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Defect formation in BAF_2 crystals doped with cadmium

A.I. Nepomnyashchikh[a], E.A. Radzhabov[a], A.V. Egranov[a,*], V.F. Ivashechkin[a], A.S. Istomin[a], T. Kurobori[b]

[a] *Vinogradov Institute of Geochemistry, Russian Academy of Sciences, Favorskii street 1a, P.O. Box 4019, Irkutsk 664033, Russia*
[b] *Department of Materials Science and Engineering, Kanazawa University, Kakuma-machi, Kanazawa-shi 920-1192, Japan*

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Abstract

Defect formation in BaF_2 single crystals doped with cadmium is investigated by optical absorption, electron paramagnetic resonance (EPR) and thermoluminescence. An optical absorption band observed in X-irradiated at 295 K crystals CaF_2 (at 3.8 eV), SrF_2 (at 3.95 eV) and BaF_2 (at 4.08 eV) is assigned to absorption of Cd^+-ions. In addition, two type hole centers: pure V_k and perturbed V_k-centers, are observed in BaF_2–1%CdF_2 crystals X-irradiated at 77 K.

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Keywords: Barium fluoride; Absorption; EPR; Luminescence

1. Introduction

BaF_2 single crystals are applied as scintillation materials for gamma-ray detection in many high-energy physics experiments. Fast timing is possible with these crystals because the very short decay time of about 0.8 ns of luminescence at 195 and 220 nm which is due to cross-luminescence transitions. BaF_2 also has an intense, slow-emission component at about 300 nm with a decay time of about 620 ns at room temperature which is due to self-trapped exciton emission. The self-trapped exciton emission is significantly suppressed in crystals of BaF_2 doped with cadmium [1].

We have investigated the defects created in the BaF_2 crystals doped with cadmium by X-irradiation using EPR, optical absorption and TL measurements.

2. Experimental technique

The crystals of undoped BaF_2 and doped with cadmium (with the concentration of cadmium up to 2 mol%) were grown using the combined Shteber–Stockbarger method. The samples were of high optical quality and no indication of oxygen

*Corresponding author. Tel.: +7-3952-511466; fax: +7-3952-464050.
E-mail address: ainep@igc.irk.ru (A.V. Egranov).

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contamination. Unirradiated (as-grown) crystals are transparent in visible and VUV spectral regions. A weak shift of fundamental absorption is only observed in these crystals. The EPR experiments were carried out on an X-band spectrometer (RE-1306) in connection with a cryostat suitable for temperatures 77 and 295 K. The absorption spectra were taken with a "Specord" spectrophotometer. The crystals were irradiated by X-rays from a Pd tube operating at 40 kV and 40 mA.

3. Results

X-irradiation of barium fluoride crystals doped with cadmium at room temperature produces a new absorption band at 4.1 eV (Fig. 1, curve 3). In some cases an additional absorption band at about 3.4 appeared after such a procedure. These results are close to those obtained in Ref. [1] and the band was attributed by Springis et al. [1] to absorption of Cd^{+} -ions. For comparison, we have also investigated the formation of Cd^{+}-centers by X-irradiation at room temperature in other alkaline earth fluoride crystals doped with cadmium. Similar bands, which are shifted to lower energy, are appeared in CaF_2 and SrF_2 doped with cadmium (Fig. 1). The peak position of optical absorption bands of Cd^{+}-centers in alkaline earth fluorides is shown in Table 1.

The EPR spectrum of BaF_2 crystals doped with cadmium after X-irradiation at 295 K is shown in Fig. 2. The simplest structure is observed for $B\|\langle 100\rangle$. The spectrum measured with $B\|\langle 100\rangle$ exhibits a well-resolved structure consisting of nine equally spaced (79×10^{-4} T) lines. This indicates a superhyperfine (SHF) interaction with eight equivalent fluorine nuclei and, therefore, Cd^{+} substitutes for a Ba^{2+}. The results are in agreement with those obtained previously [2].

X-irradiation of undoped BaF_2 at 77 K produces self-trapped hole (V_k) and F-centers [2]. No EPR or optical absorption which could be associated with F-centers were observed in BaF_2 crystals doped with cadmium X-irradiated at 77 K. The optical absorption spectrum consists of the strong absorption at 4.1 eV at 77 K, which is

Table 1
Peak position E and half-width ΔH of optical absorption bands of Cd^{+}-centers in alkaline earth fluorides

	300 K		77 K	
	E (eV)	ΔH (eV)	E (eV)	ΔH (eV)
CaF_2	3.8	0.6		
SrF_2	3.95	0.6		
BaF_2	4.08	0.64	4.1	0.54

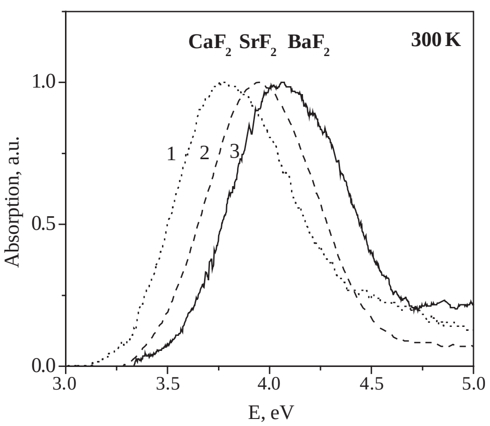

Fig. 1. Optical absorption spectra of Cd^{+}-centers at room temperature of CaF_2 (1), SrF_2 (2) and BaF_2 (3) crystals X-irradiated at 395 K.

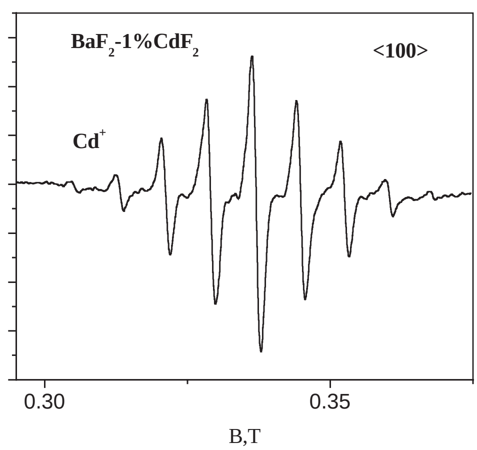

Fig. 2. EPR spectrum of Cd^{+}-ions in BaF_2 crystals at room temperature $B\|\langle 100\rangle$.

associated with Cd^+-centers and is slightly shifted to higher energy as compared with room temperature (Table 1), and the weaker absorption at 3.4 eV (Fig. 3), which is due to the absorption of self-trapped holes (V_k-centers) [3]. The strong EPR lines of two-type hole centers: pure V_k and perturbed V_k-centers (hereafter V-type centers) and the weaker lines of Cd^+ are observed in these crystals after X-irradiation at 77 K. The structure of the V-type centers will be considered later on.

Thermal annealing at about 130 K (the temperature range of decomposition of "pure" V_k-centers) leads to the destruction only some of the V_k-type and Cd^+-centers. The main part of Cd^+-centers is destroyed at about 260 K simultaneously with thermal destruction of V-type centers (Fig. 4) (EPR signal of the V-type centers is somewhat similar to V_k-centers in pure BaF_2). Some Cd^+-centers remain after heating to room temperature. No paramagnetic hole centers survive to room temperature so that it is apparent that some of the holes created at 77 K exist at room temperature in a nonparamagnetic state. It should be emphasized that the V-type centers (at least for the most part) are not formed by thermal destruction of pure V_k-centers. As pure V_k-centers they are formed immediately after X-irradiation at 77 K.

However, the thermoluminescence glow curve of X-irradiated BaF_2–1% CdF_2 crystals at 77 K shows only a weak peak (as compared with pure BaF_2), which is associated with the destruction of V_k-centers. No peak which could be associated

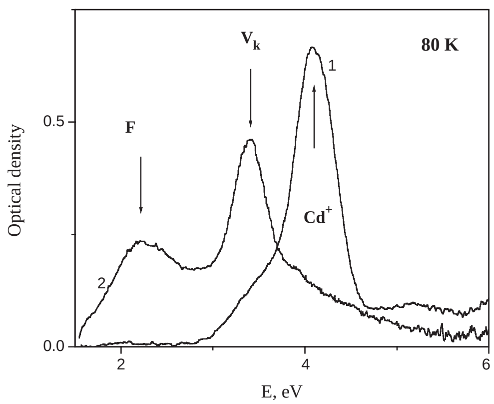

Fig. 3. Optical absorption spectra of BaF_2–1%CdF_2 (1) and pure BaF_2 (2) (for comparison) X-irradiated at 80 K.

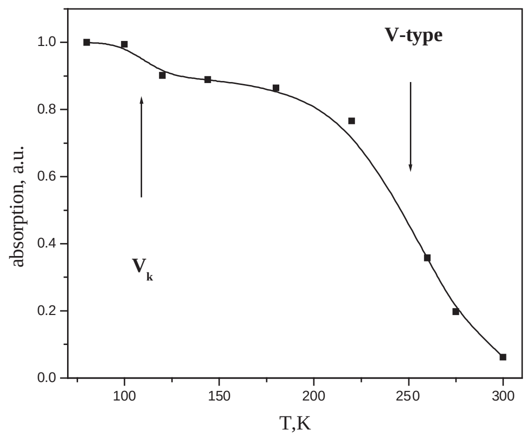

Fig. 4. Temperature annealing of Cd^+-centers in BaF_2 as determined by absorption.

with V-type centers is observed in BaF_2 crystals doped with cadmium X-irradiated at 77 K in the temperature range from 160 to 300 K.

By this it meant that, in contrast to the pure self-trapped holes (V_k-centers), the perturbed self-trapped holes (V-type centers) are not directly implicated in the radiative recombination processes. A similar effect has been reported in BaF_2 doped with lanthanum [4]. In this crystal, the self-trapped holes associated with charge-compensating interstitial fluoride ions (F_i^-) have not efficiently taken part in the radiative recombination processes.

Furthermore, from the facts that only a few number of pure V_k-centers are observed after X-irradiation at 77 K of BaF_2–1% CdF_2 and the lack of F-centers in these crystals (Fig. 3), it is conceivable that the most part of Cd^+-centers are formed by nonradiative decay of self-trapped excitons rather than by simple capture of an electron. However, no difference between the two types of Cd^+-centers formed are detected.

4. Conclusion

The exciton emission in BaF_2 can be considerably suppressed by doping with La [5,8], Cd [1], or Mg, Sr [6,7]. We found that the suppression of the exciton emission in BaF_2–LaF_3 [4] and BaF_2–CdF_2 accompany by the formation of V-type centers, which have the structure related to that of the V_k-center. In contrast to pure V_k-centers, no emission is observed in thermoluminescence at recombination at these hole centers with the electron. Therefore, such doping leads also to the suppression of the thermoluminescence. This raises the question of whether there is an interrelation between the suppression of the exciton emission and the suppression of thermoluminescence. As a check on this assumption, we plan to investigate in more detail, the V-type centers in BaF_2–LaF_3 and BaF_2–CdF_2 crystals.

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