

Divalent Rare-Earth Ions Pr, Sm, Ho, Er, Tm, and Yb in Crystals of Alkaline-Earth Fluorides

T. Yu. Sizova^{a, *}, V. Yu. Veslopolova^b, R. Yu. Shendrik^{a, b}, A. V. Egranov^{a, b},
E. A. Radzhapov^{a, b}, and A. A. Shalaev^{a, b}

^aVinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, Irkutsk, 664033 Russia

^bIrkutsk State University, Irkutsk, 664003 Russia

*e-mail: sizova@igc.irk.ru

Abstract—The absorption spectra of radiation-colored CaF₂, SrF₂, and BaF₂ crystals activated by trivalent Pr, Sm, Ho, Er, Tm, and Yb (rare-earth, RE) ions are studied. It is shown that ionizing radiation reduces the impurity ions to the divalent state. The temperature resistance of divalent RE ions of radiation-colored CaF₂ crystals correlates with the chemical stability of the compounds with divalent RE ions. The photochromic centers are produced in CaF₂-Pr crystal colored by radiation at room temperature and heated to 200°C.

DOI: 10.3103/S1062873817090234

INTRODUCTION

The optical properties of crystalline material activated by rare-earth (RE) ions are due to the valence of impurity ions. RE ions are normally incorporated into crystals of alkaline-earth fluorides (AEFs) in the trivalent state. When an external influence acts on the crystals (ionizing radiation or heating in metal vapors (additive coloring)), RE ions can be reduced to the divalent state [1–3]. Yttrium, La, Ce, Gd, Tb, and Lu, which are characterized by low third ionization potential, form photochromic centers in radiation- and additive-colored CaF₂ and SrF₂ crystals [4–6]. Such crystals can be used in holography [7].

Studying the effect different states have on valence stability of impurity ions, or on the change in their valence under an external impact, is of both practical and fundamental interest.

In [4, 5], we studied the optical properties and thermal destruction of the induced centers of CaF₂, SrF₂, and BaF₂ crystals activated by Y, La, Ce, Gd, Tb, and Lu. In this work, we studied the absorption spectra of divalent Pr, Sm, Ho, Er, Tm, and Yb ions of radiation-colored CaF₂, SrF₂, and BaF₂ crystals in the temperature range of 300–900 K.

EXPERIMENTAL

Fluoride crystals were grown using the Stockbarger technique in a three-barreled graphite crucible in a vacuum. Several percents of CdF₂ were added to the material to remove oxygen. The concentrations of PrF₃, SmF₃, HoF₃, ErF₃, TmF₃, and YbF₃ in the charges were 0.01, 0.1, and 0.3 mol %. The absorption

spectra were measured on a Lambda-950 spectrophotometer (PerkinElmer) in the range of 190–2000 nm. The radiation was produced by a BHV-12 X-ray tube at a voltage of 25 kV and a current of 20 mA over 30 min. The samples were placed directly on the outer window of the tube and were colored from both sides.

RESULTS AND DISCUSSION

Under X-ray radiation at room temperature, the RE³⁺ ions in CaF₂, SrF₂, and BaF₂ crystals activated by trivalent RE ions were partly reduced to RE²⁺ ions. The intense absorption bands of divalent RE ions (Sm, Ho, Er, Tm, Yb, Pr) are found in the visible and UV ranges of the spectrum (Fig. 1) [2, 3]. Radiation coloring also results in the formation of acceptor F₃⁻ and (F₂⁻)_{ii}-centers, along with RE²⁺-centers [8, 9].

Acceptor Centers

The (F₂⁻)_{ii}-centers in AEF crystals are holes localized on interstitial F ions oriented along axis [110] [9]. The F₃⁻-centers are a chain of three F ions (two of them are found in anion positions, and one is interstitial) oriented along axis [111] [8]. The absorption bands of the acceptor centers lie in the range of 4.1 ((F₂⁻)_{ii}-centers) [9] and 6.2 (F₃⁻-centers) [8] eV, and are masked by strong bands of divalent RE²⁺ ions. The positions of the absorption bands of the acceptor centers in the AEF crystals were determined by subtracting the absorption spectra of radiation- and additive-

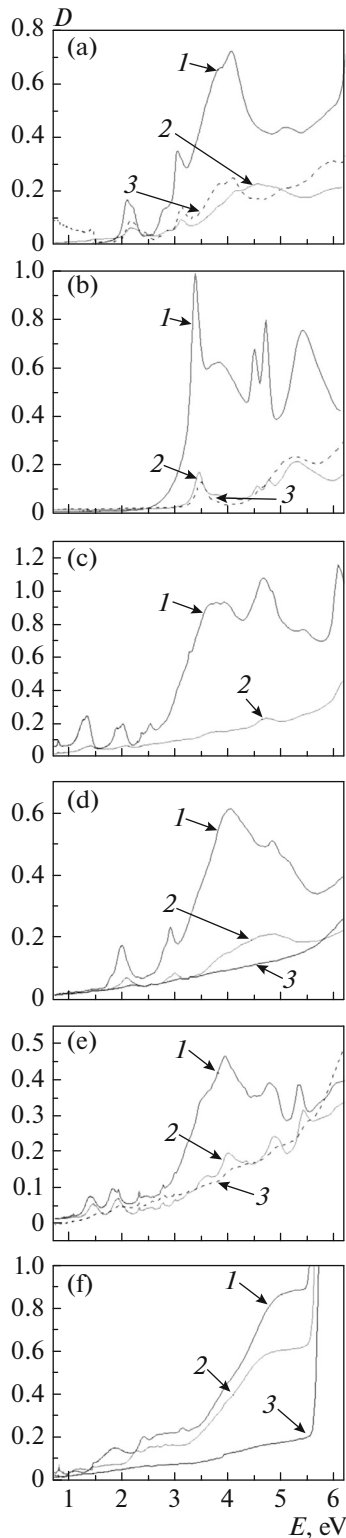


Fig. 1. Absorption spectra of radiation-colored (at room temperature) CaF_2 , SrF_2 , and BaF_2 crystals activated by trivalent Tm, Yb, Er, Sm, Ho, and Pr ions: (a) (1) CaF_2 -Tm, (2) SrF_2 -Tm, (3) BaF_2 -Tm; (b) (1) CaF_2 -Yb, (2) SrF_2 -Yb, (3) BaF_2 -Yb; (c) (1) CaF_2 -Er, (2) SrF_2 -Er, (3) BaF_2 -Er; (d) (1) CaF_2 -Sm, (2) SrF_2 -Sm, (3) BaF_2 -Sm; (e) (1) CaF_2 -Ho, (2) SrF_2 -Ho, (3) BaF_2 -Ho; (f) (1) CaF_2 -Pr, (2) SrF_2 -Pr, (3) BaF_2 -Pr. The spectra were measured at room temperature.

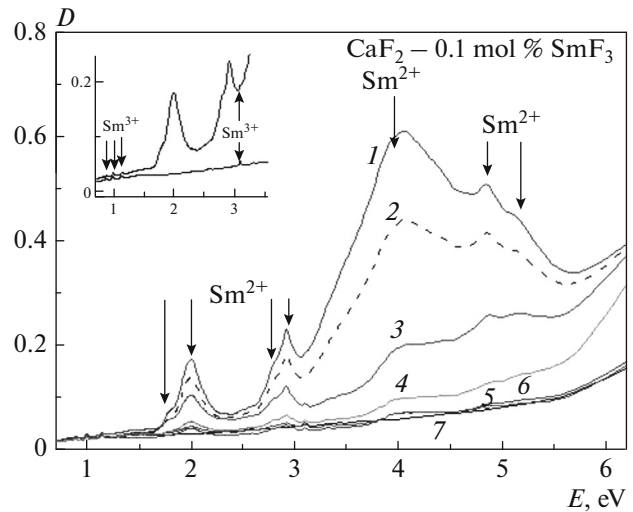


Fig. 2. Absorption spectra of CaF_2 - SmF_3 crystal measured after radiation coloring at (1) room temperature and after heating the colored crystal to (2) 100°C , (3) 200°C , (4) 250°C , and (5) 300°C . The spectra were measured at room temperature.

colored crystals [8, 9]. Additive coloring results in the formation of electron centers, while radiation coloring leads to the formation of electron and acceptor centers. The position of the absorption band is also similar for the AEF crystals activated by different RE ions [8, 10], in contrast to RE^{2+} absorption bands, which are distinct for different elements.

Divalent Rare-Earth Ions

The spectra of divalent RE ions (Sm, Ho, Er, Tm, Yb, Pr) of the CaF_2 , SrF_2 , and BaF_2 crystals are characterized by wide absorption bands in visible and UV ranges, and are caused by allowed transitions to mixed $4f$ - $5d$ -envelope [3, 8, 11–14].

The shift of the absorption band to the high-energy area in the CaF_2 - SrF_2 - BaF_2 series is caused by the crystalline field [15]. The CaF_2 crystals exhibit more efficient formation of induced centers than SrF_2 and BaF_2 crystals activated by the same impurities, due possibly to the increase in the density of the CaF_2 - SrF_2 - BaF_2 crystals. Along with absorption bands and transitions in Pr^{2+} ions in the range of 1–5 eV, the spectra of CaF_2 , SrF_2 , and BaF_2 crystals activated by Pr show intense absorption in a range of 6 eV caused by $4f$ - $5d$ transitions in Pr^{3+} -ions [16].

Figure 2 shows the curves of thermal destruction of the induced centers of the colored CaF_2 -Sm crystals. The bands of $4f^6$ - $4f^55d^1$ -transitions of Sm^{2+} are observed in the absorption spectra of CaF_2 - Sm^{3+} crystals after radiation coloring at room temperature [11]. Heating the crystals to 100°C reduces absorption in

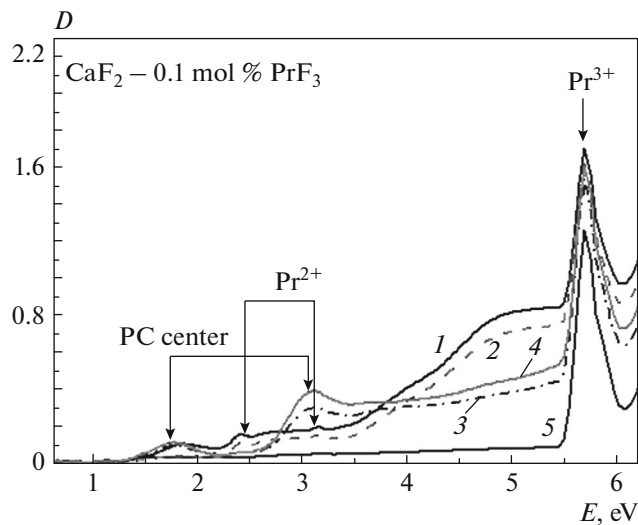


Fig. 3. Absorption spectra of $\text{CaF}_2\text{-PrF}_3$ crystal measured after radiation coloring at (1) room temperature and after heating the colored crystal to (2) 100, (3) 200, (4) 250, and (5) 300°C. The spectra were measured at room temperature.

the range of 4 eV, due to the destruction of $(\text{F}_2^-)_{ii}$ -centers [9]. The absorption band of the F_3^- -centers (the maximum of absorption band near 6 eV) is more thermally stable and is destroyed along with absorption bands of Sm^{2+} . The Sm^{2+} centers of the CaF_2 crystals are the most thermally stable of the investigated divalent ions of CaF_2 , SrF_2 , and BaF_2 crystals, and is destroyed upon heating the crystal to $\sim 700^\circ\text{C}$.

Upon heating the AEF crystals activated by Ho, Er, Tm, and Yb, the centers induced by X-ray radiation were destroyed as in the $\text{CaF}_2\text{-Sm}$ crystals. The temperatures of Ho^{2+} , Er^{2+} , Tm^{2+} , and Yb^{2+} destruction are shown in Table 1.

Figure 3 shows the curves of thermal destruction of irradiated $\text{CaF}_2\text{-Pr}$ crystals. Heating the colored crystal to 200°C alters the absorption spectra and results in the formation of the absorption band at 3 eV and the shift of maximum of the absorption band at 1.9 eV to the low-energy area. Further heating of the crystal destroyed the altered absorption spectra. All bands were destroyed upon heating to 300°C . The change in the absorption spectra was accompanied by variation

of the crystal's color. The crystal became gray and green after radiation and heating, respectively. This change in the crystal's color and its absorption spectra was observed during the formation of photochromic (PC) color centers in radiation-colored CaF_2 crystals activated by Y, La, Ce, Gd, Tb, and Lu [4, 5]. These studies also showed that the PC centers of radiation-colored CaF_2 crystals are destroyed at $300\text{--}350^\circ\text{C}$. In [16], Hayes reported that when impacting a CaF_2 crystal, trivalent Pr ions can either be reduced to the divalent state or participate in the formation of PC centers. However, no experimental results from studying these crystals were provided. It was also shown in [2, 6] that radiation coloring yields only Pr^{2+} ions from electron centers.

Neither the PC effect in $\text{CaF}_2\text{-Pr}$ crystals or the thermal destruction of the absorption spectra of induced centers in the temperature range of $80\text{--}300\text{ K}$ was studied in this work. These problems will be discussed in future works. At the same time, the character of the change of the absorption spectra upon heating a crystal, along with the temperature of the destruction of induced absorption bands, allows us to suggest that the bands with maxima of 3 and 1.7 eV belong to PC centers. No new bands were observed in the spectra of $\text{SrF}_2\text{-Pr}$ and $\text{BaF}_2\text{-Pr}$ crystals upon heating. The bands induced by radiation coloring were destroyed at 100°C .

Oxidation of the RE ions to trivalent state upon the heating of radiation-colored crystals is observed at various temperatures (see Table 1). We can see from the table that the temperatures of RE ion oxidation are different for each element.

Figure 4 compares the temperatures of oxidation of the divalent RE ions of CaF_2 crystals and their ionization potential [17]. It is known that ions with the higher third ionization potential are more stable in the divalent state [17]. The oxidation temperatures of La, Ce, Gd, and Tb ions were determined earlier in studying the PC centers of CaF_2 crystals [2, 5]. A comparison of the curves shows that oxidation of the RE ions upon the heating of CaF_2 crystals occurs at higher temperatures for the ions with the highest third ionization potential (Sm, Nd, Tm, Yb, Er), which form stable divalent compounds. The temperature resistance of the divalent RE ions of radiation-colored CaF_2 crystals correlates with the chemical stability of the

Table 1. Temperature of transformation $\text{RE}^{2+} \rightarrow \text{RE}^{3+}$ upon heating radiation-colored CaF_2 , SrF_2 , and BaF_2 crystals ($^\circ\text{C}$)

	Sm	Nd	Tm	Yb	Ho	Er	Pr
CaF_2	700	570	500	500	350	300	240 (Pr^{2+}) 300 (PC centers?)
SrF_2	600	520	400	250	200	250	100
BaF_2	300	470	300	200	100	Not induced	100

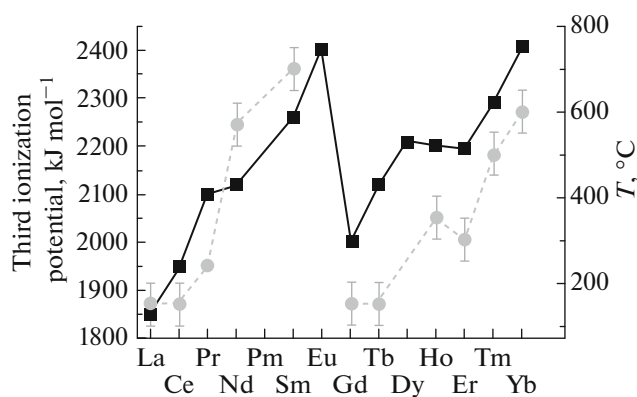


Fig. 4. Comparison of oxidation temperature of divalent RE ions in CaF_2 crystals and their third ionization potential [17].

compounds with divalent RE ions. The change in the valence of the RE ions is accompanied by the destruction of the acceptor centers produced along with divalent ions by irradiating crystals. Heating to a certain temperature thus results in the recombination of acceptor centers and divalent RE ions.

For ions with the lowest third ionization potential (La, Ce, Gd, Tb), this process is observed at lower temperatures and is accompanied by the formation of PC centers. There are two possible scenarios of the oxidation of divalent RE ions: (1) electron transfer from divalent RE ions on ionized PC centers and the formation of PC centers, and (2) the recombination of divalent RE ions with acceptor centers. Assuming that the temperatures of the transformation of ionized PC centers and the oxidation of divalent RE ions coincide, we may conclude that the first oxidation scenario is more likely.

CONCLUSIONS

The radiation coloring of CaF_2 , SrF_2 , and BaF_2 crystals activated by trivalent ions of RE elements results in the formation of divalent impurity ions, along with acceptor F_3^- - and $(\text{F}_2^-)_{\text{ii}}$ -centers. The divalent Sm ions in radiation-colored AEF crystals are the ones most thermally resistant. The temperature resistance of the divalent RE ions in radiation-colored CaF_2 crystals correlates with the chemical stability of compounds with divalent RE ions. The absorption

bands of PC centers were identified in the absorption spectra of the CaF_2 -Pr crystals.

ACKNOWLEDGMENTS

This work was performed on scientific equipment at the Shared Resource Center for Isotopic-Geochemical Research, Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences. It was supported by the Russian Foundation for Basic Research, project nos. 15-02-06514-a, 15-02-06666-a.

REFERENCES

1. McClure, D.S. and Kiss, Z., *J. Chem. Phys.*, 1963, vol. 39, p. 3251.
2. Merz, J.I. and Pershan, P.S., *Phys. Rev.*, 1967, vol. 162, p. 217.
3. Arkhangel'skaya, V.A., et al., *Opt. Spektrosk.*, 1967, p. 509.
4. Bugaenko, T.Yu., Radzhabov, E.A., and Ivashechkin, V.F., *Phys. Solid State*, 2008, vol. 50, p. 1671.
5. Sizova, T. and Radzhabov, E., *IEEE Trans. Nucl. Sci.*, 2012, vol. 59, p. 592098.
6. Catlow, C.R.A., *J. Phys. C*, 1979, vol. 12, p. 969.
7. Shcheulin, A.S., et al., *J. Opt. Soc. Am. B*, 2014, vol. 31, p. 248.
8. Radzhabov, E., *Opt. Spectrosc.*, 2016, vol. 120, p. 123.
9. Figura, P.V., Nepomnyashchikh, A.I., and Radzhabov, E.A., *Opt. Spektrosk.*, 1988, vol. 65, no. 4, p. 940.
10. Sizova, T., Radzhabov, E., Shendrik, R., Egranov, A., and Shalaev, A., *Radiat. Meas.*, 2016, vol. 90, p. 68.
11. Wood, D.L. and Kaiser, W., *Phys. Rev.*, 1962, vol. 126, p. 2079.
12. Lankhmanan, A.R. and Tiwari, S.S., *Radiat. Prot. Dosim.*, 1993, vol. 47, p. 243.
13. Weakliem, H.A. and Kiss, Z.J., *Phys. Rev.*, 1967, vol. 157, no. 2, p. 277.
14. Kaczmarek, S.M., Tsuboi, T., Ito, M., Boulon, G., and Leniec, G., *J. Phys.: Condens. Matter*, 2005, vol. 17, p. 3771.
15. Radzhabov, E. and Nepomnyashchikh, A., *Solid State Commun.*, 2008, vol. 146, p. 376.
16. Hayes, W. and Stoneham, A., in *Crystals with the Fluorite Structure: Electronic, Vibrational, and Defect Properties*, Hayes, W., Ed., Oxford: Clarendon Press, 1974.
17. Meyer, G., in *The Rare Earth Elements: Fundamentals and Applications*, Atwood, D.A., Ed., Chichester: Wiley, 2012, p. 1.

Translated by I.Yu. Melekestseva