



Spectroscopy of divalent rare earth ions in fluoride crystals



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ABSTRACT

We have studied the absorption spectra of x-ray irradiation-induced Ce^{2+} and Pr^{2+} ions in crystals of alkaline-earth fluorides. We have calculated absorption spectra of divalent praseodymium ions in SrF_2 crystals doped with Pr^{2+} for the first time. The calculated spectra agree rather well with the experimental data. In crystals containing induced Ce^{2+} ions we have found strong electron–phonon coupling. In BaF_2 , we do not observe bands corresponding to divalent Ce or Pr ions.

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1. Introduction

Rare earths are found, usually, in the +3 oxidation state. The energy difference between divalent and trivalent states is large and positive at the beginning lanthanide series indicating that the trivalent state is well-favored [1]. The negative or close to zero energy difference indicates that divalent state is more stable. It was observed for Eu, Yb and Sm ions. However, in crystals a certain fraction of any of the trivalent rare-earth ions can be reduced to the +2 oxidation state by ionizing radiation [2–4], annealing the crystals in a reducing atmosphere of metal vapor, i.e. additive coloration [5,6] or electrolytic means [7]. In reduced crystals of CaF_2 –Ce and CaF_2 –Pr divalent rare earth ions were observed [3,4]. Furthermore, they were stable at room temperature. The reduced ions occupy alkaline-earth lattice sites having the full O_h symmetry [3]. After reduction, the crystals are colored, typically having several broad, intense absorption bands extending from the near infrared through the UV region. Divalent cerium ions were also observed in SrCl_2 –Ce crystals. The bands attributed to Ce^{2+} were located in 400–700 nm region [8]. It has been found, that Pr^{2+} ions take place in energy transfer in SrF_2 –Pr and CaF_2 –Pr scintillation crystals [9,10]. Although wide investigations of SrF_2 and

BaF_2 doped with Ce and Pr ions were provided, no divalent Ce and Pr ions were found in SrF_2 and BaF_2 crystals [3–5,11].

The aim of our research is to derive from optical absorption spectra measurements and theoretical calculation an information about spin–orbital splitting and spectroscopy properties of divalent Ce and Pr ions in fluoride crystals. Part of the results was presented earlier at the paper [12]. Now a more elaborate overview and discussion of the results is given and recently obtained data are included.

2. Methodology

Crystals of CaF_2 and SrF_2 were grown from the melt by the Bridgman–Stockbarger method in graphite crucibles in vacuum and were doped with 0.1 mol% of CeF_3 or PrF_3 . In alkaline earth fluoride single crystal growth a small amount of CdF_2 was generally used as a scavenger in order to remove oxides contained in the raw materials [12–15]. The crystals of CaF_2 –Ce and CaF_2 –Pr were irradiated at 300 K by x-rays from a Pd tube operating at 35 kV and 20 mA during not more than one hour. The crystals of SrF_2 were irradiated at 77 K.

The optical absorption spectra were obtained on a Perkin-Elmer Lambda 950 UV/VIS/NIR spectrophotometer at 7, 78, and 300 K at the Baikal Analytical Center for Collective Use, Siberian

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Branch of Russian Academy of Sciences. Absorption spectra at 7 K measured using cryocooler Janis Research CCS-100/204 N.

The DFT (density functional theory) calculations were performed using embedded QM (quantum mechanical) cluster method implemented in GUESS computer code [16]. This method allows an integration of accurate quantum chemical calculations within a small defect-containing cluster and its nearest neighborhood with a classical description of the rest of crystal at molecular mechanics level. The QM cluster was surrounded by a large number (about 700 in this work) of atoms described classically with the shell model and pair potentials. About 70 cations between classical region and QM cluster were replaced with the interface atoms, which atoms have specially selected ECPs and pair potentials to minimize the distortion of electronic and spatial structure at the QM cluster edge. All atoms of the classical, interface and QM regions are allowed to relax during the geometry optimization, thus simulating the deformation and polarization of the crystal lattice by the presence of the impurity ions. For the classical region we have used the pair potentials parameters in the Buckingham form for CaF_2 and SrF_2 crystals from Ref. [17] and adjusted them so that they are compatible with GUESS code. The classical region was surrounded by several thousand of fixed-point charges to simulate the correct Madelung potential of the crystal. The GUESS code is not capable to calculate the electronic structure of QM cluster, but calls another quantum-chemical program (in this case, the Gaussian 03 [18]), and adds classic terms to find the total energy of the system. The applicability of embedded cluster calculation method for defects in ionic crystals is described in Refs. [19,20] in more details.

Calculations have been performed in a cluster containing 12 calcium or strontium ions (Me) and 32 fluorine ions, the praseodymium ion was placed in the central position instead of alkali ion $[\text{Me}_{12}\text{F}_{32}\text{Pr}^{2+}]^{-6}$ (Fig. 5). The 6–31 G* basis sets on fluorine and calcium ions, and SDD basis set on strontium and praseodymium ions were used. All cations in 6 Å vicinity of QM cluster were replaced by the interface ions, which had LANL1 ECP (Hay-Wadt large core pseudopotential) and no basis functions.

For the DFT calculations we used the modified B3LYP functional containing 40% of Hartree–Fock and 60% of DFT exchange energies which showed most adequate electron state localization and was successfully employed for DFT calculations of defects in fluoride crystals [19,20]. Optical energies and dipole matrix elements of transitions were calculated with the time-dependent DFT (TDDFT) method applied.

Note that in the previous papers [12,20] we carried out the calculations of the spatial structure and optical properties of Pr^{3+} ion in crystals of alkaline earth fluorides. The calculations have been performed on the above scheme, and showed good agreement with experiment data. This paper presents the results of calculations of Pr^{2+} single center using $[\text{Ca}_{12}\text{F}_{32}\text{Pr}^{2+}]^{-6}$ and $[\text{Sr}_{12}\text{F}_{32}\text{Pr}^{2+}]^{-6}$ cluster.

3. Experimental results

3.1. $\text{CaF}_2\text{-Ce}^{2+}$ and $\text{SrF}_2\text{-Ce}^{2+}$

After x-ray irradiation, absorption bands in a wide spectral region appear in $\text{CaF}_2\text{-Ce}$ and $\text{SrF}_2\text{-Ce}$ crystals. They are due to appear of photochromic centers [21] and divalent Ce, when trivalent Ce is reduced by x-ray irradiation. In CaF_2 these centers remain relatively stable at room temperature. In SrF_2 crystals, divalent Ce is stable only at low temperatures. Most of the Ce^{3+} ions remains unconverted after irradiation.

Fig. 1 shows the absorption spectra divalent Ce in CaF_2 and SrF_2 crystals. At low temperatures, the absorption begins at around

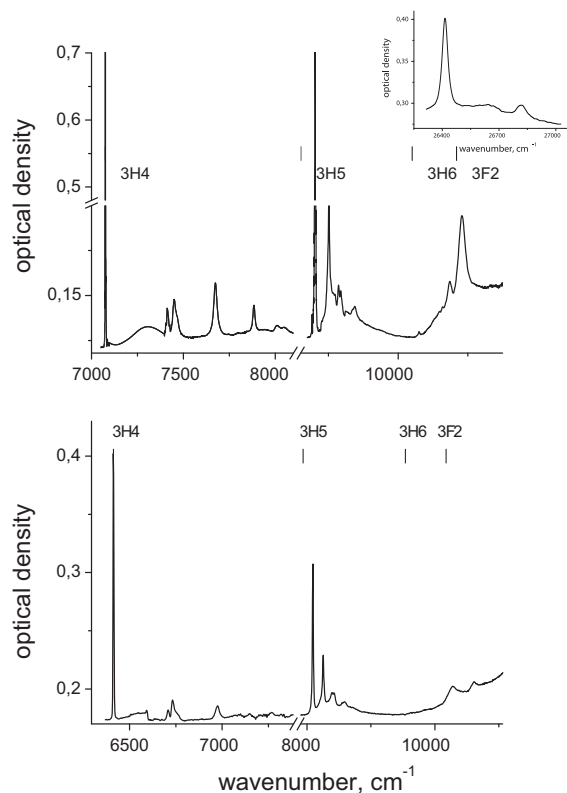


Fig. 1. Absorption spectra of $\text{CaF}_2\text{-Ce}^{2+}$ (a) and $\text{SrF}_2\text{-Ce}^{2+}$ (b) at 7 K. Energies of spin-orbital splitted 4f level of free Ce^{2+} given in the top of the figures. In the inset of (a) sharp lines in UV spectral region corresponding to Ce^{2+} are given.

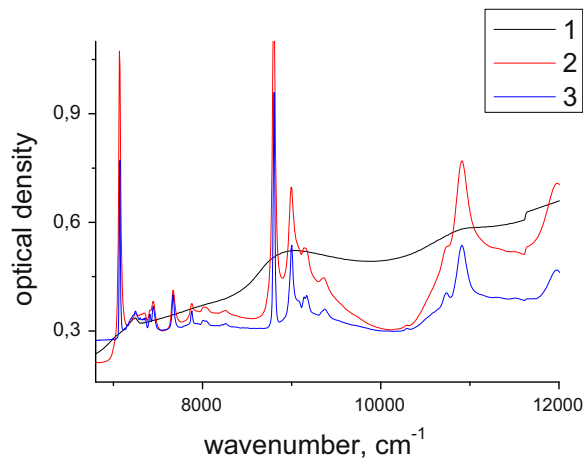


Fig. 2. Absorption spectrum of $\text{CaF}_2\text{-Ce}^{2+}$ at 300 K (1), 78 K (2), and 7 K (3).

7070 cm^{-1} in $\text{CaF}_2\text{-Ce}$ and at around 6400 cm^{-1} in $\text{SrF}_2\text{-Ce}$ and fills the whole region of the spectra. Groups of relatively sharp lines are observed at about 7070 cm^{-1} and 8800 cm^{-1} in $\text{CaF}_2\text{-Ce}$, and at about 6400 cm^{-1} and 8080 cm^{-1} in $\text{SrF}_2\text{-Ce}$. The higher energy bands except two sharp lines at $26,400\text{ cm}^{-1}$ and $26,800\text{ cm}^{-1}$ (inset to Fig. 1a) are broadened.

The spectrum exhibits a very strong temperature dependence that is shown in Figs. 2 and 3. In $\text{CaF}_2\text{-Ce}$, at 300 K and in $\text{SrF}_2\text{-Ce}$ at 77 K the various components can hardly be resolved. However, at low K temperatures some of lines are very sharp. Temperature dependences of line width of bands at 7070 cm^{-1} and 8800 cm^{-1} in CaF_2 and 6400 cm^{-1} and 8080 cm^{-1} in SrF_2 are given in Fig. 3.

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