Photochromism in Calcium and Strontium Fluoride Crystals Doped With Rare-Earths Ions

T. Sizova and E. Radzhabov

***Abstract*—This paper reports the absorption spectra of photochromic centers in CaF_2 and SrF_2 crystals doped with Ce^{3+} and Gd^{3+} impurities and thermal decay of the centers in temperature range 80–500 K. The ionized photochromic color centers are generated in crystals under low-temperature X-rays irradiation. These centers are transformed into photochromic color centers upon heating of crystals. All color centers decay at temperature about 500 K.**

***Index Terms*—Alkaline-earth fluorides, optical spectroscopy, radiation hardness, rare earths, scintillators, X-rays.**

I. INTRODUCTION

To improve the scintillation properties of alkaline-earth fluorides the doping of rare earth ions is used, although when employed with impurities doping reduces the radiation hardness of crystals. It is known, that in the crystals doped with such rare earth ions as La, Ce, Gd, Tb, Lu or yttrium the X-irradiation [1] or additive coloration [2]–[4] result in formation of photochromic centers (PC centers). Referring to optical and electron paramagnetic resonance (EPR) research, it has been suggested that the ionized (PC^+) and thermally stable photocromic centers in CaF_2 and SrF_2 crystals consist of one or two electrons bound at the anion vacancy adjacent to the trivalent impurity cation. Colored crystals exhibit a photochromic effect, i. e. they change color under exposure to light. This process is accompanied by a reversible transformation of PC center into the ionized PC center (PC^+ center) [2]. The mechanism for creating PC centers in X-irradiated crystals is not clear so far. It has been found that photocromic centers can be formed by the shallow trivalent traps, e. g. Y, La, Ce, Gd and Tb, which have the low third ionization potentials; the stronger traps with the higher ionization potentials will form divalent ions. Therefore, the anion vacancies created during x-irradiation in the crystals doped with trivalent impurities which do not change their positive charge. The optical properties of X-rays created photochromic centers and their thermal destruction in crystals of CaF_2, SrF_2, BaF_2 doped with La^{3+}, Y^{3+}, Lu^{3+} were studied in our previous papers [5], [6].

In this paper we discuss the data of studying photochromic color centers created by X-rays and their thermal decay at temperature range from 80 to 500 K in CaF_2 and SrF_2 crystals doped with Ce^{3+} and Gd^{3+}.

II. EXPERIMENTAL METHODOLOGY

The crystals of CaF_2 and SrF_2 doped with 0.01 to few mol. percent CeF_3 and GdF_3 were grown in vacuum in graphite crucible by the Stockbarger method. For the measurements the concentration of Ce and Gd was 0.3 mole% in SrF_2, while the concentrations of Gd-0.1% and Ce-0.3% in CaF_2 were chosen. Optical absorption was measure by Perkin-Elmer Lambda 950 spectrophotometer. The crystals were irradiated at 80 or 300 K by X-rays from Pd tube operating at 35 kV and 20 mA.

III. RESULTS

A. Optical Absorption Spectra of CaF_2 Doped With Gd^{3+}

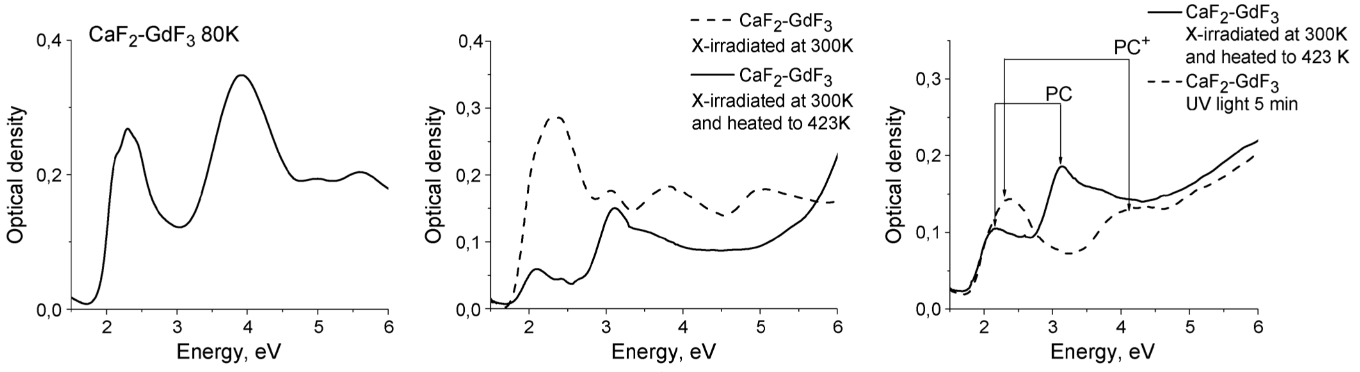
Fig. 1 illustrates the absorption spectra of X-irradiated CaF_2 doped with Gd^{3+}. The X-irradiation at 80 K of $CaF_2 - Gd^{3+}$ results in creation of absorption bands at 2.3 eV end 3.9 eV [Fig. 1(a)]. The absorption band 3.9 eV in the spectrum $CaF_2 - Gd^{3+}$ belongs to absorption V_k centers formed during irradiation process [7]. The absorption band at 2.3 eV consist of two peaks: at 2.2 eV belongs to 4f–5d transition of Gd^{2+} [8], [9], the origin of peak at 2.3 eV is unknown. But absorption bands Gd^{2+}, as well as the hole absorption at 3.9 eV are much stronger than the absorption bands in this region of the spectrum for the other rare-earth-doped CaF_2 crystals [7]. These features of absorption are also the case for the ions with low third ionization potentials (La, Lu and Y) [5], [6]. This fact can denote the contribution of the other centers absorbing within this region. The optical absorption spectrum of color centers in irradiated CaF_2 doped with Gd^{3+} at room temperature is demonstrated in Fig. 1(b). The absorption bands remain in the same region of the bands that are observed in irradiated crystals at 80 K. However, a new small peak is observed at 3.1 eV. The heating of the crystals to 400 K leads both to the appearance of absorption bands at about 2 eV and essential increase of the band at 3.1 eV [Fig. 1(b), solid curve]. These bands belong to the PC center [2]. If crystals of CaF_2 doped with Gd^{3+} are illuminated at room temperature with ultraviolet light the absorption of the PC decreases with growing absorption in the visible region and prominent absorption band at about 3.8 eV, which means absorption of the PC^+ center [Fig. 1(c)]. The process is reversed by absorption of visible light, or thermal energy.

Manuscript received November 05, 2011; revised January 19, 2012; accepted February 28, 2012. This work was supported by the Lavrentjev's grant of the Siberian Branch of Russian Academy of Science 7.11, and by the Russian Foundation for Basic Research 11-02-00717-a.

T. Sizova is with the Department of Physics of Monocrystals, Vinogradov Institute of Geochemistry, Irkutsk, 664033 Russia (e-mail: sizova@igc.irk.ru).

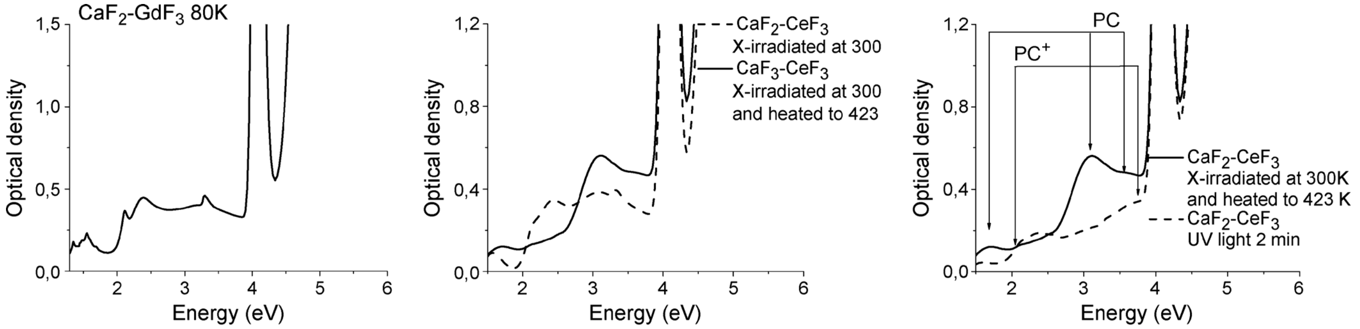
E. Radzhabov is with the Department of Physics of Monocrystals, Vinogradov Institute of Geochemistry, Irkutsk, 664033 Russia, and also with Irkutsk State University, Irkutsk 664003, Russia.

Digital Object Identifier 10.1109/TNS.2012.2190423



a b c

Fig. 1. Optical absorption of CaF_2 doped with Gd^{3+} a) after x-irradiation at 80 K, (b) after x-irradiation at 300 K (dashed curve) and after heating x-irradiated crystals to 423K (solid curve), (c) after heating x-irradiated crystals to 423K (solid curve) and after exposure of UV light (dashed curve).



a b c

Fig. 2. Optical absorption of CaF_2 doped with Ce^{3+} (a) after x-irradiation at 80 K, (b) after x-irradiation at 300 K (dashed curve) and after heating x-irradiated crystals to 423K (solid curve), (c) after heating x-irradiated crystals to 423K (solid curve) and after exposure of UV light (dashed curve).

B. *Optical Absorption Spectra of CaF_2 Doped With Ce^{3+}*

Fig. 2 displays the absorption spectra of X-irradiated CaF_2 doped with Ce^{3+}. The optical absorption spectrum of X-irradiated at 80K crystals of CaF_2 doped with Ce^{3+} contains a strong absorption band at 4 eV, which is due to the 4f–5d transition of the Ce^{3+} ion [10]; weaker absorption at 1.5 eV, is due to 4f–5d transitions of Ce^{2+} [11]; broad band with peaks at 2.1 eV end 2,3 eV is due to 4f–5d transition of Ce^{2+} [11]; and a broad band with two peaks at 3.2 eV and slight absorption at 3.7 eV [Fig. 2(a)].

Like in the case with crystals doped with La, Lu and Gd (as reported before) the absorption bands Ce^{2+} above 2 eV are much stronger than the absorption bands in the region of spectrum for the other rare-earth-doped CaF_2 crystals [7]. It can denote the contribution of the other centers absorbing in this region. The absorption spectra of X-irradiated at room temperature $CaF_2 - Ce^{3+}$ crystals [Fig. 2(b)] contains the bands, which remain at the same region of the bands observed in the irradiated crystals at 80 K. The heating crystals to 400K, like $CaF_2 - Gd^{3+}$, leads to the increase of band intensity at 3.2 eV and very poor absorption at 3.6 eV, both due to PC center [2]. The conversion of PC to PC^+ centers is presented in Fig. 2(c). With ultraviolet light at room temperature the absorption of the PC decreases with growing absorption of PC^+ centers. Their spectra are similar to the absorption of X-irradiated crystals at 80K. Comparison of the data in Figs. 1(c) and 2(c) (dashed curves) with Figs. 1(a), 2(a) indicates that the spectra of optical absorption induced by X-irradiation at 80 K are quantitatively similar to those of PC^+ centers of corresponding crystals. Thus, it can be concluded that by X-irradiation of CaF_2 doped with Ce^{3+} and Gd^{3+} at 80 K the PC^+ centers are formed.

C. *Optical Absorption Spectra of SrF_2 Doped With Gd^{3+} and Ce^{3+}*

The crystals of SrF_2 doped with Gd^{3+} and Ce^{3+} become colored only after X-irradiation at 80 K. The energies of the absorption bands of the SrF_2 doped with Gd^{3+} (2 eV, 3.8 eV, 4.8 eV) are close to those of PC^+ centers of irradiated CaF_2 doped with Gd^{3+} at 80 K [Fig. 1(a)]. Thermal decay of absorption band is given in Fig. 3(a), were the peaks are annealed alike. A shift of absorption peak at 3.8 eV at temperatures over 130 K can be due to annealing of V_k centers. The ionizing photochromic color centers are destructed at higher temperatures.

X-irradiation of the SrF_2 crystals doped with Ce^{3+} at 80K results in creating absorption bands at 2.3 eV, 3.4 eV and 4.3 eV. The strong absorption at 4.3 eV is due to 4f–5d transition of Ce^{3+}. Thermal annealing of the color centers in SrF_2 doped with Ce^{3+} is yielded in Fig. 3(b). The peak at 3.4 eV decreases faster than the 2.3 eV band. This means that these bands belong to different color centers and lie in the region of PC^+ centers absorption of CaF_2 doped with Ce^{3+} [Fig. 2(a)]. However at present the nature of these bands is not recognized yet.

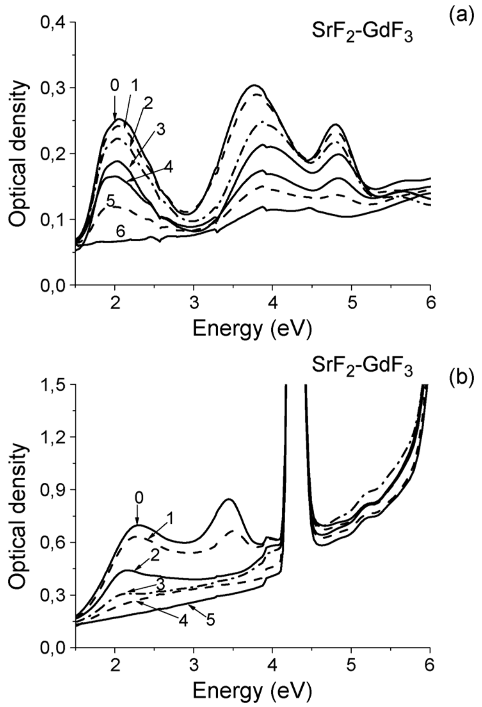


Fig. 3. Thermal decay of color centers SrF_2 doped with Gd^{3+} (a) and Ce^{3+} (b) crystals. Curve 0 is the absorption after irradiation at 80 K, 1-heating crystals to 123K, 2–158K, 3–192K, 4–220K, 5–248K, 6–273K.

IV. DISCUSSION

The absorption bands of PC^+ centers in CaF_2 doped with Ce^{3+} and Gd^{3+} were identified by linear dichroism investigation in additively colored crystals of rare-earth-doped CaF_2 [2]. The absorption band of PC^+ center in the visible region is very wide. Based on the investigation of optical absorption of rare-earth-doped CaF_2 after X-irradiation at 80 K by Merz and Pershan [7] it was also concluded that the other centers absorbing in the same region contribute to the region of absorption of divalent Ce and Gd, like for divalent La, Tb. Acquired data and experimental results allowed the inference that the PC^+ centers are formed by X-irradiation of CaF_2 doped by Ce^{3+} and Gd^{3+} as well as SrF_2 doped with Gd^{3+} at 80 K. The energy of absorption bands of PC and PC^+ centers are tabulated in Table I. The positions of absorption bands of PC and PC^+ centers in CaF_2 doped with Ce^{3+} and Gd^{3+} agree with the literary data [2]. There are no literary data on the PC and PC^+ centers for SrF_2 but the shift of the absorption bands in $SrF_2 - Gd^{3+}$ to longer wavelength relative to the bands of PC^+ centers in $CaF_2 - Gd^{3+}$ confirm the assignment of the band in $SrF_2 - Gd^{3+}$ to PC^+ centers.

Since the PC center consist of two electrons bound at anion vacancy adjacent to the trivalent impurity cation [2], the formation PC^+ centers can be described as

$$RE^{3+} \xrightarrow{XRays} RE^{3+} + e^- + V_a + F_i^0 \rightarrow PC^+ + F_i^0$$

On heating crystals to 400 K the PC^+ centers are transformed into PC centers:

$$PC^+ + e^- \rightarrow PC.$$

TABLE I
ABSORPTION BANDS OF PC AND PC^+ CENTERS IN X-IRRADIATED CaF_2 AND SrF_2

		CaF_2	SrF_2
Ce^{3+}	PC centers	1.7 eV 3.2 eV 3.6 eV	not observed
	PC^+ centers	2.1 eV 3.7 eV	?
Gd^{3+}	PC centers	2.1 eV 3.1 eV 3.7 eV	not observed
	PC^+ centers	2.2 eV 3.9 eV 4.3 eV	2 eV 3.8 eV 4.8 eV

TABLE II
FORMATION OF PHOTOCHROMIC CENTERS IN X-IRRADIATED ALKALINE-EARTH FLUORIDES

Impurity	CaF_2	SrF_2	BaF_2
Y	PC^+ 80K [5] PC 300K [1,5]	PC 300K[5]	not observed
La	PC^+ 80K [5] PC 300K [5]	PC^+ 80K [5]	
Ce	PC^+ 80K PC 300K	?	
Gd	PC^+ 80K PC 300K	PC^+ 80K	
Tb	PC^+ 80K PC 300K	not investigated	
Lu	PC^+ 80K [6] PC 300K [6]	not observed	

The photochromic behavior of these crystals arises from ionization of PC centers, forming PC^+ and trapping the ionized electron on the isolated RE^{3+} ion:

$$PC + RE^{3+} \underset{VIS,kT}{\overset{UV}{\rightleftarrows}} PC^+ + RE^{2+}$$

The data on formation of photochromic color centers in crystals of alkaline-earth fluorides doped with trivalent rare-earth ions are summarized in Table II. The PC centers are formed in CaF_2 doped with Y, La [5], Ce, Gd, Tb and Lu [6] at room temperature, while at 80K the PC^+ center in these crystals are formed. In SrF_2 the PC centers are formed in the crystals doped with Y [5] and PC^+ centers are formed in SrF_2 doped with La [5] and Gd. In BaF_2 crystals neither PC nor PC^+ centers are observed. The PC centers are created in combining the rare-earth ion and fluorine vacancy. We assume that loose lattice of BaF_2 favors a lower probability of combining the rare-earth ion and fluorine vacancy, therefore PC centers are not formed in these crystals.

V. CONCLUSION

After x-irradiation at 80K the optical absorption of PC^+ centers is observed in CaF_2 doped with Ce^{3+}, Gd^{3+}. At temperatures 350–450 K the PC^+ centers are transforms into PC centers. $SrF_2 - Ce^{3+}$, $SrF_2 - Gd^{3+}$ cannot be colored by X-irradiation at 300 K. The absorption bands of PC^+ centers were recognized in SrF_2 doped by Gd^{3+} after x-irradiation at 80K. Their absorption bands are shifted to the lower energy relative to the absorption bands of PC^+ in CaF_2. In SrF_2 doped with Ce^{3+} the absorption bands at 2.3 eV, 3.4 eV and 4 eV (4d–5f transition of Ce^{3+}) are the case. The nature of the band at 2.3 eV and 3.4 eV has not been identified yet. This is to be implemented in the future research.

REFERENCES

[1] J. R. O. Connor and J. H. Chen, "Color centers in alkaline earth fluorides," *Phys. Rev. B*, vol. 130, pp. 1790–1791, 1963.

[2] D. L. Staebler and S. E. Schnatterly, "Optical studies of a photochromic color center in rare-earth-doped CaF_2," *Phys. Rev. B.*, vol. 3, pp. 516–527, 1971.

[3] C. H. Anderson and E. S. Sabisky, "EPR studies of photochromic CaF_2," *Phys. Rev. B.*, vol. 3, pp. 536–545, 1971.

[4] R. C. Alig, "Theory of photochromic centres in CaF2," *Phys. Rev. B.*, vol. 3, pp. 536–545, 1971.

[5] T. Y. Bugayenko, E. A. Radzhabov, and V. P. Ivashechkin, "Temperature decay of photochromic clor centers," *Phys. Solid State*, vol. 50, no. 9, pp. 1671–1673, 2008.

[6] T. Y. Sizova and E. A. Radzhabov, "The investigation of photochromism in CaF_2, SrF_2, BaF_2," in *Book of Abstracts of XIV Int. Feofilov Symp.*, 2010, vol. 138.

[7] J. L. Merz and P. S. Pershan, "Charge conversion of irradiated rare earth ions in CaF_2," *Phys. Rev.*, vol. 162, no. 9, pp. 217–235, 1967.

[8] D. S. McClure and Z. Kiss, "Survey of the spectra of the divalent rare-earth ions in cubic crystals," *J. Chem. Phys.*, vol. 39, no. 12, pp. 3251–3257, 1963.

[9] K. E. Johson and J. N. Sandoe, "An interpretation of the spectra of bivalent rare-earth ions in crystals," *J. Chem. Soc.*, vol. (A), pp. 1694–1697, 1969.

[10] E. Loh, "Ultraviolet absorption spectra of Ce^+ in alkaline-earth fluorides," *Phys. Rev.*, vol. 154, pp. 270–276, 1967.

[11] R. C. Alig, Z. J. Kiss, J. P. Brown, and D. S. McClure, "Energy levels of Ce^{2+} in CaF_2," *Phys. Rev.*, vol. 186, pp. 276–284, 1969.