density functional calculations were performed with BHHLYP exchange-correlation functional, as more reliable for “crystal” calculations than B3LYP. For calculations of NN centre (C<sub>4v</sub> symmetry) we use Me<sub>6</sub>F<sub>17</sub> quantum cluster. For calculation of NNN centre (C<sub>4v</sub> symmetry) a larger cluster Me<sub>4</sub>F<sub>27</sub> (a cube 3 × 3 × 3 of smallest fluorine cubes with 4 Me ions inside) was used. All ions of quantum cluster were free during geometry optimisation, while core potentials and point charges remain frozen. Both clusters show very minimal lattice distortions without impurity ions.

## 3 Results

### 3.1 Absorption, emission, excitation and decay

Shift of fundamental absorption edge to low energies was observed in vacuum ultraviolet region of CaF<sub>2</sub> crystals doped with YF<sub>3</sub> or LaF<sub>3</sub> impurity (Fig. 1). The more impurity concentration the larger shift was

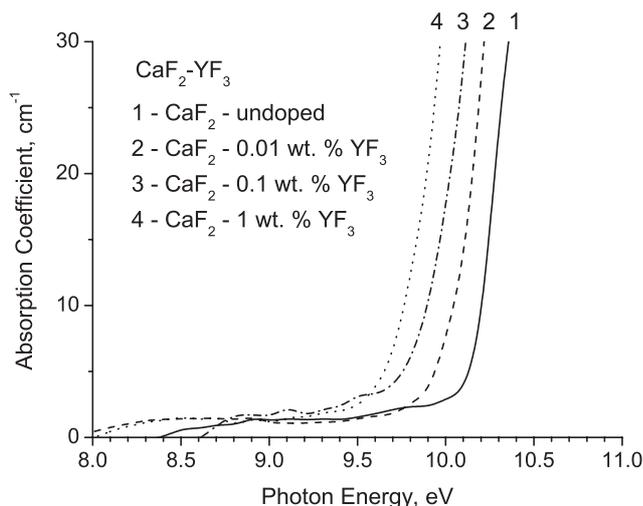
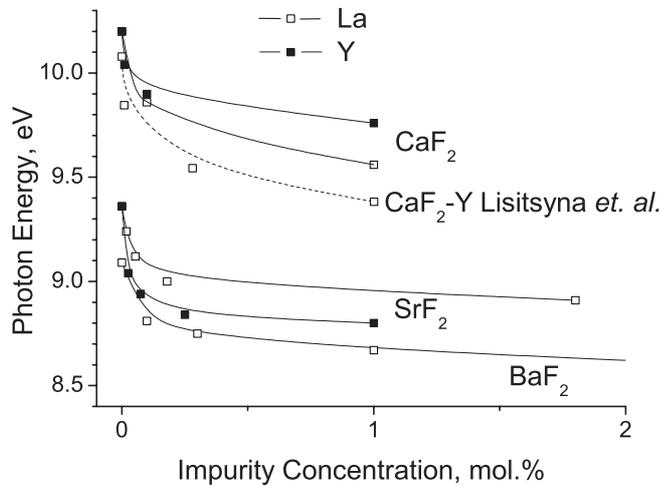


Fig. 1 Absorption spectra of CaF<sub>2</sub> crystals doped by YF<sub>3</sub> impurity at room temperature.

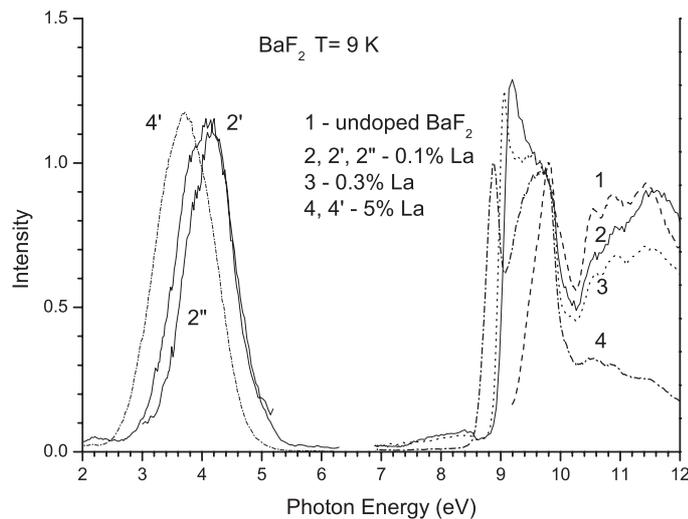


**Fig. 2** Shift of vacuum ultraviolet absorption edge of alkaline-earth fluorite crystals doped with LaF<sub>3</sub> or YF<sub>3</sub> impurities. Absorption energies of each curve were taken at 10 cm<sup>-1</sup> of absorption coefficient. Dashed curve shows the results obtained in Ref. [1]. It seems that the discrepancy is caused by different choice of edge energy.

observed. Evidently the impurity absorption bands are very closed to exciton absorption bands so one could not observe the impurity band maximums. The shift becomes near 0.65 eV for 1% of LaF<sub>3</sub> and near 0.4 eV for 1% of YF<sub>3</sub> impurity.

Shift of absorption edge was observed also for SrF<sub>2</sub> and BaF<sub>2</sub> crystals containing Y or La impurities (Fig. 2). Absorption curves can be described by appearing new absorption band, which is very close to exciton absorption band. However the parameters of new bands can be obtained from absorption spectra with large uncertainty. Therefore we found the maximums of bands from the excitation spectra (see later).

New luminescence bands are observed in all cases under excitation into impurity region. The luminescence band at 4.05 eV of BaF<sub>2</sub>-La crystals are observed under excitation in impurity region. The narrower exciton emission band at 4.15 eV are excited at band-to-band region (see Fig. 3). The La related



**Fig. 3** Emission and excitation spectra of BaF<sub>2</sub> and BaF<sub>2</sub>-La crystals at 9 K. Excitation spectra measured for 4.0 eV. Emission spectra measured with excitation 8.9 eV (4'), 9.2 eV (2') and 19.2 eV (2'').

emission slightly shifts to lower energies to 3.8 eV in crystals containing more than 1% of  $\text{LaF}_3$  impurity (Fig. 3) (see also [12]). The maximum of excitation bands at low La concentration was observed at 9.1–9.2 eV (see Fig. 3). Small dip on excitation curve appeared at 9.2 eV in crystal  $\text{BaF}_2$ –0.3 mol%  $\text{LaF}_3$ . At higher concentration the dip at 9.2 eV becomes more evident (see Fig. 3) corresponding to maximum of La impurity absorption band.

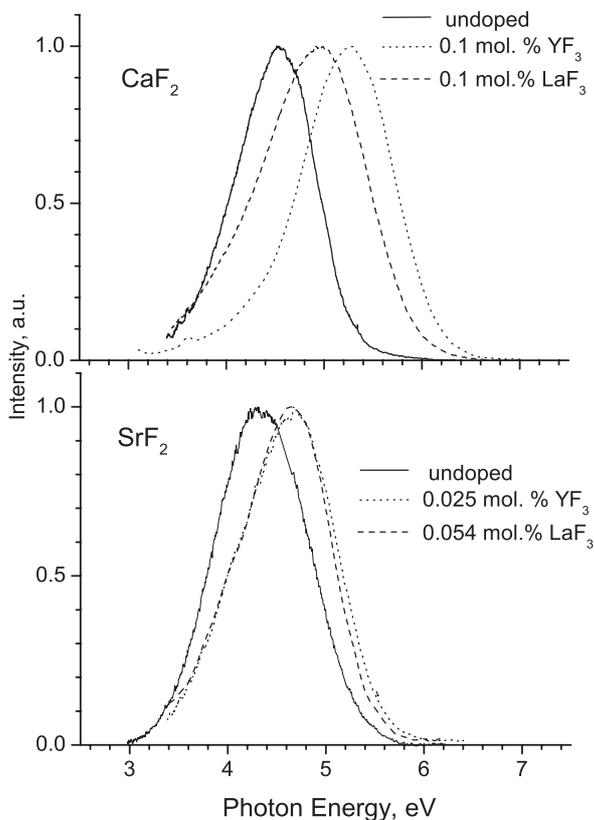
The band at 5.25 eV was observed in  $\text{CaF}_2$ –Y crystals at low temperatures under excitation in 9–10 eV region (Fig. 4). Maximum of excitation band shifts to lower energies with increasing of yttrium concentration. The band decreased above 150 K and partially transformed into another band having maximum at 4.6 eV, showing similar excitation spectrum at impurity region 9–10 eV. The 4.6 eV band only observed in  $\text{CaF}_2$ –Y crystal above 200 K. This 4.6 eV band is very close to band of exciton emission.

The bands at 5.03 eV was observed in  $\text{CaF}_2$ –La crystals at low temperatures having excitation band within La impurity region 9.2–9.8 eV (see Fig. 4). At room temperature the band at 5.10 eV remains while another two bands at 4.5 eV and weak band at 3.5 eV appear.

The bands at 5.25 eV and 5.03 eV well separated from exciton emission band at 4.55 eV (see Fig. 4). The Stokes shift for these emissions is less then for exciton emission. Both bands were not observed under excitation into band-to-band region or under X-ray excitation. Both initial emission bands can transforms over potential barrier to another emission 4.5 eV, which are very close to exciton emission band.

New emission bands at 4.8 eV were observed in La- or Y-doped  $\text{SrF}_2$  crystals under excitation into impurity region (see Fig. 4).

Decay of Y-related emission in  $\text{BaF}_2$  is exponential with tau 1.7  $\mu\text{s}$  at room temperature. The fastest decay time becomes 2.1  $\mu\text{s}$  and another slower decay components appeared at lower temperatures. At least three exponential decay components with tau 2.1, 10 and 80  $\mu\text{s}$  needs to describe the observed de-



**Fig. 4** Emission spectra of  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals doped by  $\text{LaF}_3$  and  $\text{YF}_3$  impurities at 80 K. Emission was excited by resonance lines 9.6 eV ( $\text{SrF}_2$ ) and 10.0 eV ( $\text{CaF}_2$ ) of discharge lamps.

**Table 1** Experimental and calculated energies in eV of excitation and luminescence bands in Y or La doped alkaline-earth fluoride crystals. Fastest decay components are shown also. Experimental data were taken at 80 K. All experimental data were measured for concentration of impurities near 0.1 wt%.

crystal	impurity	$E_{\text{exc exp.}}$	$E_{\text{exc calc.}}$ (TDDFT)	$E_{\text{em exp.}}$	$E_{\text{em calc.}}$ (HF)	$\tau_{\text{exp}}$ $\mu\text{s}$
CaF <sub>2</sub>	La	10.1	9.34	5.03	4.79	3.0
	Y	9.8	9.4	5.24	4.56	3.5
SrF <sub>2</sub>	La	9.3	9.0	4.82	4.24	4.1
	Y	9.3	9.1	4.87	4.02	4.6
BaF <sub>2</sub>	La	9.1	9.1	4.05	4.26	2.7
	Y	9.0	9.1	4.00	3.94	2.1

cay curve at 170 K and 80 K. Similar decay behaviours were observed in other cases. Slower components appeared below 50 K in CaF<sub>2</sub>–Y, and below 150 K in SrF<sub>2</sub>–Y. Fastest decay components are collected in the Table 1. Observed decay components can be considered as originated from three sublevels of excited triplet state, splitted by spin-orbital coupling.

### 3.2 Calculations

Geometry optimisation shows the significant distortion in the ground state. Me<sup>3+</sup> ion and interstitial F<sub>i</sub><sup>-</sup> attract to each other, the distance between La–F reduced to 2.42 Å (CaF<sub>2</sub>) and 2.52 Å (BaF<sub>2</sub>), while the calculated distance in (LaF)<sup>2+</sup> molecule is 2.055 Å. The calculated energies of transitions from interstitial fluorine to impurity metal have the energies near 1.5–2 eV less than that of transitions in pure crystal cluster. The oscillator strengths of these transitions are 10<sup>-4</sup>–10<sup>-3</sup>. The calculation of isolated pair (LaF)<sup>2+</sup>, having internuclear distances 2.4–2.5 Å, shows the oscillator strength of lowest energy transitions in the same range. Calculated energies are shown in Table 1.

Much less distortion of cluster was obtained in triplet excited state, when hole localised on interstitial fluorine and excited electrons occupied the Y or La ion. Triplet–singlet luminescence energies were treated as difference between total energies of cluster in triplet and singlet states. At first the geometry of cluster was optimised for triplet excited state and then the total energy of singlet ground state was calculated for that cluster.

All calculated transitions are in good correlation with experimental values (see Table 1). Emission energies were calculated using LANL2DZ basis and BHLYP correlation functional also. The calculated energies were near 1 eV larger than those calculated using Hartree–Fock method.

## 4 Discussion

In early paper [12] we conclude that emission at 3.82 eV excited in impurity region 8–9 eV in BaF<sub>2</sub>–3% LaF<sub>3</sub> belong to strongly perturbed excitons. However the results of measurements on CaF<sub>2</sub> and SrF<sub>2</sub> show that Y or La-impurity emission bands shifted to high energy side against exciton band (see Fig. 4). In the case of CaF<sub>2</sub>–Y the shift becomes 0.75 eV. This is too high to be explained by perturbation of exciton. Moreover in many cases the new emission transformed at relatively high temperature to perturbed exciton emission, which emission band slightly shifted to low-energy side. Our calculations of relatively large cluster, containing La or Y impurity ion and F interstitial show that the configuration of triplet Me<sup>2+</sup>–F<sub>i</sub><sup>0</sup> has markedly less energy than that of exciton near impurity. Therefore we conclude that observed emission and excitation bands belong to Me<sup>3+</sup>–F<sub>i</sub><sup>-</sup> pairs.

Shift of fundamental absorption edge in vacuum ultraviolet region was observed in CaF<sub>2</sub> crystals doped by YF<sub>3</sub> or by NaF impurities [1]. Both impurities leads to continuous shift of absorption edge to low energies. The addition of both impurities in equal molar concentration result in very small shift of

absorption edge [1]. Later it was shown that in double activated crystals  $\text{CaF}_2\text{-Na}$ ,  $\text{Ce}$  the charge compensating interstitial fluorine and anion vacancies are not observed [10]. The  $\text{CaF}_2$  doped with equal molar concentration of  $\text{Ce}^{3+}$  and  $\text{Na}^+$  ions contains predominantly cubic  $\text{Ce}$  ions due to large distances between  $\text{Ce}^{3+}$  and  $\text{Na}^+$  ions [11]. Therefore the shift of absorption edge of alkaline-earth fluorides doped with trivalent metal impurities is mainly due to presence of charge compensating interstitial fluorines.

From experimental investigations [7–9] and theoretical calculations [13, 14] it follows that in a row of  $\text{CaF}_2$ ,  $\text{SrF}_2$ ,  $\text{BaF}_2$  the ratio of concentrations of NNN to NN  $\text{Me}^{3+}\text{-F}_i^-$  dipoles drastically increased. Also in the same crystal the ration NNN to NN dipoles growth with decreasing ionic radius of rare-earth ion. It means that in particular crystal the concentration of NNN dipoles should be higher with Y impurity than that with La impurity. For relatively large La impurity the NN-centres are predominant in  $\text{CaF}_2$  and  $\text{SrF}_2$ , and becomes near 0.1 against NNN centres in  $\text{BaF}_2$  [9]. For relatively small Y impurity ion the number of NN centres become 0.1 or less against that of NNN centres in  $\text{SrF}_2$  and  $\text{BaF}_2$  crystals [7, 8]. From our calculation the NNN centres should have luminescence bands with maximums less than 2 eV, due to large lattice relaxation. However no red luminescence bands were observed not in  $\text{SrF}_2$  not in  $\text{BaF}_2$  crystals. The calculated oscillator strengths of NNN centre absorption near 5 time less than that of NN centres, due to larger separation between impurity ion and interstitial fluorine. However the fast component of decay time weakly depends on host lattice (see Table 1). Therefore the observed luminescence belong to radiative transitions of nearest  $\text{Me}^{3+}\text{-F}_i^-$  pairs. Taking into account that the number of NNN centres in  $\text{BaF}_2$  is several time larger than that of NN centres one should conclude that relatively large number of NNN centres should absorb incident vacuum ultraviolet photons. It seems that the absence of luminescence of NNN centres is due to quenching.

The decrease of energy of luminescence band of  $\text{Me}^{3+}\text{-F}_i^-$ -centres in a row of  $\text{CaF}_2\text{-SrF}_2\text{-BaF}_2$  is larger than that of exciton band. Indeed, if the energy in  $\text{CaF}_2$  is 0.3–0.5 eV larger than exciton band, the maximums of emission bands become 0.2–0.3 eV less than exciton band in  $\text{BaF}_2$ . It is not surprising because the electron part of exciton is F centre, the radiuses of which depends on lattice. The electron part of  $\text{Me}^{3+}\text{-F}_i^-$  centre is  $\text{Re}^{3+}$ , which radius not depends on lattice. In latter case the lattice relaxation in  $\text{BaF}_2$  is significantly larger than that in  $\text{CaF}_2$ .

## 5 Conclusion

The experimental and calculation results lead us to conclusion that the observed Y or La-impurity absorption or excitation belong to transitions from charge compensating fluorines to trivalent impurity metals. The observed new luminescence bands are due to back radiative triplet-singlet transitions from impurity metal to interstitial fluorines  $\text{Me}^{3+}\text{-F}_i^-$ .

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