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## Divalent Cerium and Praseodymium Ions in Crystals of Alkaline-Earth Fluorides

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**Abstract**—We have studied the absorption spectra of radiation-induced divalent cerium and praseodymium ions in crystals of alkaline-earth fluorides. Using ab initio quantum-mechanical methods, we have calculated absorption spectra of divalent praseodymium ions in  $\text{CaF}_2$  crystals for the first time. The theoretical spectrum agrees rather well with the experimentally registered spectra.

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### INTRODUCTION

Rare-earth ions mainly form stable trivalent compounds (e.g.,  $\text{LaF}_3$ , etc.). At the same time, the possibility of formation of divalent compounds based on rare-earth ions is being studied rather intensely. Stable divalent compounds are formed with Eu, Yb, and Sm ions, which have high third ionization potentials. The least stable divalent compounds are formed with La, Ce, Gd, Tb, and Lu ions, which have low third ionization potentials, i.e., with ions that form photochromic centers in alkaline-earth fluorides [1]. A similar situation is observed for alkaline-earth fluorides doped with rare-earth ions.

However, divalent rare-earth ions can also be formed in additively colored or irradiated crystals; in the majority of cases, such centers are stable only at a boiling temperature of liquid nitrogen or at lower temperatures. In absorption spectra, divalent rare-earth ions give rise to absorption bands in the visible and infrared ranges of the spectrum [2]. The ground state of the majority of divalent rare-earth ions is located rather close to the conduction band [3].

Divalent Pr ions that are formed in alkaline-earth fluorides as a result of the absorption of ionizing radiation participate in energy-transfer processes in these compounds. Their participation leads to a lengthening in the scintillation time and, correspondingly, to a lowering of the light yield of crystals  $\text{CaF}_2\text{-Pr}^{3+}$ ,  $\text{SrF}_2\text{-Pr}^{3+}$ , and  $\text{BaF}_2\text{-Pr}^{3+}$  [4, 5]. It is necessary to further study the formation processes of these ions, as well as their characteristics, for the purpose of eliminating their influence in the course of energy transfer. In crystals that are doped with cerium, divalent rare-earth ions can also participate in energy-transfer processes [6, 7].

Divalent rare-earth ions can also be observed upon formation of photochromic centers. There are two types of centers, namely, so-called PC and  $\text{PC}^+$  centers. A photochromic center in a crystal of an alkaline-earth fluoride is a complex that consists of a trivalent rare-earth ion and an anionic vacancy and that has captured two electrons. Under the action of UV light, a passage from PC to  $\text{PC}^+$  centers is possible. Absorption spectra of PC centers are simpler and, to some extent, are similar to absorption spectra of perturbed F centers. Absorption spectra of  $\text{PC}^+$  centers are more complex. In some cases, they have been attributed to spectra of divalent rare-earth ions, and many absorption bands have been rather reasonably associated with transitions in these ions. In crystals doped with Ce, bleaching of PC centers led to the formation of  $\text{PC}^+$  centers. At the same time, the spectrum of divalent cerium ions was also clearly observed and it was impossible to separate one spectrum from the other [8].

Ab initio calculations of the energy structure of divalent rare-earth ions have also almost not been performed. Semiempirical calculations of centers of divalent rare-earth ions were performed in [8]. The authors of that work confirmed that bands observed in absorption spectra of  $\text{CaF}_2\text{-Ce}$  are indeed related to transitions in divalent cerium ions. In [10], based on empirical calculations, it was concluded that the probability of occurrence of  $\text{Ce}^{2+}$  centers in  $\text{CaF}_2$  crystals is small, and  $\text{Ce}^{4+}$  centers prove to be more stable. No theoretical calculations of energy levels of  $\text{Pr}^{2+}$  ions in  $\text{CaF}_2$  crystals have been made.

Therefore, investigation of Ce and Pr divalent ions is important both for the understanding the energy-transfer processes in alkaline-earth fluorides, which are promising scintillation materials [6, 7, 11], and for

more detailed investigation of mechanisms of formation and transformation of photochromic centers. This paper will present results of our investigations of  $\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals with radiation-induced  $\text{Ce}^{2+}$  and  $\text{Pr}^{2+}$  centers. In order to study these centers in this work, we registered optical absorption spectra in the IR, visible, and UV ranges of the spectrum. We also performed ab initio quantum-mechanical calculations of absorption spectra of  $\text{Pr}^{2+}$  ions in the  $\text{CaF}_2$  crystal.

## EXPERIMENTAL TECHNIQUE

$\text{CaF}_2$ ,  $\text{SrF}_2$ , and  $\text{BaF}_2$  crystals doped with praseodymium ions with concentrations of 0.05, 0.1, and 1 mol % and  $\text{CaF}_2$  and  $\text{SrF}_2$  crystals doped with 0.1 mol % of  $\text{Ce}^{3+}$  were grown by the Stockbarger method in graphite crucibles in vacuum. The crystals under study did not contain oxygen impurities, which was verified via the absence of a characteristic emission under UV excitation [12, 13]. The concentration of the dopant was also monitored by the ICP-MS methods on a Finnigan spectrometer [6].

Absorption spectra were measured on a Lambda 950 PerkinElmer spectrophotometer in the spectral range between 200 and 2500 nm (6.2–0.5 eV). Spectra at a temperature of 80 K were measured in a vacuum cryostat with quartz windows. Measurements at liquid helium temperatures were implemented using a Janis Research closed-cycle helium cryostat with quartz windows. To measure spectra in the range of 2500–10000 nm (0.5–0.12 eV), an FT-801 Fourier-transform spectrometer was used.

Crystals were irradiated using an X-ray tube with a Pd anode; the tube voltage was 35 kV, its current was 20 mA, and the irradiation time was varied from 30 min to 1 h. The thicknesses of examined specimens did not exceed 1.5 mm. Low-temperature irradiation of crystals was performed in a vacuum cryostat.

Calculations were performed by the embedded-cluster method using the GUESS software package [14]. In the crystal lattice, a quantum-mechanical cluster was separated that contained a defect and its nearest environment. Around this cluster, ~700 atoms were separated, which were described classically with pair potentials (the classical region). To correctly reproduce the Madelung potential inside the system, the quantum cluster, along with the classical region, was surrounded by ~7000 point motionless charges. The GUESS software package itself does not calculate the electronic structure of the quantum-mechanical cluster, but calls up another quantum-chemical program (in our case, this is Gaussian 03 [14]) and adds classical terms for finding the total energy of the system.

In more detail, the application of the embedded cluster method to fluoride crystals was described in [15–18].

Calculations were implemented in terms of the DFT (density functional theory) method using the B3LYP hybrid functional, which contained 40% of the HF exchange and 60% of the Becke exchange. In [16–18], it was shown that it is this functional that ensures the correct degree of localization of the electron density in calculations of the optical properties of defects in crystals of alkaline-earth fluorides. As a basis set for calcium and fluorine ions, we used the 6–31G all-electron basis set, while, for the praseodymium ion, we used the SDD basis set. Excited states and energies of optical transitions were both calculated by the time-dependent DFT (TD DFT) method. In order to avoid the distortion of the electron density at the boundary of the quantum-mechanical cluster, interface atoms are singled out in the classical region. In the case of purely ionic crystals, it suffices to replace several dozen cations at the boundary quantum cluster–classical region with the LANL1 pseudopotential.

We note that, in our previous work [17], we carried out a series of calculations of the spatial structure and optical properties of  $\text{Ce}^{3+}$  and  $\text{Pr}^{3+}$  ions in crystals of alkaline-earth fluorides. These calculations were done according to the scheme indicated above and showed good agreement with experiment. In this work, we present results of calculations of a single  $\text{Pr}^{2+}$  center using a cluster  $\text{Ca}_{12}\text{F}_{32}\text{—Pr}^{2+}$ .

## RESULTS

### *Crystals Doped with Praseodymium Ions*

After irradiation of  $\text{CaF}_2$  crystals doped with  $\text{Pr}^{3+}$  ions, their absorption spectra exhibit a series of new bands in the IR and visible ranges of the spectrum. Figures 1a and 1b show the absorption spectra of  $\text{CaF}_2$  crystals doped with 0.1 and 1 mol % of  $\text{Pr}^{3+}$  ions. Curve 1 corresponds to the absorption spectrum of the unirradiated crystal. Narrow lines in the ranges of 0.7 and 2.7 eV are related to transitions inside of the *f* shell of  $\text{Pr}^{3+}$  ions. The figure does not show intense bands that are caused by *4f–5d* transitions in  $\text{Pr}^{3+}$  ions, which are located in the UV range. After the X-ray irradiation of crystals for 30 min at room temperature, broad bands with energies of 0.4, 1.1, 1.8, 2.4, 2.7, and 3 eV appear in their absorption spectrum. At a temperature of 10 K, no fine structure is observed in these bands. They are seen most clearly in the absorption spectrum of the crystal  $\text{CaF}_2\text{—}0.1$  mol %  $\text{Pr}^{3+}$ ; in crystals with higher concentrations, these bands can also be observed against the background of intense bands of the *f–f* absorption of  $\text{Pr}^{3+}$  ions.

The absorption spectra of  $\text{BaF}_2$  crystals doped with 0.1 and 0.3 mol % of  $\text{Pr}^{3+}$  ions are presented in Fig. 1c. Curves 1–1 and 2–1 correspond to the absorption spectra of the unirradiated crystals  $\text{BaF}_2\text{—}0.1$  mol %  $\text{Pr}^{3+}$  and  $\text{BaF}_2\text{—}0.3$  mol %  $\text{Pr}^{3+}$ . Narrow bands in the energy range below 1 eV in the absorption spectra are

related to  $f-f$  transitions in  $\text{Pr}^{3+}$  ions. A sharp increase in the optical density above 5.5 eV corresponds to the  $4f-5d$  absorption in  $\text{Pr}^{3+}$  ions. After the X-ray irradiation of crystals for 30 min at a boiling temperature of liquid nitrogen, a series of broad bands with energies of 2.15, 3.4, 4, and 4.5 eV appear in their absorption spectrum. In the absorption spectra of the irradiated crystal  $\text{BaF}_2-0.1 \text{ mol } \% \text{ Pr}^{3+}$ , the optical density of these bands is lower than that in the spectrum of the crystal  $\text{BaF}_2-0.3 \text{ mol } \% \text{ Pr}^{3+}$  that was irradiated for the same period of time. We also measured the absorption spectra of irradiated crystals  $\text{BaF}_2-0.05 \text{ mol } \% \text{ Pr}^{3+}$ ; in these crystals, the optical density of the appearing bands was even lower.

Irradiation of  $\text{SrF}_2-\text{Pr}^{3+}$  crystals almost does not induce the occurrences of additional bands.

#### Crystals Doped with Cerium Ions

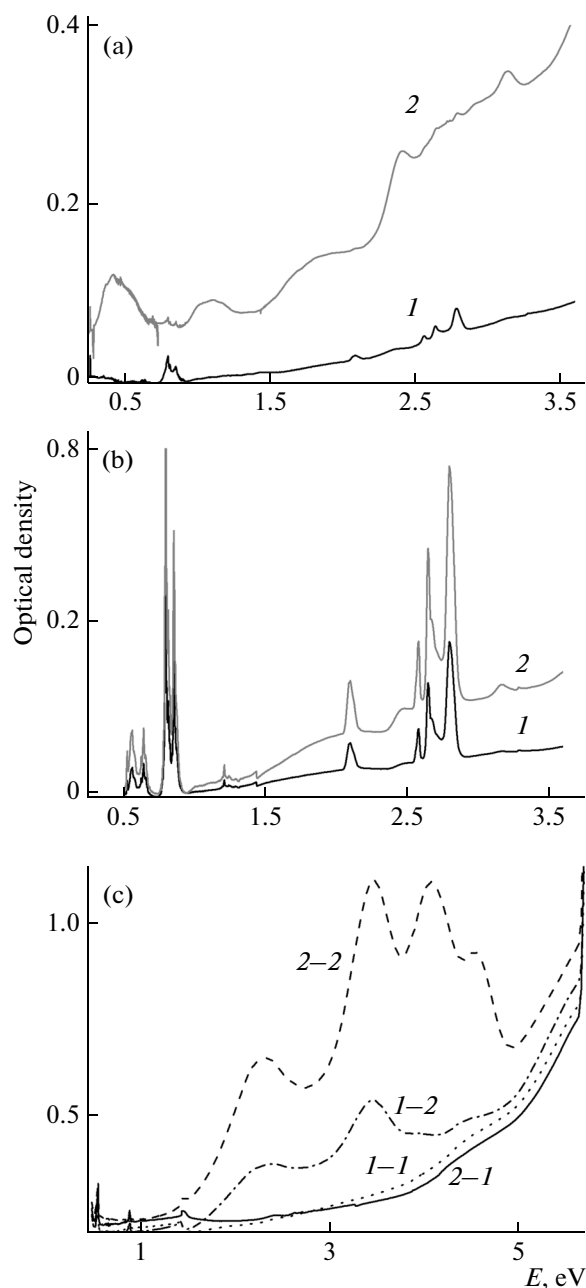
The absorption spectra of  $\text{CaF}_2-\text{Ce}^{3+}$  and  $\text{SrF}_2-\text{Ce}^{3+}$  crystals prior to and after their irradiation are shown in Fig. 2. The absorption spectrum of the unirradiated crystal  $\text{CaF}_2-0.1 \text{ mol } \% \text{ Ce}^{3+}$  shows intense bands in range of 4–6 eV, which are related to  $4f-5d$  transitions in  $\text{Ce}^{3+}$  ions. After irradiation at a temperature of boiling of liquid nitrogen, the spectrum exhibits a series of additional bands, namely, a set of narrow lines at 0.8, 1.2, and 1.3 eV and broad bands in the range of 2.1 and 2.4 eV.

In the spectrum of unirradiated  $\text{SrF}_2-\text{Ce}^{3+}$  crystals, intense bands are observed in the UV range, which are related to the  $4f-5d$  absorption of  $\text{Ce}^{3+}$  ions. After irradiation at a boiling temperature of liquid nitrogen, the absorption spectrum reveals a series of bands: broad bands at 1.7, 2.2, and 2.7 eV and a set of narrow lines with energies of  $\sim 1$  eV.

## DISCUSSION

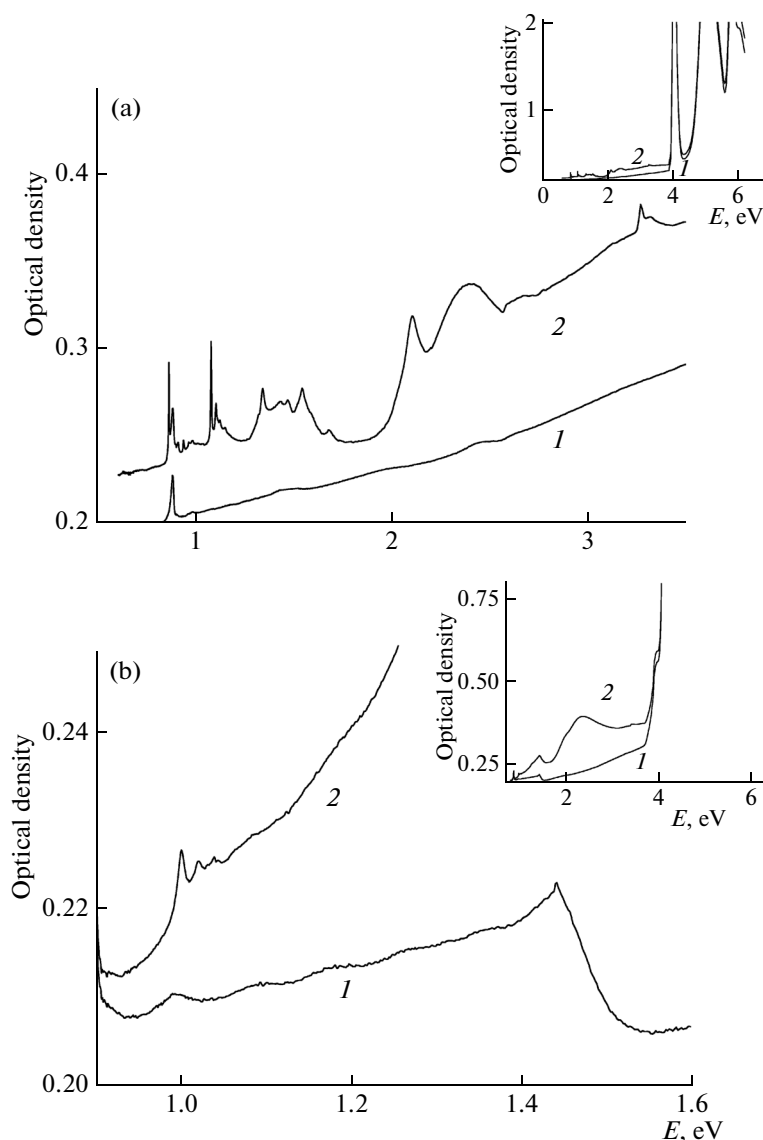
After the irradiation, a series of bands appears in the absorption spectrum of  $\text{CaF}_2-\text{Pr}^{3+}$  crystals. Previously, bands of the same energies were observed in [2, 19] in spectra of radiatively and additively colored crystals.

These bands are related to  $4f-5d$  transitions in divalent praseodymium ions. In [2], the transition with the energy of 0.4 eV corresponds to the splitting from the ground state  $4f^3-^4I_{9/2}$  to the lowest level of the split state  $4f^25d$ . Transitions with higher energies correspond to transitions from the  $f$  state to higher levels of the  $d$  state, which lie in the conduction band of  $\text{CaF}_2$  [6]. Therefore, these lines in the absorption spectrum are rather broad and remain unresolved upon lowering of the temperature. It is worth noting that  $\text{Pr}^{2+}$  ions in  $\text{CaF}_2$  crystals are stable at room temperature. The authors of [19] measured the magnetic



**Fig. 1.** Absorption spectra of crystals (1–1)  $\text{CaF}_2-0.1 \text{ mol } \% \text{ Pr}^{3+}$ , (1–2)  $\text{CaF}_2-1 \text{ mol } \% \text{ Pr}^{3+}$ , (2–1)  $\text{BaF}_2-0.1 \text{ mol } \% \text{ Pr}^{3+}$ , and (2–2)  $\text{BaF}_2-1 \text{ mol } \% \text{ Pr}^{3+}$ . The absorption spectra of the unirradiated crystals are shown by curves 1, 1–1, and 2–1, while the absorption spectra of the irradiated specimens are shown by curves 2, 2–1, and 2–2.

circular dichroism in additively colored  $\text{CaF}_2-\text{Pr}^{2+}$  crystals. For bands with the energy of 1.8 eV, the right-hand polarization was more pronounced, whereas the left-hand polarization was in remaining bands. This can testify to the fact that transitions that are related to these bands differ from the transition with the energy of 1.8 eV.



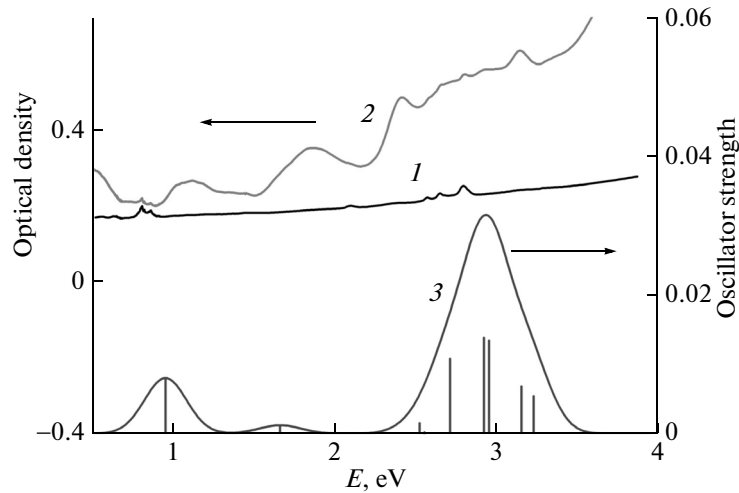
**Fig. 2.** Absorption spectra of (1) unirradiated and (2) irradiated crystals (a)  $\text{CaF}_2\text{-}0.1 \text{ mol } \% \text{Ce}^{3+}$  and (b)  $\text{SrF}_2\text{-}0.1 \text{ mol } \% \text{Ce}^{3+}$ . The insets show the absorption spectra in a wider energy interval.

In order to refine the scheme of energy levels in crystals under investigation, we performed quantum-chemical calculations. Initially, we calculated the deformation of the lattice caused by the occurrence of  $\text{Pr}^{2+}$  ions. In the course of relaxation of the lattice, displacements of nearest fluorine ions were  $0.08 \text{ \AA}$ , displacements of calcium ions were  $0.05 \text{ \AA}$ , and, in this case, displacements of fluorine ions were directed away from praseodymium ions. This pattern of displacements is caused by the fact that the ionic radius of the  $\text{Pr}^{2+}$  ion is somewhat greater than the ionic radius of the  $\text{Ca}^{2+}$  ion ( $1.187$  and  $1.04 \text{ \AA}$ , respectively).

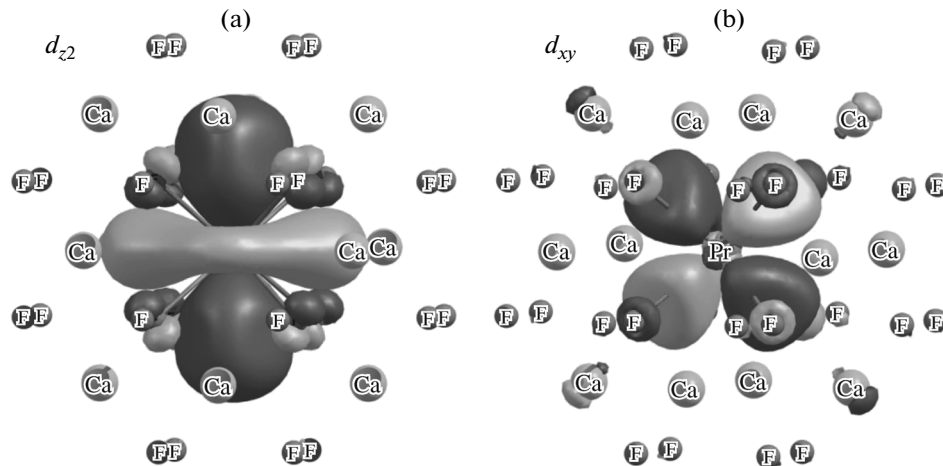
Applying the TD DFT method and using the optimized geometry of the ground state, we calculated the energies and oscillator strengths for transitions  $4f^3 \rightarrow$

$4f^25d$  of the  $\text{Pr}^{2+}$  ion. For a single center, two groups of bands are observed, which are related to the splitting of the  $5d$  state into two levels,  $e_g$  and  $t_{2g}$ . This splitting is caused by the occurrence of a field of a cubic symmetry. The calculated spectrum of  $4f^3 \rightarrow 4f^25d$  transitions is shown in Fig. 3 (curve 3). The low-energy band is caused by transitions to the  $e_g$  state, which is localized in the band gap of the crystal. The high-energy band is caused by a set of transitions to the  $t_{2g}$  state, which are in the conduction band and contain a substantial fraction of  $4s$  and  $3d$  orbitals of calcium ions. One-electron orbitals of some  $5d$  states are presented in Fig. 4.

Good agreement between calculation results and experimental absorption spectra (Fig. 3, curves 2 and



**Fig. 3.** Comparison of absorption spectra of (1) unirradiated and (2) irradiated crystal  $\text{CaF}_2$ -0.1 mol %  $\text{Pr}^{3+}$  with (3) calculated absorption spectrum.



**Fig. 4.** One-electron orbitals of the (a)  $e_g$  and (b)  $t_{2g}$  levels of the  $5d$  state of the  $\text{Pr}^{2+}$  ion.

3). Therefore, to the transition from the  $4f$  ground state to the lowest level  $e_g$  of the  $5d$  state, which is split by the crystal field, the band with the energy of 1.1 eV corresponds, whereas the bands with the energies of 2.4, 2.7, and 3 eV are related to transitions  $\bar{n}$  from the  $4f$  ground state to the level  $t_{2g}$  of the  $5d$  state. The nature of the bands with energies of 1.8 and 0.4 eV requires further research. The splitting of the  $5d$  state can be estimated from the absorption spectrum, the value of this quantity is about 1.3–1.4 eV or 10400–11200  $\text{cm}^{-1}$ , which is close to splitting of the  $5d$  state in other divalent rare-earth ions (10500–13000  $\text{cm}^{-1}$ ) presented in [19]. Theoretical calculations yield a value of about 1.55 eV or on the order of 12500  $\text{cm}^{-1}$ .

The spectra of  $\text{BaF}_2$ -Pr crystals irradiated at a boiling temperature of liquid nitrogen also show

absorption bands (Fig. 1c). Their optical density depends in directly proportionally on the concentration of  $\text{Pr}^{3+}$  ions. This allows us to conclude that these bands in the absorption spectrum are related to praseodymium ions. The revealed bands are quite consistent with the absorption bands of divalent praseodymium in  $\text{CaF}_2$  crystals (Figs. 1a, 1b). However, they are shifted toward the range of higher energies, which is observed for  $\text{BaF}_2$  crystals doped with other divalent rare-earth ions. This is related to the fact that, in  $\text{BaF}_2$ , the splitting of the  $5d$  state by the crystal field is smaller than for  $\text{CaF}_2$  crystals. The splitting of the  $5d$  state can also be estimated from the absorption spectrum assuming that the energy of the transition from the ground  $f$  state to the lowest level of the  $5d$  state is about 1.1 eV (9200  $\text{cm}^{-1}$ ).  $\text{Pr}^{2+}$  centers

in  $\text{BaF}_2\text{-Pr}$  crystals are less stable than in  $\text{CaF}_2\text{-Pr}$  and are destroyed upon heating above 200 K.

### Crystals Doped with Cerium Ions

The structure of absorption spectra of crystals  $\text{CaF}_2\text{-Ce}^{3+}$  irradiated at a boiling temperature of liquid nitrogen is more complex than in crystals doped with  $\text{Pr}^{3+}$  ions. In the spectrum, two types of bands can be singled out, namely, a set of narrow lines in the range of 0.8, 1.2, and 1.3 eV and broad bands in the range of 2.1 and 2.3 eV. Similar absorption spectra were measured in [8]. It was proved that narrow lines correspond to transitions from the ground state  $4f5d$  to split levels of the  $f$  state. Broad bands are related to the absorption of photochromic  $\text{PC}^+$  centers [9].

The absorption spectrum of the  $\text{SrF}_2\text{-Ce}^{3+}$  crystal irradiated at 80 K also exhibits the appearance of a series of narrow lines in the range of 1 eV and broad bands at 1.4 and 2.3 eV (Fig. 2b). In [9], based on the similarity of the absorption spectra with the spectrum of the crystal  $\text{CaF}_2\text{-Ce}$ , broad lines were attributed to  $\text{PC}^+$  centers.

Narrow lines, with respect to their structure, are similar to the  $4f5d\text{-}4f$  absorption of  $\text{Ce}^{2+}$  ions (see Fig. 2a). It should be noted that, in the absorption spectrum of the irradiated crystal  $\text{SrF}_2\text{-Ce}$ , only one group of narrow lines is observed, which is distinct from the spectrum of the crystal  $\text{CaF}_2\text{-Ce}$ , in which three groups of lines are clearly pronounced. It is likely that this is related to the fact that, in the spectrum of the crystal  $\text{SrF}_2\text{-Ce}$ , almost all split  $4f$  levels fall into the range of the conduction band, which leads to a considerable broadening of lines that superimpose on broad absorption bands related to  $\text{PC}^+$  centers. Indeed, the spacing between the ground  $4f5d$  state and the bottom of the conduction band is estimated to be 1.6 eV in  $\text{CaF}_2\text{-Ce}^{2+}$  and 1.3 eV in  $\text{SrF}_2\text{-Ce}^{2+}$  [20, 21]. Correspondingly, if we assume that the energy position of split  $4f$  states depends weakly on the host matrix, since the  $f$  shell is screened, the next group of  $5d4f\text{-}4f^2$  absorption bands should fall into the range of the conduction band.

### CONCLUSIONS

In this work, we have investigated the absorption spectra of irradiated crystals of alkaline-earth fluorides doped with trivalent cerium and praseodymium ions. After the irradiation, divalent praseodymium ions are formed in  $\text{CaF}_2\text{-Pr}^{3+}$  and  $\text{BaF}_2\text{-Pr}^{3+}$  crystals. In this case,  $\text{Pr}^{2+}$  ions are most stable in  $\text{CaF}_2\text{-Pr}$  crystals, and such centers are efficiently induced and are not destroyed even at room temperatures. In  $\text{BaF}_2\text{-Pr}^{3+}$

crystals,  $\text{Pr}^{2+}$  ions are formed only upon irradiation at low temperatures.

Upon irradiation of  $\text{CaF}_2\text{-Ce}^{3+}$  and  $\text{SrF}_2\text{-Ce}^{3+}$  crystals at a temperature of 80 K, apart from photochromic centers, absorption spectra exhibit narrow lines in the IR range of the spectrum that are related to  $\text{Ce}^{2+}$  ions.

### REFERENCES

1. S. Cotton, *Lanthanide and Actinide Chemistry* (Wiley, New York, 2006).
2. D. McClure and Z. Kiss, *J. Chem. Phys.* **39**, 3251 (1963).
3. P. Dorenbos, *J. Phys.: Cond. Matt.* **15**, 2645 (2003).
4. R. Shendrik and E. Radzhabov, *IEEE TNS* **59**, 2089 (2012).
5. R. Shendrik, E. Radzhabov, and V. Nagirnyi, *IOP Conf. Series: Mat. Sci. Eng.* **15**, 012083 (2010).
6. R. Y. Shendrik, E. A. Radzhabov, and A. I. Nepomnyashchikh, *Rad. Meas.* **56**, 58 (2013).
7. R. Y. Shendrik, E. A. Radzhabov, and A. I. Nepomnyashchikh, *Tech. Phys. Lett.* **39** (7), 587 (2013).
8. R. C. Alig, Z. J. Kiss, J. P. Brown, and D. S. McClure, *Phys. Rev.* **186**, 276 (1969).
9. T. Sizova and E. Radzhabov, *IEEE TNS* **59**, 2098 (2012).
10. R. Visser, J. Andriessen, P. Dorenbos, and C. W. E. Van Eijk, *J. Phys.: Cond. Matt.* **5**, 5887 (1993).
11. R. Y. Shendrik and E. A. Radzhabov, *IEEE TNS* **57** (3), 1295 (2010).
12. A. V. Egranov and E. A. Radzhabov, *Spectroscopy of Oxygen and Hydrogen Defects in Alkali Halide Crystals* (Nauka, Novosibirsk, 1992).
13. A. I. Nepomnyashchikh, A. A. Shalaev, A. K. Subanakov, A. S. Paklin, N. S. Bobina, A. S. Myasnikova, and R. Yu. Shendrik, *Opt. Spektrosk.* **111** (3), 442 (2011).
14. P. V. Sushko, A. L. Shluger, and C. R. A. Catlow, *Surf. Sci.* **450** (3), 153 (2000).
15. M. J. Frisch, G. W. Trucks, H. B. Schlegel, et al., *Gaussian*, 03 (Gaussian Inc., Pittsburgh, 2007).
16. A. S. Mysovsky, P. V. Sushko, E. A. Radzhabov, M. Reichling, and A. L. Shluger, *Phys. Rev. B* **84**, 064133 (2011).
17. A. Myasnikova, E. Radzhabov, and A. Mysovsky, *IEEE TNS* **59** (5), 2065 (2012).
18. A. S. Myasnikova, A. S. Mysovskii, and E. A. Radzhabov, *Opt. Spektrosk.* **114** (3), 445 (2013).
19. H. A. Weakliem, C. H. Anderson, and E. S. Sabisky, *Phys. Rev. B* **2**, 4354 (1970).
20. K. E. Johnson and J. Sandoe, *J. Chem. Soc. Am.* 1694 (1969).
21. C. Pedrini et al., *J. Physique* **42**, 323 (1981).

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