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OPTICAL INVESTIGATION OF CATION DEFECTS IN IRRADIATED RbBr

(Presented by Ch. Lushchik)

An X-ray or UV irradiation of RbBr crystals at 80 and 190 K creates Br_3^- centers oriented along $\langle 100 \rangle$ directions. The photodissociation of these centers creates V_F centers. X-irradiation also brings about an absorption band at 5.4 eV, stable up to 425 K, which can be interpreted as the absorption of interstitial dipoles $\text{Rb}_i^+\text{Br}_i^-$.

Introduction

Basic data on radiation defects in alkali halides have been obtained for KCl and KBr crystals [1, 2]. In these crystals X-irradiation at 4.2 K creates pairs of anion Frenkel defects: either the anion vacancies v_a^- (α centers) and interstitial halogen ions i_a^- (I centers), or F and H centers ($v_a^-e^-$ and i_a^0). Recently it has also been shown that in some alkali halides X-irradiation creates pairs of cation Frenkel defects: the cation vacancies v_c^- and interstitial cations i_c^+ as well as complex associations of defects with cation vacancies and holes as their components — V_F centers ($v_c^-e^+$) and V_4 centers ($v_c^-e^+i_a^0$) [3-7].

The aim of the present study is to investigate optically cation defects in RbBr which become apparent in the X-irradiation-induced absorption and optical dichroism spectra and thermally stimulated luminescence (TSL).

In [8] the absorption spectra of RbBr X-rayed at 16 K were investigated, and the absorption bands of I centers (5.45 and 5.20 eV), H centers (3.25 eV) and a broad band with the maximum at 4.18 eV were detected. The intensity of the latter is proportional to the square of the H -band intensity and, according to [8], it is associated with di- H -centers. The annealing of I centers in the region of 40 to 60 K was studied in [9]. The V_K centers in RbBr are described in [10]. Cation Frenkel defects in RbBr have not practically been studied.

In the absorption spectrum of RbBr at 80 K the bands at 6.6 and 7.08 eV correspond to the e^0 excitons.

Experimental

The crystals of RbBr were grown by the method of sixty-fold recrystallization at the Institute of Physics of the Academy of Sciences of the Estonian SSR [11]. The investigation of ionic conductivity showed that the transition to the intrinsic conductivity occurs at 290 °C, which testifies to the high purity of the crystals relative to divalent metals ($\text{C}(\text{Me}^{2+}) \leq 10^{-2}$ ppm). RbBr platelets of approximately $10 \times 10 \times 1.5$ mm³ freshly cleaved along the $\{100\}$ planes were studied. The crystal was placed into

a cryostat with a sorption pump and was X-irradiated through a beryllium window using a tube with a tungsten target operating at 60 kV and 15 mA. The exposure time (5 h) corresponds to the absorbed dose of 50 Mrd.

The absorption spectra were recorded at 80 K before and after the irradiation on a «Specord UV VIS» spectrophotometer. In the figures, the spectra of the absorption induced by X-irradiation are shown. To determine the orientation of color centers, the X-rayed crystals were bleached by linearly polarized light and subsequently the optically induced linear dichroism was investigated according to [12-14]. The polarization degree of the light obtained by using polaroids, was about 100 per cent in the region of 3.5 to 5.1 eV. The bleaching was performed with the light from an SVD-120A Hg discharge lamp or a powerful DDS-400 deuterium lamp through an MDR-23 monochromator. The integral TSL in the region of 80 to 450 K was recorded mostly at the heating rate $\beta=0.15$ K/s, in the region of 4.2 to 80 K — $\beta=0.015$ K/s.

Experimental results

The absorption spectra of RbBr induced by X-irradiation at 80, 190, and 300 K, are shown in Fig. 1. In the spectra an intensive F band (1.81 eV), an α band (6.02 eV), and a β band (6.31 eV) can be seen. The absorption band in the region of 5.8 to 5.0 eV typical of I centers, in the region of 5.0 to 3.7 eV typical of V_2 and V_4 centers, and in the region of 3.6 to 2.7 eV typical of V_K , V_F , and H centers are observable. The broad absorption bands in the regions of 5.8 to 5.0 eV and of 5.0 to 3.7 eV (half-width $\delta > 1$ eV) are non-elementary. To divide them into elementary components the pulse annealing of X-rayed crystals was used: the crystal was heated up to definite temperatures (exposure

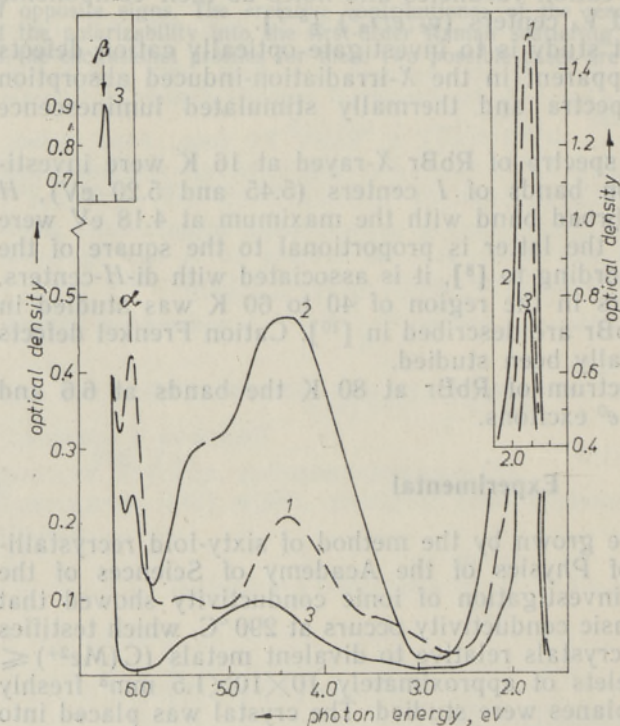


Fig. 1. Absorption spectra of RbBr X-irradiated at 80 K (1), 190 K (2), and 300 K (3).

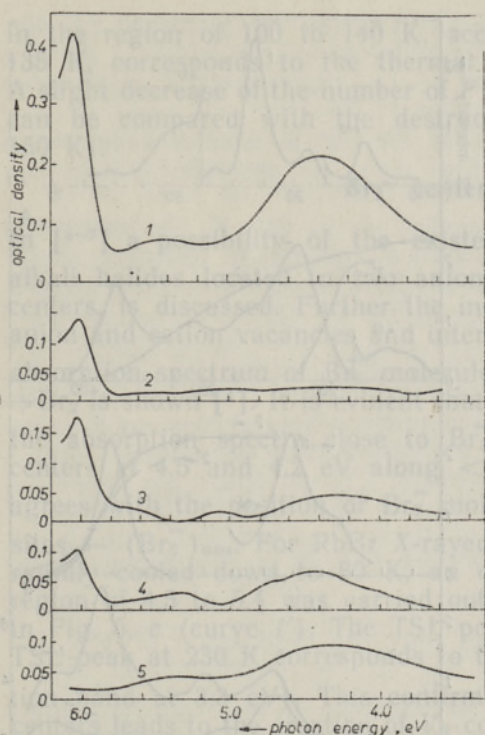


Fig. 2. Absorption spectrum of RbBr after an X-irradiation at 80 K (1) and the decrease of the absorption after heating from 80 to 170 K (2), from 170 to 240 K (3), from 240 to 300 K (4), and from 300 to 400 K (5).

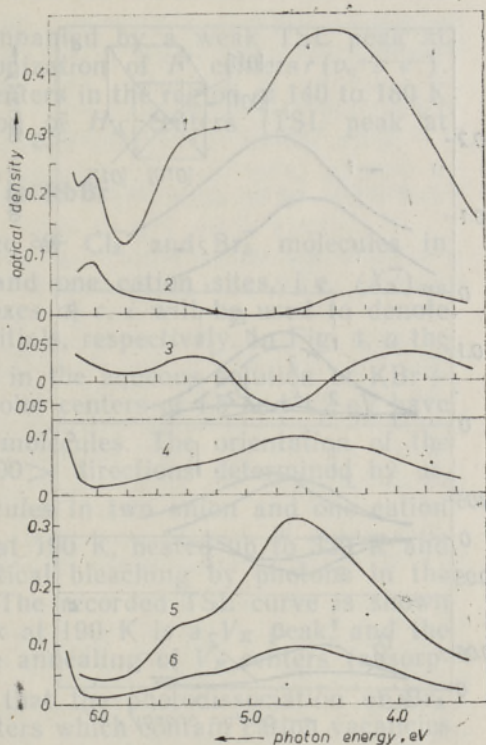


Fig. 3. Absorption spectrum of RbBr X-irradiated at 190 K (1) and the decrease of the absorption after heating from 240 to 280 K (2), from 280 to 320 K (3), from 320 to 360 K (4), from 360 to 400 K (5), and from 400 to 425 K (6).

2 min), rapidly cooled down to 80 K, and then the absorption spectra were measured.

The absorption spectra of RbBr crystals X-rayed at 80 or 190 K and annealed in the definite temperature region, are shown in Figs. 2 and 3. An analysis of the data presented in these figures shows that in the region of 5.8 to 5.0 eV low-temperature (annealed up to 240 K) and high-temperature (annealed up to 425 K) I centers can be distinguished. In the region of 5.0 to 3.7 eV for the crystals X-rayed at 80 K, it is possible to single out the centers with the absorption maxima at 4.2 and 4.5 eV and for the crystals X-rayed at 190 K, the absorption bands at 4.2, 4.5, and 4.8 eV.

For a more detailed analysis of 5.0 to 3.7 eV region, a selective bleaching of crystals by 4.68 or 3.97 eV photons (propagation vector parallel to $[100]$) was performed. After bleaching RbBr with light, the electric vector being parallel to $[001]$ (subsequently the term « $[001]$ light» will be used), the absorption measured with $[001]$ light decreases, and the absorption measured with $[010]$ light slightly increases (see Fig. 4, c). The optical dichroism along the C_4 axis was determined as the difference of absorption coefficients $D_4 = K_{010} - K_{001}$ (see Fig. 4, b, d). Analogously, after the bleaching with $[011]$ light, the absorption spectra with $[011]$ and $[0\bar{1}1]$ lights were measured. Dichroism along the axis C_2 was determined as $D_2 = K_{011} - K_{0\bar{1}1}$ (see Fig. 4, b, d).

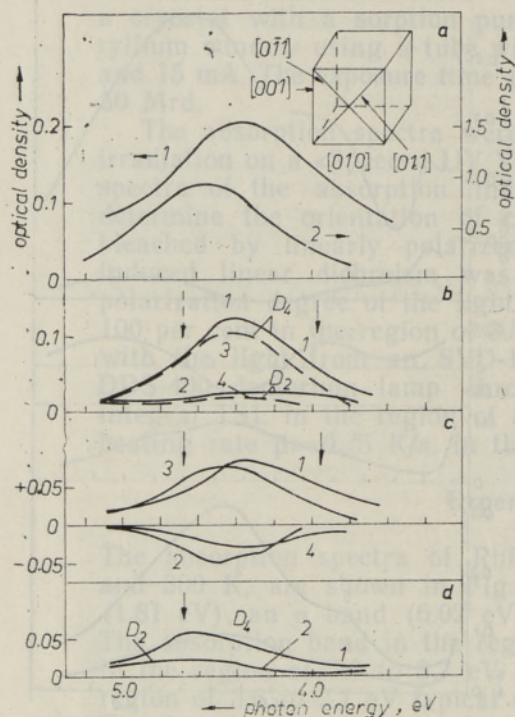


Fig. 4. Optical spectra of a RbBr crystal. *a* — Absorption spectra of Br_3^- molecules in RbBr X-irradiated at 80 K (1) and in an aqueous solution at 300 K (2). *b* — Optical dichroism induced by bleaching with [001] (1, 3) and [011] light (2, 4) in RbBr X-irradiated at 80 K. Energy of photons is 3.97 eV (1, 2) and 4.68 eV (3, 4). *c* — Decrease of [001] light absorption (1, 3) and increase of [010] light absorption (2, 4) in RbBr X-irradiated at 80 K after bleaching with [001] light. Energy of the photons is 3.97 eV (1, 2) and 4.68 eV (3, 4). *d* — Optical dichroism induced by bleaching with [001] (1) and [011] (2) light (4.68 eV photons) in RbBr X-irradiated at 190 K.

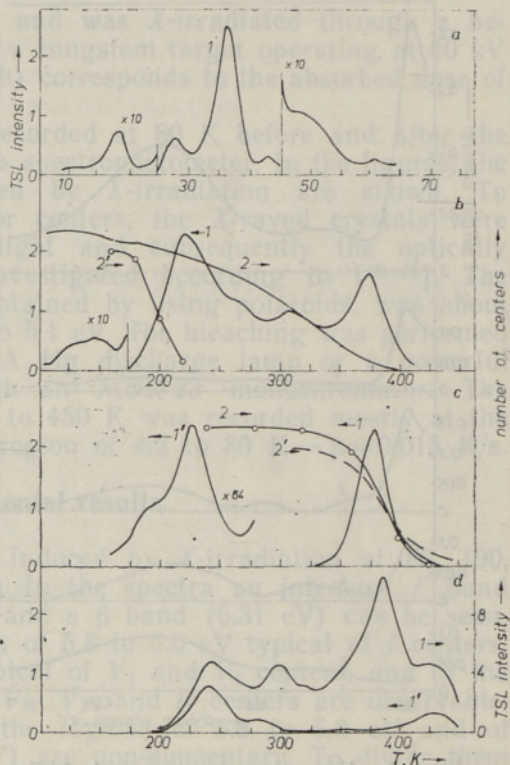


Fig. 5. Integral intensity of thermally stimulated luminescence (I , I') and thermal bleaching of color centers (2, 2') for RbBr after an X-irradiation at 4.2 (a), 80 (b), 190 K (c) and after an illumination at 190 K (d, ratio of doses 1:130) with heating rates 0.015 K/s (a), 0.15 K/s (b, c) and 0.3 K/s (d). Thermal bleaching of F band at 1.81 eV (2b, 2c), of EPR signal of V_K center (2'b) and of absorption band at 5.37 eV (2'c).

Linear oscillators are oriented along C_4 axis (i.e. along $\langle 100 \rangle$ directions) if the dichroism D_4 is present and D_2 is absent [12]. It is this case that takes place for color centers with the absorption maxima at 4.2 and 4.5 eV. In the region of 4.8 to 5.1 eV very weak dichroism D_4 and D_2 can be observed (see Fig. 4, d), which may direct the orientation of color centers at 4.8 eV along $\langle 110 \rangle$ directions.

In Fig. 5 the TSL curves of RbBr crystals X-rayed at 4.2, 80, and 190 K are presented. The curves of the thermal bleaching of F centers ($\propto F^m \cdot T^{1/2}$ is taken as the number of F centers), and the centers with the absorption at 5.37 eV measured in the regime of continuous heating, are given as well. The data on the pulse annealing of F centers and the electron paramagnetic resonance (EPR) signal of V_K centers are presented in Fig. 5 (curves 2c and 2'b). The increase of the number of F centers

in the region of 100 to 140 K, accompanied by a weak TSL peak at 135 K, corresponds to the thermal ionization of F' centers ($v_a^+e^-e^-$). A slight decrease of the number of F centers in the region of 140 to 180 K can be compared with the destruction of H_A centers (TSL peak at 150 K).

Br_3^- centers in RbBr

In [4-7] a possibility of the existence of Cl_3^- and Br_3^- molecules in alkali halides located in two anion and one cation sites, i.e. $(X_3^-)_{aca}$ centers, is discussed. Further the indexes a , c , i will be used to denote anion and cation vacancies and interstitials, respectively. In Fig. 4, a the absorption spectrum of Br_3^- molecules in the aqueous solution of $\text{KBr} + \text{Br}_2$ is shown [4]. It is evident that color centers of 4.5 and 4.2 eV have the absorption spectra close to Br_3^- molecules. The orientation of the centers at 4.5 and 4.2 eV along $\langle 100 \rangle$ directions determined by us, agrees with the position of Br_3^- molecules in two anion and one cation sites — $(\text{Br}_3^-)_{aca}$. For RbBr X -rayed at 190 K, heated up to 320 K and rapidly cooled down to 80 K, an optical bleaching by photons in the region of 4.5 to 5.4 was carried out. The recorded TSL curve is shown in Fig. 5, c (curve I'). The TSL peak at 190 K is a V_K peak, and the TSL peak at 230 K corresponds to the annealing of V_F centers (absorption band at 3.3 eV). This confirms that the photodissociation of Br_3^- centers leads to the creation of V_F centers which contain cation vacancies [10, 15]. Thus the absorption band at 4.5 eV corresponds to $(\text{Br}_3^-)_{aca}$ centers and at 4.2 eV (as with KBr [5] and KCl [7]), to $(\text{Br}_3^-)_{aca}\text{Rb}_i^+\text{Br}_i^-$ centers.

A theory of linear Br_3^- molecules is considered in [16, 17]. The absorption at 4.5 eV corresponds to $^1\Sigma_g \rightarrow ^1\Sigma_u$ transition into the excited state with a repulsive potential, which leads to the photodissociation of Br_3^- centers with the creation of halogen atoms Br^0 (i.e. H centers). The creation of H centers in KBr and KCl due to the photodissociation of Br_3^- and Cl_3^- centers is mentioned in [4, 5].

The weak TSL peaks at 43, 49, and 52 K (Fig. 5, a) for the RbBr crystals X -rayed at 4.2 K correspond to the annealing of H centers [9]. At 80 K and especially at 190 K H centers in RbBr crystals migrate to large distances and interact easily with F centers and other defects of a crystal lattice.

Practically no absorption band appears at 4.8 eV after an irradiation at 80 K when v_c^- in RbBr are immobile. The band is rather intensive in the crystals X -rayed at 190 K and especially at 300 K. The number of the centers involved increases with heating crystals from 200 to 320 K when v_c^- and $v_c^-e^+$ become mobile. A similar band at 5.8 eV in KCl was interpreted as the absorption of $(\text{Cl}_2^0)_2$ associations [7]. According to [16], this association should be regarded as a T -shaped Cl_4^0 molecule.

Interstitial dipoles $\text{Rb}_i^+\text{Br}_i^-$

I centers (single interstitial halogen ions i_a^-) are described in [8] for RbBr crystals X -rayed at 16 K. The TSL curve of RbBr crystal X -rayed at 4.2 K, is shown in Fig. 5, a . The main peak at 37 K corresponds to bimolecular annealing of single I centers whose recombination with F centers leads to the creation of conduction electrons [9]. The recomb-

nation of electrons with V_K centers causes the luminescence of self-trapped excitons (both π emission with a maximum at 2.11 eV and σ emission at 4.15 eV). TSL peaks at 11, 18, and 27 K correspond to α , I correlation pairs.

More stable I_A centers annealed at $T < 250$ K simultaneously with α centers (absorption of a halogen near ν_a^+), are observed in KBr—Na and KBr—Li crystals [18].

It follows from Fig. 2 that if heated up to 240 K, the annealing of both low-temperature I centers and α centers in RbBr is simultaneous. This part of I centers is probably localized near Na^+ and K^+ ions. However, the absorption band at 5.4 eV (typical of I centers) remains even after the heating up to 300 K. The annealing of this band occurs only in the region of 350 to 425 K (Fig. 5, c , curve 2'). As in KCl crystals [7, 19], the high-temperature I centers in RbBr (absorption band at 5.4 eV) can be connected with the creation of interstitial dipoles $\text{Rb}_i^+\text{Br}_i^-$. In KCl the reorientation of such dipoles occurs at 160 K, and the annealing at $T > 400$ K [19]. In RbBr the annealing of the 5.4 eV absorption band occurs in the temperature range of 350 to 425 K, but the reorientation of dipoles has not been studied yet.

When irradiating RbBr at 80 K, interstitial dipoles must appear (see below) near Br_3^- centers. Therefore at the photodissociation of Br_3^- centers by 4.67 eV photons, not only the destruction of Br_3^- but also $\text{Rb}_i^+\text{Br}_i^-$ centers is expected due to the recombination of ν_c^- and i_c^+ . In fact, after the optical destruction of Br_3^- centers created by X -irradiation at 80 K, the proportional bleaching of the absorption band at 5.4 eV (which we consider to be the absorption of interstitial dipoles) takes place as well.

In RbBr crystals X -rayed at 190 K the majority of interstitial dipoles appear far from Br_3^- centers. In this case a small number of dipoles is destroyed by 4.67 eV photons. Up to now we have not succeeded in the selective bleaching of the absorption band at 5.4 eV or in studying optically-induced dichroism of dipoles in RbBr X -rayed at 80 K.

Creation of cation defects by irradiation

With the increase of the X -irradiation dose of RbBr crystal, the number of V_F centers (TSL peak at 230 K) increases, and the absorption bands at 4.2, 4.5 eV (Br_3^- centers) and 5.4 eV ($\text{Rb}_i^+\text{Br}_i^-$ centers) grow linearly.

Characteristics of color centers in RbBr

Absorption band, eV	Decay temperature, K	Symbol	Model
6.31	—	β	$e^0\nu_a + e^-$
6.02	—	α	$e^0\nu_a^+$
5.45; 5.20	37	I	i_a^- [8, 9]
5.4	400	—	$i_a^- i_c^+$
4.8	—	Br_4^0	—
4.5	380	Br_3^-	$\nu_c^- e^+ i_a^0$
4.2	—	Br_3^-	$\nu_c^- e^+ i_a^0 \dots i_c^+ i_c^-$
1.81	—	F	$\nu_a^+ e^-$
3.22	190	V_K	e^+ [10, 15]
3.3	230	V_F	$\nu_c^- e^+$
3.25	52	H	i_a^0 [8, 9]

In the region of 320 to 450 K the ionic conductivity of RbBr X-rayed at 190 K grows as well. These facts testify to the creation of cation Frenkel defects by X-irradiation.

In Table the positions of the absorption bands, decay temperatures, conventional designations, and models of the investigated color centers in RbBr, are compiled.

Five basic mechanisms of v_c^- and i_c^+ creation in alkali halides are proposed:

1. At double ionization of a halogen ion a non-stable association of seven positively charged ions arises in the crystal, the decay of which may cause the creation of cation defects [20].
2. Cation defects arise due to the decay of cation excitons which can be formed in RbBr by 16—17 eV photons.
3. Cation defects in RbBr may be generated by the decay of self-trapped anion excitons formed by 6.5—7.0 eV photons [3].
4. The association of two H centers may create a complex defect $v_c^-e^+i_a^0 \dots i_c^+i_a^-$ [21].
5. According to [22], the interaction of H and V_K centers creates $v_c^-e^+i_a^0 \dots i_c^+$ centers.

In order to elucidate the basic creation mechanisms of cation defects in RbBr, we investigated the radiation defects produced by the 6.5—7.0 eV photons using the TSL method. These photons create selectively anion excitons, but they cannot cause double ionization of halogen ions, cation excitons or a large number of holes. At such an excitation, some of the mechanisms mentioned above are impossible (1, 2) or improbable (5).

At 190 K a RbBr crystal was irradiated by 6.7 eV photons ($N=10^8$ photons/cm².s) which were distinguished from CO₂-discharge by a VMR-2 vacuum monochromator. The curves of integral TSL measured after the irradiation with the heating rate of 0.3 K/s, are shown in Fig. 5, *d*. After 1h irradiation (about 10^{17} excitons/cm³ were obtained), V_F centers (peak at 240 K) and the centers responsible for TSL peak at 430 K arose. After an irradiation with a 130 times greater dose, in addition to V_F peak a TSL peak at 370—380 K which corresponds (as was pointed above) to $(Br_3^-)_{aca}$ centers, was distinctly observed. Thus, at a small dose anion excitons create V_F centers in RbBr, at a large irradiation dose, however, both V_F and $(Br_3^-)_{aca}$ centers are created, which agrees well with mechanism 3.

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KIIRITATUD RbBr KRISTALLIDE KATIOONSETE DEFEKTIDE OPTILINE UURIMINE

RbBr kristallide kiiritamisel temperatuuril 80 ja 190 K tekivad kaht tüüpi Br_3^- -tsentrid, mis on orienteerunud suundades $\langle 100 \rangle$ ja neelavad piirkonnas 4,5 või 4,2 eV. Nende tsentrite fotodissotsieerumisel tekivad V_F -tsentrid (katioonvakantsi juures lokaliseeruv auk). Röntgenkiiritus tekitab veel neeldumisriba 5,4 eV, mis on stabiilne kuni temperatuurini 425 K ja mida võib tõlgendada kui sõlmedevahelise $\text{Rb}_i^+\text{Br}_i^-$ dipooli neelamist. On käsitletud katioonsete Frenkeli defektide tekkimise võimalikke mehhanisme.

А. ЛУЩИК

ОПТИЧЕСКОЕ ИССЛЕДОВАНИЕ КАТИОННЫХ ДЕФЕКТОВ В ОБЛУЧЕННЫХ КРИСТАЛЛАХ RbBr

В случае облучения кристаллов RbBr при 80 и 190 К создаются Br_3^- -центры двух типов, ориентированные по направлениям $\langle 100 \rangle$ и поглощающие в области 4,5 и 4,2 эВ. При фотодиссоциации этих центров создаются V_F -центры (дырка, локализованная около катионной вакансии). Облучение рентгеновскими лучами приводит, кроме того, к появлению стабильной до 425 К полосы поглощения 5,4 эВ, которая может быть интерпретирована как поглощение междоузельных диполей $\text{Rb}_i^+\text{Br}_i^-$. Обсуждаются возможные механизмы создания катионных френкелевских дефектов.