

Radiation defects in BaF₂–Cd

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Received 26 September 2013, revised 12 December 2013, accepted 10 June 2014

Published online 4 July 2014

Keywords EPR, fluorides, luminescence, radiation defects

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Radiation defects in barium fluoride single crystals doped with cadmium have been investigated by luminescence and absorption spectroscopy, as well as by electron spin resonance spectroscopy. Three types of Cd⁺ centers differing by the local environment with the point symmetries O_h, C_{3v} and C_{2v} have been identified, although in barium fluoride crystals doped with

cadmium only the cubic Cd⁺ centers are usually formed, as was reported in the previous paper [J. Phys.: Condens. Matter **20**, 465213 (2008)]. We believe that these features may arise from the difference in the spatial distribution of the impurities in the crystals.

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1 Introduction It has been found that alkaline earth fluoride crystals that have not been deliberately doped with impurities are much less susceptible to coloration at room temperature by X-irradiation than most alkali halides. Undoped CaF₂ and SrF₂ crystals may be colored by X-rays much more readily at 4 K or at 77 K than at room temperature but the coloration efficiency, especially in the case of CaF₂ is still much slower than in most alkali halides [1, 2]. The extremely slow coloration rate of undoped alkaline earth fluorides by X-irradiation is due to inefficient separation of close F–H pairs. It has also been found [3, 4] that the holes complementary to the F centers produced by X-irradiation at both 77 and 4 K are V_k centers. In alkali halides, by contrast, the irradiation in the helium temperature range generally produces more H centers than V_k centers [5].

Introduction of some cationic impurities in alkaline fluorides leads to a significant increase in coloration of the crystals by ionized irradiation. It has been found that in some cases the composition of the radiation defects includes anion vacancies that in general is unusual, as in the undoped crystals, they are not created with such efficiency. Some propositions on the matter were made by us in the previous papers [6–8]. The influence of cationic impurities on the formation of intrinsic defects in the anion sublattice can be reduced to two essentially different processes:

(i) The centers, including the impurity ion and anion vacancy are created at the temperatures higher than the onset of the motion of anion vacancies. The onset of the motion of anion vacancies in CaF₂ crystal is at about 200 K. In this case,

the formation of anion vacancies is presumably due to the nonradiative decay of self-trapped excitons [1, 9]. Impurity charge defects stimulate the separation of charged intrinsic α–I(F^{–i}) defects [6, 7] by their electric fields. The formation of F_{2A}⁺ in CaF₂–Na [10], Cd⁺(C_{3v}) in CaF₂ and SrF₂ [6, 7] and Mn/F-centers in CaF₂–Mn [11] is apparently connected with the motion of anion vacancies.

(ii) The centers, including the impurity ion and anion vacancy are created at 77 K and their formation is not related to the heat-activation process of the motion of anion vacancies. It seems that the formation is linked to the configuration instability at the impurity ion trapping an electron (maybe a hole) [8]. The photochromic centers are produced either by X-irradiation or by additive coloration (by heating the crystals in a calcium atmosphere) of CaF₂ crystals doped with certain rare-earths ions (La, Ce, Gd, Tb, and Lu) or Y [12–14]. It has been found [15, 16] that X-irradiation at 77 K of CaF₂ and SrF₂ crystals doped with the impurities that can form the photochromic centers, results in creation of PC⁺ and V_k centers (self-trapped holes that have the structure of a molecular ion – F₂[–]). The chemical instability of the divalent compounds of these ions [17] leads to the formation of the PC⁺ centers, instead of the divalent ions in alkaline-earth fluorides.

While the second type of the processes occurs much less frequently than the first, it is not limited only to the photochromic centers that formed in alkaline earth fluorides activated by some rare-earth ions. So, in CaF₂–Co the defects consisting of an F center nearest to a Co²⁺ ion in a substitutional position are created at 300 and 80 K [18].

In crystals of calcium and strontium fluorides activated by divalent ions of cadmium, radiation leads to formation of monovalent cadmium centers perturbed by one or two anion vacancies, located in the immediate environment, which lowers the symmetry of the center to C_{3v} and C_{2v} , respectively [6, 7]. Usually in crystals of barium fluoride Cd^{+} centers only in a cubic environment are created. However, in some cases it is possible to produce in these crystals the centers similar to those obtained in other alkaline-earth fluorides such as CaF_2 and SrF_2 [19]. In this paper, radiation defects in barium fluoride single crystals doped with cadmium have been investigated by luminescence and absorption spectroscopy, as well as by electron spin resonance spectroscopy. Three types of Cd^{+} centers differing by the local environment with the point symmetries O_h , C_{3v} , and C_{2v} have been identified. We discuss the reasons for the formation of Cd^{+} centers with low symmetry in these crystals.

2 Experimental technique The crystals of BaF_2 doped with cadmium (with the concentration up to 1 mol%) used for the measurements described in the previous papers [6, 7, 20] and used for the measurements described in this paper were grown from the melt by the Bridgman–Stockbarger method. The specimens used for the measurements in previous studies, about 10 mm in diameter and 50 mm in length, were obtained and we denote them as “small.” Studies of the formation of radiation Cd^{+} centers, X-ray luminescence [21] and atomic emission analysis from different parts of the boule suggest that the impurity in these crystals are randomly (for low concentrations) or uniformly (for concentrations of about 1 mol%) distributed over the crystal. The specimens used for the measurements in this study, about 60 mm in diameter and 150 mm in length, were obtained and we denote them as “large.” In the latter, a strongly nonuniform distribution of cadmium over the crystal is observed from time to time.

In alkaline-earth fluorides single-crystal growth a small amount of CdF_2 is generally used as a scavenger in order to remove oxides and oxyfluorides contained in the raw materials by the reaction $CdF_2 + BaO \rightarrow CdO + BaF_2$. CdO and excess CdF_2 evaporate completely from the melt before crystallization begins [22, 23]. Because of the appreciable vapor pressure of CdF_2 at the melting point of BaF_2 it was necessary to confine the impurity-doped melt in the crucible by means of a floating graphite plug, which reduced the open surface area of the melt and thus decreased the impurity evaporation. The samples were of high optical quality with no indication of oxygen contamination. The atomic emission spectrometry analyses were carried out on several samples in order to determine the concentration of Cd in the grown crystals. Optical absorption measurements were made with a Lambda 950 UV/VIS/NIR spectrophotometer. Luminescence measurements were made with a LS 55 Luminescence Spectrometer Perkin Elmer with PMP R928. The crystals were irradiated at 77 or 295 K by X-rays from a Pd tube operating at 50 kV and 50 mA for not more than one hour.

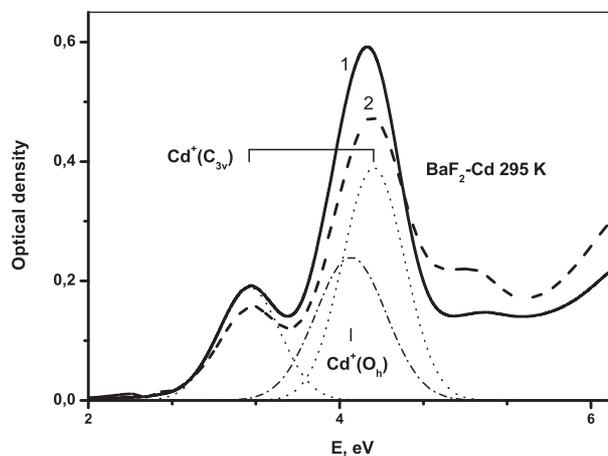


Figure 1 Spectra of optical absorption at 295 K (1,2) of the “large” BaF_2 -Cd crystal with strongly nonuniform distribution of the impurity after X-irradiation at 295 K (1) and subsequent optical bleaching by 3.7 eV light at 295 K (2). Dotted curves are Gaussian bands to simulate the measured spectrum.

The EPR experiments were done on an X-band spectrometer Fourier Transform EPR Spectrometer ELEXSYS Series Bruker.

3 Experimental results

3.1 Absorption X-irradiation at 77 K of BaF_2 crystals doped with cadmium results in the creation of absorption bands at 4.1 eV of reduced cadmium centers with cubic symmetry – $Cd^{+}(O_h)$ [20] and 3.4 eV of V_k centers [24]. In some crystals the Cd^{+} centers with cubic symmetry created by X-irradiation at 77 K are converted to Cd^{+} centers with lower symmetry by heating up to room temperature. X-irradiation at room temperature of BaF_2 -Cd crystals leads to the same results. There are two absorption bands with peaks at 3.28 and 4.27 eV with an approximate intensity ratio of 1:2 in the absorption spectra of the crystals BaF_2 -Cd after X-ray irradiation at room temperature (Fig. 1). By analogy with the results obtained for other alkaline-earth fluorides [6, 7], these bands are assigned to Cd^{+} centers that consist of a fluorine vacancy and the nearest-neighboring Cd^{+} ion. In this case, the symmetry center is reduced to C_{3v} ($Cd^{+}(C_{3v})$), which determines the presence of two absorption bands. The centers are optically bleached by light in the second absorption band with a maximum at 4.27 eV and the high-energy absorption at about 5.0 eV is increased, which is associated with the formation of cadmium centers $Cd^{+}(C_{2v})$ (by analogy to the previous results [6, 7]) (Fig. 1).

Experimental data on the splitting of the absorption band of $Cd^{+}(C_{3v})$ centers in alkaline-earth fluorides (Fig. 2) are presented in Table 1. From the table, it is clear that the splitting of the p-state of $Cd^{+}(C_{3v})$ center in all crystals has approximately the same value of about 1 eV. In this case, Δ_1 monotonically increases from CaF_2 to BaF_2 and Δ_2 has the opposite behavior.

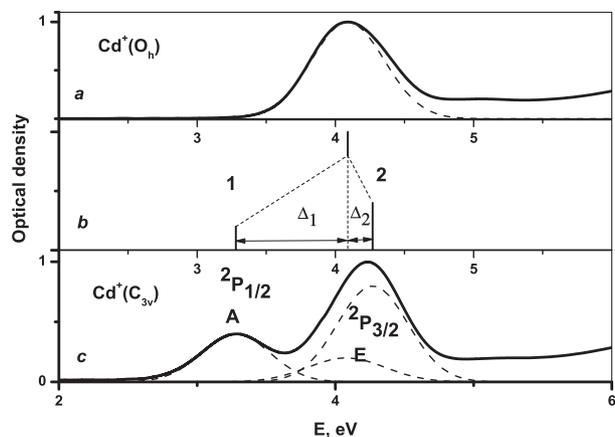


Figure 2 Schematic representation of the level splitting of Cd⁺ ions under lower symmetry. (a) The absorption spectrum of Cd⁺(O_h) ions in cubic environment (e.g., the absorption spectrum of the “small” BaF₂-Cd crystal with random distribution of the impurity after X-ray irradiation at 295 K is shown). (b) Δ₁ and Δ₂ shift of the absorption bands of Cd⁺(C_{3v}) centers relative to the absorption band of Cd⁺(O_h) centers. (c) The absorption spectrum of Cd⁺(C_{3v}) ions, which are localized near the anion vacancy (e.g., the absorption spectrum of the “large” BaF₂-Cd crystal with strongly non-uniform distribution of the impurity after X-ray irradiation at 295 K is shown).

3.2 EPR The EPR spectrum of a BaF₂-Cd crystal X-irradiated at 295 K is shown in Fig. 3. There are two groups of lines that are related to the centers of monovalent cadmium ions with different symmetry. The more intense group consisting of nine lines refers to the ions Cd⁺(O_h) in a cubic environment. The spectrum is due to superhyperfine interaction of the unpaired electron with eight equivalent fluorine nuclei. This is similar to what was observed earlier [20, 25]. Another group with eight lines is the EPR spectrum of monovalent ions of cadmium Cd⁺(C_{3v}), with an adjacent anion vacancy, as indicated by the absence of one fluorine nuclei in this spectrum. In addition, there is a weakly resolved structure, which could not be observed at the temperature of liquid nitrogen. Although the centers are oriented along the C₃-axis, the simplest structure is observed for B||⟨100⟩, since the angles between eight different positions of the anion vacancy on the tops of the cube, the electron and the direction of the external magnetic field are the same. The fact that the cadmium ion does not experience a significant shift from the

Table 1 Splitting of absorption band of the Cd⁺(C_{3v}) centers in alkaline-earth fluorides (for definitions see Fig. 2)

crystal	Δ ₁	Δ ₂	Δ ₀ =Δ ₁ +Δ ₂	T (K)
CaF ₂	0.17	0.73	0.9	295
	0.25	0.73	0.98	80
SrF ₂	0.65	0.44	1.09	295
	0.67	0.44	1.11	80
BaF ₂	0.8	0.19	0.99	295
	0.85	0.15	1.0	80

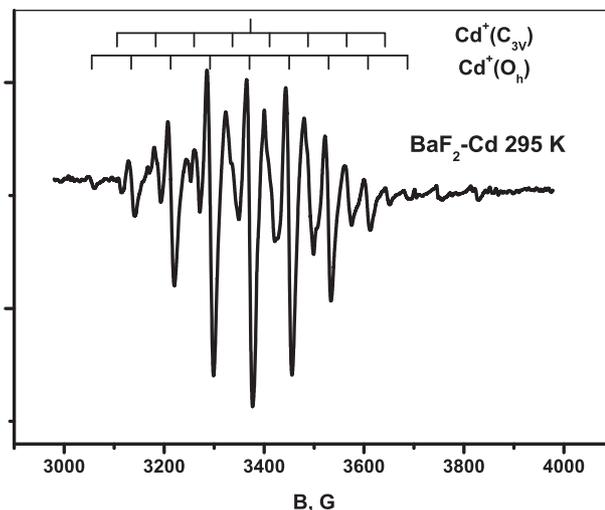


Figure 3 EPR spectrum of the “large” BaF₂-Cd crystal after X-irradiation at 295 K, B||⟨100⟩.

center indicates similar values of superhyperfine splitting for the ions in the cubic environment and disturbed anion vacancy. It should be noted that although the EPR signal from Cd⁺(O_h) is more intense than that of Cd⁺(C_{3v}) centers absorption spectra show that the concentration of Cd⁺(C_{3v}) centers is higher than that of the Cd⁺(O_h) centers.

3.3 Luminescence Figure 4 shows the emission and excitation spectra of Cd⁺(C_{2v}) centers in BaF₂ crystals. For comparison, the spectra of similar centers in other alkaline-earth fluorides are also shown. Photoexcitation at room temperature in the absorption band of Cd⁺(C_{2v}) centers at about 5.0 eV (Fig. 1), which is formed in BaF₂-Cd crystals by X-irradiation and subsequent optical bleaching with

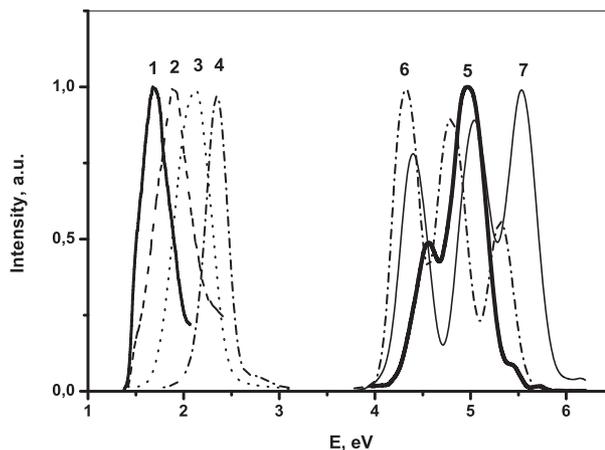


Figure 4 Spectra of emission (1,2) and excitation (5) of the “large” BaF₂-Cd crystals at 80 (1,5) and 295 K (2) after X-ray irradiation at 295 K and subsequent bleaching with 3.7 eV light at 295 K. For comparison, the spectra of excitation (6,7) and emission (3,4) of Cd⁺(C_{2v}) centers in crystals of CaF₂ (4,7) and SrF₂ (3,6) at 77 K are shown.

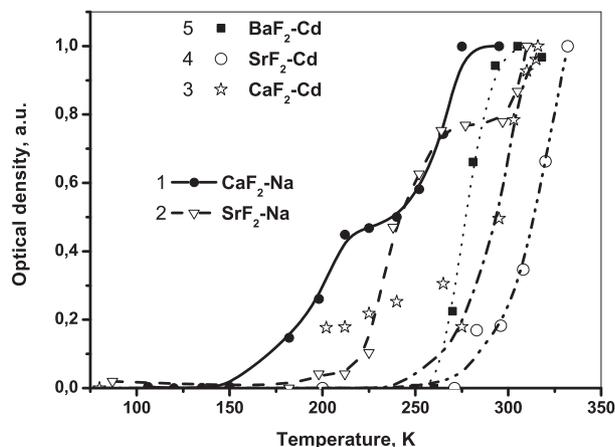


Figure 5 Temperature dependence of the formation of $F_2^+(\text{Na})$ centers in $\text{CaF}_2\text{-Na}$ (1), $\text{SrF}_2\text{-Na}$ (2) crystals and $\text{Cd}^+(\text{C}_{3v})$ centers in $\text{CaF}_2\text{-Cd}$ (3), $\text{SrF}_2\text{-Cd}$ (4), and $\text{BaF}_2\text{-Cd}$ (5) crystals. Measurements were carried out at 77 K. The samples were held for 2 min at each temperature.

3.7 eV light at 295 K, leads to the appearance of red emission with peak at 1.9 eV, which shifts to 1.7 eV at 77 K. Unlike the $\text{Cd}^+(\text{C}_{3v})$ centers for which the splitting of p-state changes little on going from CaF_2 to BaF_2 for $\text{Cd}^+(\text{C}_{2v})$ centers largest splitting is observed in CaF_2 crystals, and the smallest in BaF_2 crystals. This leads to the fact that, unlike CaF_2 and SrF_2 , the two excitation bands are only observed in BaF_2 crystals, the intensity of the high-energy band is twice that of the low-energy band, indicating that the former arises from the two unresolved transitions to the excited p-state.

3.4 Temperature dependence Figure 5 shows the temperature dependence of the formation of the centers having in its composition anionic vacancies. In the case of formation of $F_2^+(\text{Na})$ centers in CaF_2 the dependence is close to that reported by Tijero and Jaque [10]. In agreement with Tijero and Jaque [10], the experimental data obtained from X-ray-irradiated at 77 K $\text{CaF}_2\text{-Na}$ and $\text{SrF}_2\text{-Na}$ crystals show that the $(F_2^+)_A$ centers are created in two stages: the low-temperature stage is associated with a short-range reorientation, while an anion-vacancy-diffusion process operates in the high-temperature zone. There is some distinction between the temperature range of the formation of F_{2A}^+ and $\text{Cd}^+(\text{C}_{3v})$ centers. Apparently, the temperature dependence is not caused by the motion of free anion vacancies but probably results from motion within the Coulomb interaction of impurity–vacancy pairs.

4 Discussion In our previous papers [6, 7], three types of Cd^+ or Zn^+ centers differing by the local environment with the point symmetries O_h , C_{3v} , and C_{2v} have been identified in CaF_2 and SrF_2 crystals. The formation of the last two is the result of the interaction between the reduced impurity centers and anion vacancies. The latter are intrinsic radiation defects and are not essentially created by X-irradiation in the undoped crystals. It has been suggested that under X-ray

radiation of the crystals charged defects such as Cd^+ or Zn^+ in cubic symmetry sites are created and their electric field promotes the separation of intrinsic radiation defects ($\alpha\text{-I}$ pairs) formed by radiationless decay of self-trapped excitons near the charged impurity centers. Radiation formation of the anion vacancies occurs, apparently, near the charged impurity defect, at a distance of several lattice constants (because the next process of the formation of the impurity–anion vacancy complex is thermally activated). Formation of the anion vacancies occurs owing to two competing processes. On the one hand, this is the random formation of an exciton near the charged impurity defect, which probability increases on increasing the number of anion sites, so with increasing the distance from the impurity defect. On the other hand, the strength of the electric field that promotes the separation of $\alpha\text{-I}$ pairs decreases on increasing the distance from the charged impurity ion. It is necessary to make the remark, although there is no doubt that the $F_{2A}^+(\text{Na})$ and $\text{Cd}^+(\text{C}_{3v})$ centers include an anion vacancy, there are no F-centers (except F_A in the Na-doped crystals) and attempt to produce from these anion vacancies F-centers by additional radiation in the temperature range from 77 to 300 K of the crystals previously irradiated at 77 K fails. This indicates that these anionic vacancies cannot be considered as free but as interacting with the charged impurity ion, even at 77 K.

At the same time the strength of the electric field is determined by distribution of the charged impurity defects in crystals. Low concentrations of charged defects in crystals generate random electric fields characterized by Holtmark distributions [26–28]. This case was described in our previous papers [6, 7] and the efficiency of the formation of the $\text{Cd}^+(\text{C}_{3v})$ centers having in its composition anionic vacancy decreases from CaF_2 to SrF_2 and in BaF_2 crystals the centers are not created under X-irradiation at room temperature. In most cases, in barium fluoride crystals doped with divalent ions of cadmium, X-ray irradiation at room temperature leads to the formation of $\text{Cd}^+(\text{O}_h)$ centers in cubic environment.

With increasing concentration of impurities, the distribution is constantly changing from random to uniform as the number of crystal lattice sites is limited. At this uniform distribution, by symmetry, the electric field is zero everywhere and separation of $\alpha\text{-I}$ pairs does not occur and anion vacancies are not created. As a result $\text{Zn}^+(\text{O}_h)$ centers in a cubic environment are only created after X-irradiation of SrF_2 doped with at about 1 mol% ZnF_2 at room temperature as it was earlier observed in our previous study [6, 7]. At lower concentration the impurity centers incorporating an anion vacancy such as $\text{Zn}^+(\text{C}_{3v})$ and $\text{Zn}^+(\text{C}_{2v})$ are observed.

By the difference in the conditions of crystal growth nonuniform distribution of impurity in crystals is also possible. In this case it is expected that the region with higher strength of electric field in comparison with random distribution exists. Two types of the $\text{BaF}_2\text{-Cd}$ crystals have been produced – “small” with a diameter of 10 and 50 mm length and “large” with a diameter of 60 and 150 mm length. In the latter, a strongly nonuniform distribution of cadmium in the crystal is observed from time to time. Cd^+ centers with

lower symmetry in BaF₂-Cd are produced in “large” crystals, in which there is a strong non-uniform distribution of cadmium.

5 Conclusions Experimental results obtained in this and the previous works [6, 7] can be interpreted as follows. The impurity distribution in the crystals is essential for the separation of the intrinsic radiation defects (α -I pairs). Three main types of the spatial distribution of impurities in crystals can be identified in order of increasing strength of the internal electric fields of the charged defects – uniform, random, and nonuniform. Usually, at low concentration of impurities a random distribution is realized. In this case, the efficiency of the formation of the Cd⁺(C_{3v}) and Cd⁺(C_{2v}) centers having in its composition one or two anion vacancies decreases from CaF₂ to SrF₂, and in BaF₂ crystals the centers are not created under X-irradiation at room temperature. In most cases, in BaF₂ crystals doped with divalent ions of cadmium the X-ray irradiation at room temperature leads to the formation of Cd⁺(O_h) centers in cubic environment. However, for a strong nonuniform distribution of the impurities in BaF₂-Cd crystals, centers with low symmetry are also created. The spatial distribution aspires to uniformity with increasing concentration of impurities. In this case, only centers with a cubic symmetry are created and this process begins in SrF₂ crystals, standing between CaF₂ and BaF₂.

Acknowledgements This work was partially supported by The Ministry of Education and Science of the Russian Federation.

References

- [1] W. Hayes (ed.), Crystals with Fluorite Structure. Electronic, Vibrational, and Defect Properties (Clarendon Press, Oxford, 1974).
- [2] P. Call, W. Hayes, J. Stott, and A. Hughes, *J. Phys. C, Solid State Phys.* **7**, 2417–2428 (1974).
- [3] W. Hayes and R. Lambourn, *J. Phys. C, Solid State Phys.* **6**, 11–26 (1973).
- [4] W. Hayes and R. Lambourn, *Phys. Status Solidi B* **57**, 693–699 (1973).
- [5] W. Kanzig and T. Woodruff, *J. Phys. Chem. Solids* **9**, 70–92 (1959).
- [6] A. Egranov, E. Radzhabov, V. Ivashechkin, M. Semenova, and I. Vasil’eva, *J. Phys.: Condens. Matter* **20**, 465213 (2008).
- [7] A. Egranov, E. Radzhabov, A. Nepomnyashchikh, V. F. Ivashechkin, and I. Vasil’eva, *Phys. Solid State* **50**, 1740–1746 (2008).
- [8] A. Egranov and T. Y. Sizova, *J. Phys. Chem. Solids* **74**(3), 530–534 (2013).
- [9] K. Song and R. Williams, *Self-Trapped Excitons*, Springer Series in Solid State Sciences, Vol. 105 (Springer-Verlag, Berlin, 1993).
- [10] J. Tijero and F. Jaque, *Phys. Rev. B* **41**, 3832–3836 (1990).
- [11] S. McKeever, B. Jassemjad, J. Landreth, and M. Brown, *J. Appl. Phys.* **60**, 1124 (1986).
- [12] C. Anderson and E. Sabisky, *Phys. Rev. B* **3**, 527–536 (1971).
- [13] D. Staebler and S. Schnatterly, *Phys. Rev. B* **3**, 516–526 (1971).
- [14] R. Alig, *Phys. Rev. B* **3**, 536–545 (1971).
- [15] T. Bugaenko, E. Radzhabov, and V. Ivashechkin, *Phys. Solid State* **50**, 1671–1673 (2008).
- [16] T. Sizova and E. Radzhabov, *IEEE Trans. Nucl. Sci.* **59**, 2098–2101 (2012).
- [17] S. Cotton, *Lanthanide and Actinide Chemistry* (John Wiley & Sons Ltd, Chichester, UK, 2006).
- [18] R. Alcalá and P. Alonso, *Phys. Rev. B* **18**, 5506–5513 (1978).
- [19] M. Springis, A. Veispals, P. Kulis, U. Rogulis, I. Tale, and J. Trokss, in: *SCINT95: Proc. Int. Conf. on Inorganic Scintillators and their Applications*, edited by P. Dorenbos and C. W. E. van Eijk (Delft University Press, The Netherlands, 1996), pp. 403–406.
- [20] A. Nepomnyashchikh, E. Radzhabov, A. Egranov, V. Ivashechkin, A. Istomin, and T. Kurobori, *Nucl. Instrum. Methods Phys. Res. A* **537**, 27–30 (2005).
- [21] E. Radzhabov, A. Istomin, A. Nepomnyashchikh, A. Egranov, and V. Ivashechkin, *Nucl. Instrum. Methods Phys. Res. A* **537**, 71–75 (2005).
- [22] D. Stockbarger, *J. Opt. Soc. Am.* **39**(9), 731–740 (1949).
- [23] B. Sobolev, *Crystallogr. Rep.* **47**(Suppl. 1), S63–S75 (2002).
- [24] A. I. Nepomnyashchikh, E. A. Radzhabov, A. V. Egranov, V. F. Ivashechkin, and A. S. Istomin, *Radiat. Eff. Defects Solids* **157**(6–12), 715–719 (2002).
- [25] V. Krutikov, N. Silkin, and V. Stepanov, *Sov. Phys. Solid State* **18**, 1725–1729 (1976).
- [26] J. Holtsmark, *Ann. Phys. (Leipzig)* **363**, 577–630 (1919).
- [27] D. Redfield, *Phys. Rev.* **130**, 914–915 (1963).
- [28] D. Redfield, *Trans. New York Acad. Sci.* **25**, 590–598 (1964).