ISSN 1063-7834, Physics of the Solid State, 2008, Vol. 50, No. 9, pp. 1671–1673. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © T.Yu. Bugaenko, E.A. Radzhabov, V.F. Ivashechkin, 2008, published in Fizika Tverdogo Tela, 2008, Vol. 50, No. 9, pp. 1607–1609.

PROCEEDINGS OF THE XIII FEOFILOV SYMPOSIUM "SPECTROSCOPY OF CRYSTALS DOPED BY RARE-EARTH AND TRANSITION-METAL IONS"

(Irkutsk, July 9–13, 2007)

Thermal Decay of Photochromic Color Centers in CaF_2, SrF_2, and BaF_2 Crystals Doped by La and Y Impurities

T. Yu. Bugaenko, E. A. Radzhabov, and V. F. Ivashechkin

Vinogradov Institute of Geochemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1A, Irkutsk, 664033 Russia

e-mail: eradzh@igc.irk.ru

Abstract—The absorption spectra of photochromic centers in CaF_2, SrF_2, and BaF_2 crystals doped by La and Y impurities and thermal decay of the centers in the temperature range 80–600 K are investigated. Under low-temperature x-ray irradiation, ionized photochromic color (PC^+) centers are generated in La- and Y-doped CaF_2 crystals and in a La-doped SrF_2 crystal. It is revealed that, upon heating of the CaF_2–LaF_3 crystal, PC^+ centers are transformed into photochromic color (PC) centers. In the SrF_2–YF_3 crystal irradiated at room temperature, photochromic color centers are generated as well. All color centers decay at a temperature of approximately 600 K. After irradiation of the BaF_2–YF_3 crystal at a temperature of 80 K, absorption bands are observed at energies of 2.25 and 3.60 eV, which are related to neither PC centers nor PC^+ centers.

PACS numbers: 78.70.-g, 78.70.Dm

DOI: 10.1134/S1063783408090151

1. INTRODUCTION

Barium fluoride BaF_2 is known as the fastest inorganic scintillator. An important factor limiting the use of the BaF_2 fluoride as a fast scintillator is that it has an intense slow luminescence component (approximately 620 ns) due to self-trapped anion excitons. The suppression of the undesirable prolonged luminescence in barium fluoride at a wavelength of 310 nm with retention of the specific light yield of the fast component can be achieved by introducing rare-earth impurities into the matrix of the crystal [1]. It is known that additive coloration of the calcium fluoride CaF_2 doped by La, Ce, Gd, Tb, Lu, and Y impurities, as well as radiation-induced coloration of the CaF_2, SrF_2, and BaF_2 fluorides doped by yttrium, results in the formation of photochromic color (PC) centers [2, 3]. A photochromic color center consists of two electrons captured by a complex nucleus composed of a rare-earth ion and the nearest neighbor anion vacancy [4]. Colored crystals exhibit a photochromic effect; i.e., they change color under exposure to light. This process is accompanied by a reversible transformation of a PC center into an ionized PC (PC^+) center [2].

The objective of this work was to investigate the optical absorption of photochromic color centers and their thermal decay at temperatures in the range from 80 to 600 K in radiation-colored crystals CaF_2, SrF_2, and BaF_2 doped by trivalent ions La^{3+} and Y^{3+}.

2. SAMPLE PREPARATION AND EXPERIMENTAL TECHNIQUE

Calcium, strontium, and barium fluoride crystals doped by lanthanum and yttrium impurities served as the object of our investigation. The concentration of La and Y impurities was 0.1 mol % in calcium fluoride and approximately 1.0 mol % in strontium and barium fluorides. The crystals were grown under vacuum in a graphite crucible according to the Stockbarger technique. The absorption spectra were measured on a Specord UV–VIS spectrophotometer in the range 1.5–6.0 eV. The samples were exposed to x-ray irradiation (35 kV, 20 mA, Pd) at room temperature and at 80 K.

3. RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra of the CaF_2, SrF_2, and BaF_2 crystals doped by LaF_3 and YF_3 impurities and irradiated at temperatures of 80 and 300 K. The energies of the observed bands are presented in the table. The absorption bands in the spectra of the CaF_2–LaF_3 and CaF_2–YF_3 crystals irradiated at room temperature (Fig. 1b) are shifted toward lower energies with respect to the bands observed in the spectra of the same crystals irradiated at a temperature of 80 K (Fig. 1a). In the spectra of the additively colored crystals of calcium fluoride doped by La and Y impurities, absorption bands of photochromic color centers were observed at energies of 1.6, 3.1, and 4.8 eV (CaF_2–LaF_3) and 2.1, 3.1, and 3.6 eV (CaF_2–YF_3) [2]. It is known that, under exposure to light, PC centers are transformed into PC^+

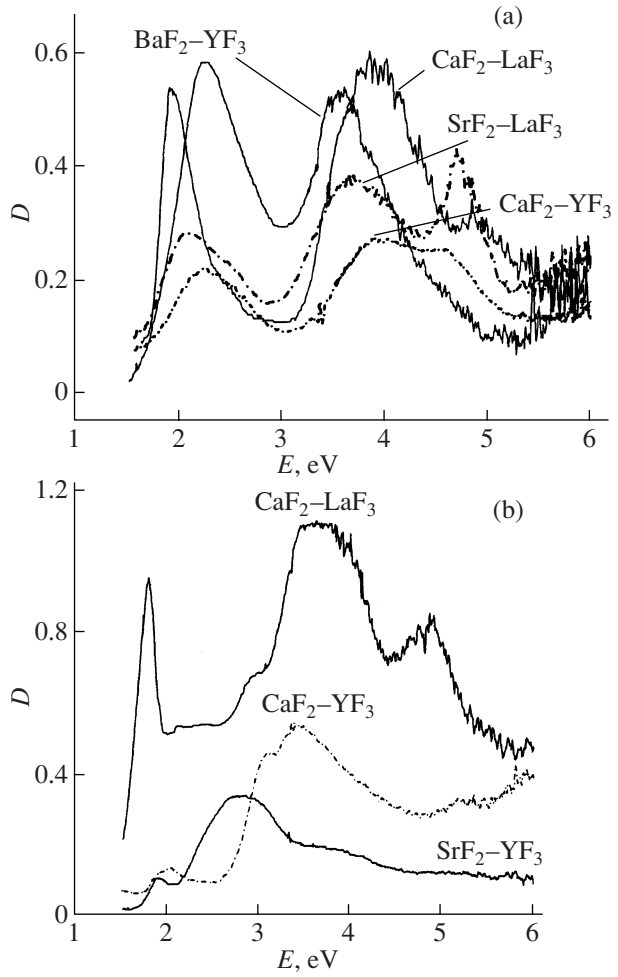

Fig. 1. Absorption spectra of the CaF_2, SrF_2, and BaF_2 crystals doped by LaF_3 and YF_3 impurities: (a) after irradiation at a temperature of 80 K (the spectra were measured at 80 K) and (b) after irradiation at a temperature of 300 K (the spectra were measured at 300 K).

centers. The absorption bands of PC^+ centers are shifted toward higher energies with respect to the absorption bands of PC centers. In CaF_2–LaF_3 crystals, the absorption bands of PC^+ centers were observed at energies of 1.8, 3.8, and 4.9 eV [2]. The absorption bands observed

Energies of absorption bands in the spectra of CaF_2, SrF_2, and BaF_2 crystals doped with LaF_3 and YF_3 impurities and irradiated at temperatures of 80 and 300 K

80 K		300 K	
crystal	*E*, eV	crystal	*E*, eV
CaF_2–LaF_3	2, 3.9, 4.8	CaF_2–LaF_3	1.8, 3.7, 4.8
CaF_2–YF_3	2.2, 3.9, 4.6	CaF_2–YF_3	2, 3, 3.5
SrF_2–LaF_3	2.1, 3.7, 4.7	SrF_2–LaF_3	1.9, 2.9, 3.7
BaF_2–YF_3	2.25, 3.6		

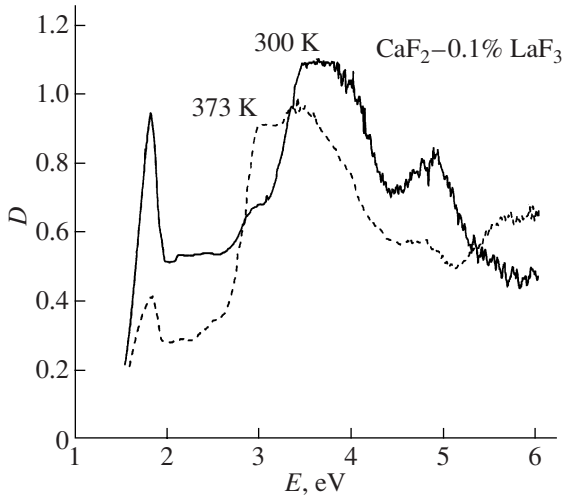

Fig. 2. Absorption spectra of the CaF_2–LaF_3 crystal irradiated at a temperature of 300 K and heated to 373 K. The spectra were measured at T = 300 K.

upon irradiation of the CaF_2–LaF_3 crystal at a temperature of 80 K in our study (see table) are assigned to PC^+ centers. Upon heating of the CaF_2–LaF_3 crystal, the spectrum is shifted toward lower energies, which indicates a transformation of color centers: PC^+ centers are transformed into PC centers (Fig. 2).

The analysis of the absorption spectra of the CaF_2–YF_3 crystal has demonstrated that irradiation of the crystal at 80 K gives rise to PC^+ centers (Fig. 1a), whereas irradiation at 300 K results in the appearance of the bands attributed to PC centers (Fig. 1b).

The energies of the absorption bands of the SrF_2–LaF_3 crystal are close to those of the CaF_2–LaF_3 crystal irradiated at 80 K (see table); i.e., the irradiation of the SrF_2–LaF_3 crystal results in the formation of PC^+ centers. The crystal becomes colored only at a temperature of 80 K.

Upon radiation-induced coloration of the SrF_2–YF_3 crystal, absorption bands of photochromic color centers were observed at energies of 2.0, 2.6, and 3.6 eV [3]. Our studies revealed that the absorption spectra of the SrF_2–YF_3 crystal irradiated at room temperature contain bands at energies of 1.9 and 2.9 eV and a weak maximum at 3.7 eV. These bands are attributed to PC centers. In contrast to the data reported in [3], our SrF_2–YF_3 crystals did not become colored at 80 K.

Irradiation of the BaF_2–YF_3 crystal leads to the appearance of absorption bands at energies of 2.25 and 3.60 eV. These bands are attributed to neither PC centers (1.7, 2.2, 2.7, 4.7 eV [3]) nor PC^+ centers. Similar results were obtained earlier in studies of BaF_2–LaF_3 crystals [5]. The nature of these bands remains unknown.

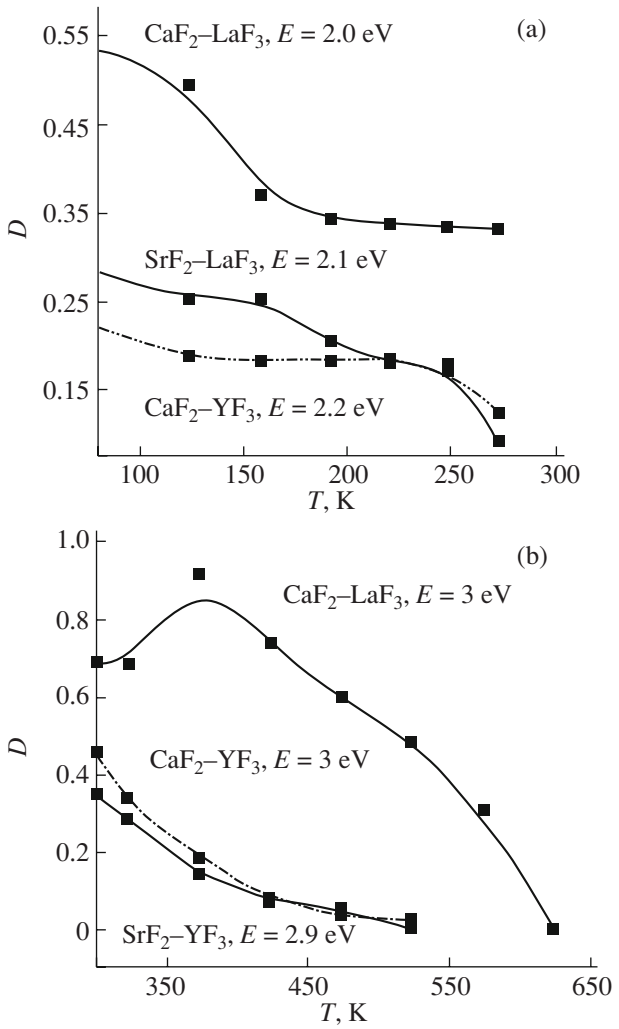

Fig. 3. Thermal decay of photochromic color centers in CaF_2–LaF_3, CaF_2–YF_3, SrF_2–LaF_3, and SrF_2–YF_3 crystals irradiated at temperatures of (a) 80 and (b) 300 K.

Figure 3a shows the thermal decay curves of PC^+ centers in the CaF_2–LaF_3, CaF_2–YF_3, and SrF_2–LaF_3 crystals irradiated at 80 K. Upon irradiation of the CaF_2–LaF_3 crystal at 300 K and its subsequent heating to 373 K, PC^+ centers are transformed into PC centers and, then, the latter centers decay. A similar decay of PC centers is observed in the CaF_2–YF_3 and SrF_2–YF_3 crystals irradiated at 300 K (Fig. 3b).

4. CONCLUSIONS

Thus, it has been found that x-ray irradiation at 80 K leads to the formation of PC^+ centers in La- and Y-doped CaF_2 crystals and in a La-doped SrF_2 crystal. At temperatures in the ranges 350–450 K (in CaF_2–LaF_3) and 250–350 K (in CaF_2–YF_3), PC^+ centers are transformed into PC centers. Photochromic color centers are also generated in the SrF_2–YF_3 crystal irradiated at room temperature, whereas the crystal irradiated at 80 K does not become colored. All color centers decay upon heating of the crystals to approximately 600 K.

For the BaF_2–YF_3 crystal irradiated at 80 K, absorption bands are observed at energies of 2.25 and 3.60 eV. These absorption spectra are assigned to neither PC centers nor PC^+ centers.

ACKNOWLEDGMENTS

This study was supported by the Russian Foundation for Basic Research (project no. 07-02-01057).

REFERENCES

1. B. P. Sobolev, E. A. Krivandina, S. E. Derenzo, W. W. Moses, and A. C. West, in *Proceedings of the MRS Symposium on Scintillator and Phosphor Materials Pittsburgh, PA, United States, 1994* (Pittsburgh, 1994), Vol. 348, p. 277.
2. D. L. Staebler and S. E. Schnatterly, Phys. Rev. B: Solid State **3**, 516 (1971).
3. J. R. O'Connor and J. H. Chen, Phys. Rev. **130**, 1790 (1963).
4. *Crystals with Fluorite Structure*, Ed. by W. Hayes (Clarendon, Oxford, 1974).
5. E. A. Radzhabov, A. Shalaev, and A. I. Nepomnyashikh, Radiat. Meas. **29**, 307 (1998).

Translated by V. Artyukhov