



OPTICAL SPECTRA OF OXYGEN DEFECTS IN BaFCl AND BaFBr CRYSTALS

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Abstract—Oxygen impurities enter BaFCl and BaFBr crystals as oxygen-vacancy centers. As in other ionic crystals, these defects in the barium fluorohalide crystals have several absorption bands and one photoluminescence band. The defects also are involved in aggregation and photochemical reactions. We have found two kinds of oxygen-vacancy centers in barium fluorohalide crystals and denoted them as centers of types I and II. On the basis of the growth conditions, absorption spectra and other data one may conclude that centers of the first type consist of oxygen substituting at F^- sites and neighboring Cl^- or Br^- vacancies. Oxygen-vacancy centers of the second type seem to be completely on either the Cl or the Br sublattice.

Keywords: A. optical materials, B. crystal growth, D. defects, D. luminescence, D. optical properties.

1. INTRODUCTION

BaFBr crystals activated with europium are used as X-ray image plates [1]. Usually BaFBr:Eu contains large amounts of oxygen (100 ppm and more) [2]. The oxygen significantly enhances F center generation under X-irradiation [3]. Nevertheless only a few data on the optical spectra of oxygen defects in barium fluorohalide crystals have been reported [2, 3]. Oxygen enters alkaline-earth fluoride crystals as oxygen-anion vacancy ($O^{2-} \rightarrow v_a^+$) centers [4-6]. These centers in alkali halide crystals easily aggregate and photodissociate [7, 8]. The first absorption band of oxygen-vacancy aggregates was observed at higher energy than that of the isolated centers in alkali halides as well as in alkaline-earth fluorides [5, 8]. Both processes are caused by the presence of the anion vacancies.

In this paper we study the optical spectra of oxygen-vacancy centers and reactions related with these defects. Some previous results on BaFCl were published in Ref. [9]. Sometimes we will use X^- to denote Cl^- or Br^- .

2. EXPERIMENTAL

The crystals were grown by the Kyropoulos, Stockbarger or Stöber methods under a He atmosphere or vacuum in graphite crucibles. Some crystals were grown from a mixture of previously melted BaBr₂ or BaCl₂ and BaF₂. The other samples were

regrown from the crystals. The mixture was dried and then melted in a vacuum of about 10^{-2} torr. In all such prepared crystals several bands in the ultraviolet region were detected. The oxygen O^{2-} centers are known to give several absorption bands in the ultraviolet up to the exciton edge [7, 8]. The 4.98 eV absorption band in BaFBr crystals has been associated with O^{2-} -vacancy defects [2]. Therefore, these ultraviolet bands in undoped crystals may arise from oxygen defects. All our spectroscopic studies show that these oxygen centers are oxygen ions associated with anion vacancies. To reduce the oxygen concentration the melt was vacuum-dried for different times from 1 h to 24 h. In this way several BaFBr, BaFCl crystals with different oxygen contents and u.v. absorption bands were prepared (for BaFBr see Fig. 1). The purest BaFBr crystals were grown in a He atmosphere with the addition of pieces of Teflon $[C_2F_4]_n$ near the heater. This method has been applied in the growth of oxygen-free CaF₂ crystals as well as crystals with different oxygen concentrations [10]. In our case the purest specimens of BaFBr have no absorption bands in the ultraviolet and no visible photoluminescence.

Before the measurements, the crystals were annealed at 600°C and cooled in air to room temperature. The crystals were cleaved perpendicular to the *c*-axis, and all optical measurements taken with $E \perp c$ -axis.

The spectra in the vacuum u.v. region were obtained from a home-made spectrophotometer.

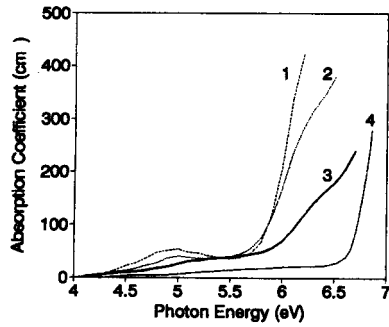


Fig. 1. Absorption spectra of BaFBr crystals with different oxygen concentrations at 295 K: curve 1—without drying; curve 2—mixture was previously dried in air; curve 3—the melt was vacuum-dried for 24 h; curve 4—the crystal was grown with $[C_2F_4]_n$ addition (see text).

Absorption spectra in the near u.v. and visible region were obtained with a "Specord M40" spectrophotometer. Samples were colored with X-rays through the beryllium window of a cryostat by a Pd tube operating at 40 kV and 50mA. The spectra resulting from the formation of F centers by u.v. light were measured with a MDR2 grating monochromator and a 400 watt deuterium discharge lamp. The emission spectra were not corrected for the spectral response of the spectrometer, as the spectrometer sensitivity did not vary significantly in the range of the measured emission.

The photoluminescence of oxygen defects is rather efficient at room temperature. This property gives an easy method for checking for the presence of oxygen in BaFBr and BaFCl by visible luminescence under u.v. irradiation, but one must be sure that other luminescent impurities are not present.

3. RESULTS

Two types of oxygen-related centers were found in BaFCl and BaFBr crystals, having different absorption, emission, excitation, aggregation and photochemical properties. Centers with a first absorption band near 5 eV were found in crystals grown from powder, and are denoted as type I centers. The second type of centers have a first absorption band at 4.2 eV for BaFBr and at 4.5 eV for BaFCl (see Table 1). These centers were found in crystals that were regrown in vacuum.

3.1. The type I centers

3.1.1. *BaFBr*. From the absorption spectra obtained with different oxygen concentrations one can see two distinct bands with maxima at 5.0 and near 6.3 eV (Fig. 1). The intensity ratio between the 6.3 and 5.0 eV bands is about 8. In carefully-prepared BaFBr crystals there are no oxygen bands at all

Table 1. The bands of type I and II oxygen-vacancy centers (in eV) in BaFBr and BaFCl crystals at 80 K. The data for BaF₂ [5] were added for comparison. The numbers in parentheses are the halfwidth of emission bands

Crystal	Type I		Type II	
	Absorb.	Emission	Absorb.	Emission
BaFBr	5.0	2.5 (0.45)	4.2	2.05 (0.4)
	6.3		5.28	
	> 7		6.35	
BaFCl	4.9	2.30 (0.4)	4.5	2.45 (0.4)
	6.3		5.6	
	7.3		6.5	
			7.4	
BaF ₂	5.2	2.38		
	6.05			
	7.2			
	8.4			

(see Fig. 1). Above 6.7 eV excitation absorption starts [11].

The one emission band at 2.5 eV was excited in the range from 4 to 7 eV in crystals with a rather high oxygen content (Fig. 2). In crystals with a low oxygen concentration, there is a weak broad luminescence band at 3.4 eV of unknown nature. The excitation spectrum of the 2.5 eV luminescence consists of bands at 4.95, 6.3 and 7.0 eV. The first two bands coincide well with the oxygen absorption bands, so it seems that the 2.5 eV photoluminescence band corresponds to oxygen defects. Above 7 eV the oxygen emission band reduces and an asymmetric band with a maximum at 4.2 eV increases simultaneously (see Fig. 2). The energy range of conversion of the 2.5 eV emission band to the 4.2 eV band shifts to higher energies for samples with higher oxygen concentration. This process can be described as competition for photon absorption between the excitons and the oxygen defects. In crystals with low oxygen concentration there is a weak 5.0 eV emission band together with one at 4.2 eV. Since the 5.0 eV emission band is

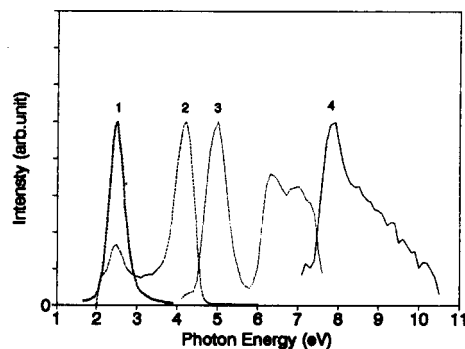


Fig. 2. Emission (1, 2), and excitation (3, 4) spectra of BaFBr crystals at 80 K. Excitation spectra were measured with appropriate filters which were transparent to the 2.5 eV band (3) and to the 4.2 eV one (4). Emission spectra were measured under 5.0 eV (1) and 7.7 eV (2) light irradiation.

resonant with direct excitation of oxygen centers this band is depressed in oxygen-doped crystals. Therefore the 4.2 and 5.0 eV bands must be attributed to the excitons [12].

Under irradiation by u.v. light at room temperature the oxygen absorption bands at 6.3 and 5.0 eV decrease and several bands increase, the strongest of these being at 2.15 eV. Weak bands at 3.3, 2.5 eV and one with a maximum at lower energy than the marginal 1.4 eV were created (Fig. 3). The bands at 2.15 and 2.5 eV correspond to $F(Br^-)$, $F(F^-)$ centers, respectively [13, 14]. The relative height of the band with $E < 1.4$ eV grows with increasing oxygen concentration. It is possible that this absorption belongs to F-center colloids (as in the case of BaFCl [15]). The formation spectrum of $F(Br^-)$ centers shows that a photochemical reaction is efficient with light energies above 5.2 eV (see Fig. 3). The formation spectrum consists of 6.2 eV and higher energy bands.

Under X-irradiation at liquid nitrogen temperature 3.35, 2.08 and weak 2.45 eV bands appear. There is a proportionality between the 3.35 and 2.08 eV bands during the X-irradiation (Fig. 4). These bands also bleach proportionally under irradiation with 3.4 eV light at 80 K. Under heating, the 3.35 eV band disappears in the 110–140 K region and the 2.08 eV one decreases to one half of its initial intensity (see Fig. 4). According to our results the 3.35 eV band possesses $\langle 110 \rangle$ but not $\langle 100 \rangle$ dichroism. The defect with its axis along $[111]$ must also lead to $\langle 110 \rangle$ but not to $\langle 100 \rangle$ dichroism. The observed 3.35 eV band is associated with V_k centers, which at 1.5 K have two absorption bands at 3.4 and 1.28 eV [3]. Our results are consistent with the assignment of this band to out-of-plane Br_2^- centers, known [3] to be the predominant V_k centers formed and to have their axes close to $[111]$. The other two absorption bands at 2.45, 2.08 eV are found to be shifted to lower energies from the $F(F^-)$ and $F(Br^-)$ bands at 2.65 and 2.15 eV [14], respectively. These bands could obvi-

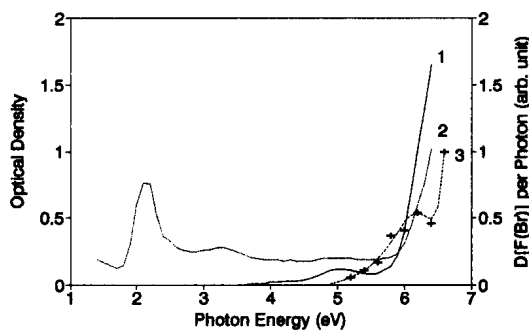


Fig. 3. Absorption spectra of BaFBr crystals at 295 K after quenching (1) and subsequent ultraviolet irradiation (2). (3)—Formation spectrum of $F(Br^-)$ centers.

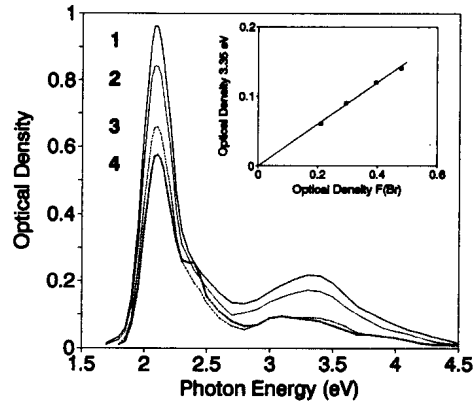


Fig. 4. Absorption spectra of BaFBr crystals at 80 K after X-irradiation at 80 K (1) and heating up to 120 (2), 140 (3), 180 K (4). The upper set shows the correlation of the intensities of the 2.08 and 3.35 eV bands during X-irradiation.

ously be caused by slightly disturbed $F(F^-)$ and $F(Br^-)$ centers. A similar $F(Br^-)$ perturbed band was observed earlier [3].

3.1.2. *BaFCl*. There are bands at 4.9, 6.3 and above 7 eV in the absorption spectra of BaFCl crystals containing oxygen (Fig. 5). A photoluminescence band at 2.35 eV (with halfwidth 0.5 eV) at 80 K was excited within the 4–8 eV region (see Fig. 5). The excitation spectrum of the 2.35 eV emission band consists of 4.5, 6.3 and 7.4 eV bands, and above 8 eV the 2.35 eV band sharply decreased and a 3.35 eV band appeared (see Fig. 5), which is obviously related to excitons [12, 16].

The crystals can be colored by u.v. light with photon energies above 5.5 eV. The 4.9 and ~ 7.3 eV absorption bands decreased and several new bands appeared at 295 K (Fig. 6). The 2.24 and 2.42 eV bands were most intense in colored crystals. The 2.24 eV band corresponds to $F(Cl^-)$ centers [15] and the 2.42 eV one can be ascribed to the $F(Cl^-)$ centers

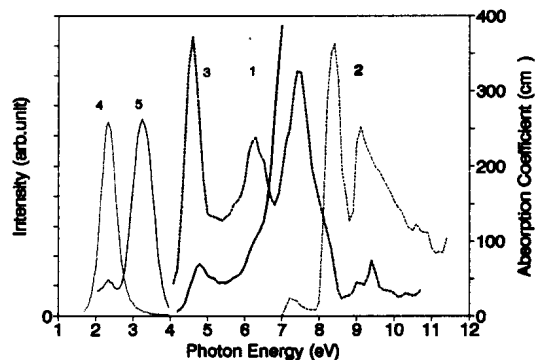


Fig. 5. Absorption (1), emission (4, 5) and excitation (2, 3) spectra of BaFCl crystals at 80 K. Photoluminescence spectra were measured under 7.7 (4) and 8.4 eV (5) light irradiation. Excitation spectra were measured for the 2.35 (3) and 3.35 eV (2) emissions.

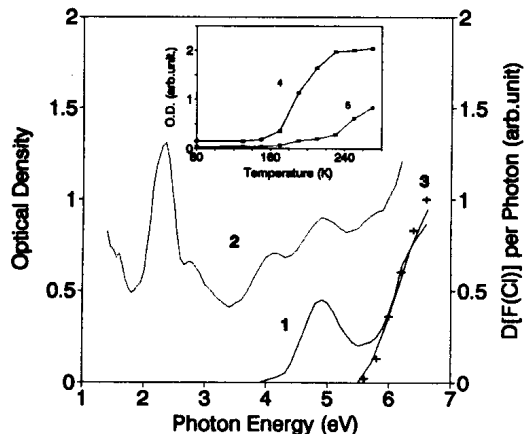


Fig. 6. Absorption spectra of BaFCl crystals at 295 K after quenching (1) and subsequent ultraviolet irradiation (2). (3)—Formation spectrum of $F(Cl^-)$ centers. The upper set shows the temperature dependence of efficiency of photochemical production of $F(Cl^-)$ centers (4) and F-aggregates (at $E < 1.4$ eV) (5).

perturbed by some defects. The weak band near 3 eV is associated with $F(F^-)$ centers and the band with $E < 1.4$ eV with some F center aggregates [15]. The 2.42 eV centers can be transformed optically into unperturbed $F(Cl^-)$ centers at 80 K, while reverse transformation is ineffective. Heating of the crystal reduces the 2.42 eV band in the range of 220–270 K. Along with this, the formation of $F(Cl^-)$ as well as F-aggregates ($E < 1.4$ eV) is observed. Above 280 K the 2.42 eV band was sharply reduced. The coloration efficiency by u.v. light decreased in the range from 270 to 160 K, and has a constant value below 160 K (see Fig. 6). When quenched BaFCl crystals were annealed at 160°C the 4.9 eV band was shifted to higher energies, perhaps due to aggregation of oxygen centers.

3.2. The type II centers

Oxygen centers of the second type have three absorption bands in BaFBr and four in BaFCl crystals (Fig. 7). The centers in both crystals have their own luminescence bands (see Table 1). The excitation bands of this luminescence coincide well with oxygen absorption bands. These luminescence bands are found to be shifted from bands of type I centers by 0.45 eV to lower energies in BaFBr and by 0.15 eV to higher energies in BaFCl crystals.

After u.v. irradiation at room temperature all oxygen absorption bands were decreased and $F(X^-)$ bands appeared. A photochemical reaction is effective when the crystal is irradiated into the second or third absorption bands. The bands of the formation spectrum of $F(Br^-)$ centers coincide with absorption bands of oxygen centers (see Fig. 7). The photochemistry is much less effective at 80 K than at room temperature.

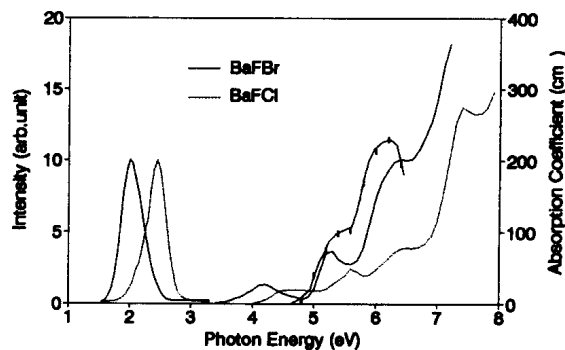


Fig. 7. Absorption (right), emission (left) and $F(Br^-)$ formation spectrum (points) of type II oxygen-vacancy centers in BaFCl and BaFBr crystals at 80 K. Emission spectra are measured with excitation light from the first low-energy absorption bands.

The long storage of BaFCl, BaFBr at room temperature or short heating to 100°C completely changes the initial spectrum: the first and second absorption bands disappear and two new bands between them are created. Moreover, weak absorption bands from aggregated oxygen centers appeared at 80 K in the spectrum of a rapidly quenched BaFCl crystal. Similar transformations of absorption spectra due to aggregation of oxygen-vacancy centers in alkali halides and alkaline-earth fluorides were observed earlier [5, 8].

4. DISCUSSION

The similarities between oxygen defects in BaFCl, BaFBr and oxygen-vacancy centers in alkali halides and alkaline-earth fluorides [5, 7, 8] allow us to conclude that oxygen defects in barium fluorohalides are oxygen-vacancy centers. Such defects in other ionic crystals have several absorption and photoluminescence bands and participate in aggregation and photochemical reactions [7, 8].

Experimental results show that there are two types of oxygen-vacancy centers in barium fluorohalide crystals. The absorption and emission bands are listed in Table 1. Some recent data [5] for oxygen-vacancy centers in BaF_2 are also included.

4.1. Type I and II centers

The barium fluorohalide lattice contains two kinds of anions: F and X (Cl, Br or I). Therefore, the oxygen-vacancy centers can occupy three different positions in a lattice: F-F, X-X and F-X pair sites.

When single crystals were prepared from powders, only stoichiometric ones grew well [17]. First we discuss the structure of the oxygen-vacancy centers in stoichiometric crystals. Photodissociation of the oxygen-vacancy centers leads to creation of O^- ions [2, 3] and F centers [mainly $F(Br^-)$ or $F(Cl^-)$] (see Figs 3

and 6). The $F(X^-)$ centers are efficiently produced by X-irradiation at 80 K, when free electrons are captured by oxygen-vacancy centers and holes are self trapped (see later). The efficiency of $F(F^-)$ creation is more than 10 times smaller than that for $F(X^-)$ in both cases. Obviously the anion vacancy of the type I center occupies a bromine or chlorine site but not a fluorine one. At room temperature X-irradiation of BaFBr:Eu containing oxygen, O^- centers, substituting for F^- , are formed [2]. The oxygen ion (O^{2-}) is believed to substitute for fluorine with charge compensation provided by a bromine vacancy [2]. These facts allow us to conclude that the O^{2-} -vacancy center of type I in stoichiometric barium fluorohalide crystals consists of an oxygen ion substituting for F^- and a neighboring Cl^- or Br^- vacancy. It is also possible to grow F-rich or X-rich BaFX crystals [13]. Under X-irradiation of F-rich crystals, $F(X^-)$ centers were mainly created and vice versa [13, 17]. From these results one would generally expect that in F-rich crystals the oxygen-vacancy centers must be in the X-sublattice and in X-rich crystals they must be in the F-sublattice. When a crystal is regrown in vacuum more BaX_2 must evaporate from the melt than BaF_2 due to the higher vapor pressure, and oxygen-vacancy centers are expected to be in the X-sublattice. The energy of the first absorption band of type II centers in BaFCl, BaFBr is lower than that of type I by nearly 0.4–0.8 eV (see Table 1). The first absorption band of the oxygen-vacancy centers is related to transitions from the ground state (mainly oxygen p -orbitals) to an excited one (mainly vacancy s -orbitals) [18]. The ground level of the oxygen-vacancy center in alkali halide crystals is not far above the top of the halide valence band [18]. In barium fluorohalide crystals, the upper valence band derives from chlorine or bromine [11], and the fluorine valence band is about 3 eV lower [19]. The qualitative scheme of the zone bands of barium fluorohalide crystals shows that the energy of the first absorption band of the (F–X) or (F–F) oxygen-vacancy centers has to be larger than that of (X–X) centers (Fig. 8). Some doubts exist about the presence of a band gap between fluorine and halide valence bands. Nevertheless, the same general scheme for the energy levels of oxygen-vacancy centers has to be valid for both cases. We therefore assume that oxygen ions of type II centers occupy the chlorine or bromine sites. As in the case of type I centers, photodissociation of type II oxygen-vacancy centers leads mainly to the creation of $F(X^-)$ centers (see Fig. 7). It is reasonable to conclude that the O^{2-} -vacancy type II defect in barium fluorohalide crystals occupies the X–X pair sites.

The energies of the first bands of the (F–X) and (F–F) oxygen-vacancy centers have to be almost

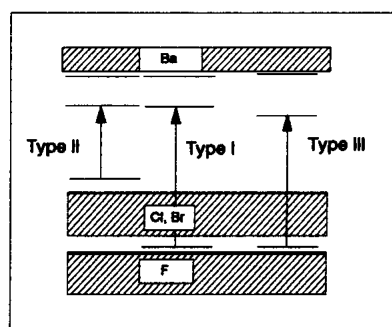


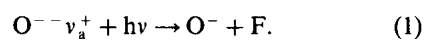
Fig. 8. The qualitative scheme of zone bands of barium fluorohalide crystals and energy levels of oxygen-vacancy defects of three different types. The arrows show the allowed transitions which form the first absorption bands.

equal because the energy difference between the ground levels of $F(F^-)$ and $F(Br^-)$ is about a few tenths of an eV (see Fig. 8). The absorption and emission bands of type I oxygen-vacancy centers in BaFX agree closely with those in BaF_2 (see Table 1). Consequently, the absorption and emission bands of (F–F) and (F–X) oxygen-vacancy centers are expected to be in close agreement. In spite of the similarity of the optical spectra, the (F–F) type centers can be distinguished from (F–X) ones by differences in photodissociation and low temperature X-ray coloration. $F(F^-)$ type centers have to be the most prominent product of these processes. The relatively small $F(F^-)$ -like band was observed in a photobleached crystal as well as in the X-irradiated one (see Figs 3, 4 and 6). Perhaps these results arise from the presence of a small fraction of $F(F^-)$ type III oxygen-vacancy centers as well as those of (F–X) type I.

Although we have no results that point clearly to the coexistence of different types of oxygen-vacancy centers, this is probably not impossible. For example, if the oxygen concentration exceeds the deficit for bromine ions, (Br–Br) type II oxygen-vacancy centers are likely to be present as well as “normal” (F–Br) type I ones. This coexistence will be easily detected from the rather different absorption and emission bands of type I and II centers (see Table 1), particularly in the case of BaFBr.

4.2. Photodissociation

Photodissociation of oxygen-vacancy centers in alkali halide crystals above 200 K follows the reaction [8, 20]:



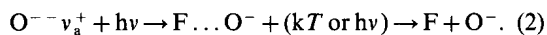
The reaction is not effective when a crystal is irradiated into the low absorption band [8]. The O^- ions

were detected by ESR [21] and optical absorption techniques [20]. Photodissociation of the oxygen defects in BaFCl and BaFBr crystals also occurs by irradiation into second (and higher) absorption bands (Figs 3, 6). Recently the creation of O^- ions substituting for F^- as well as $F(Br^-)$ centers was observed in a BaFBr crystal after u.v. irradiation (4.5–5.7 eV region) at room temperature [2]. The authors concluded that the photoionisation of O^{2-} ions and subsequent capture of electrons by Br^- vacancies leads to the creation of O^- and $F(Br^-)$ centers [2]. Obviously their results correspond to ours (see Fig. 3).

During the photodissociation process of the type I oxygen-vacancy centers in BaFCl and BaFBr at low temperature, perturbed $F(X^-)$ centers were created as well as unperturbed ones. The perturbed centers possess the following properties:

- the absorption bands of the centers are found to be shifted to higher energies by 0.15 (BaFBr) or 0.2 eV (BaFCl);
- the concentration of the centers formed below the temperature of their destruction is more than or comparable to that of $F(X^-)$ centers;
- with increasing temperature the centers partly transform to unperturbed $F(X^-)$;
- under light irradiation at 80 K the perturbed centers transform to $F(X^-)$.

It is reasonable to assume that the perturbed $F(X^-)$ centers are the intermediate defects on the way to creation of unperturbed $F(X^-)$ centers. Then we can write:

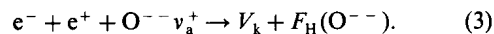


Here $F \dots O^-$ means F and O^- centers, which are separated by a few interionic distances. Similar F centers perturbed by neighboring sulphur ions were observed in NaBr- S^- crystals [22]. Perhaps the irradiation of BaFCl or BaFBr into the F band at low temperature leads to an optically stimulated motion of the F centers away from the O^- ions.

4.3. X-Ray coloration

The main effect of the presence of oxygen impurities is the enhancement of the efficiency of X-ray coloration [2]. V_k as well as perturbed $F(Br^-)$ centers are produced by X-irradiation of BaFBr at low temperature ($T < 150$ K) (see Fig. 4). Under X-irradiation free electrons and holes are produced in a crystal. At low temperature, some of the electrons are captured by oxygen centers and the corresponding

holes are self-trapped. This process in LiF, CaF_2 follows the reaction [23]:



The additional electron is captured in states that originated mainly from the anion vacancy, and leads to the production of an F center disturbed by a neighboring O^{2-} ion. Due to the oxygen ions, the absorption band of the $F(Br^-)$ centers is slightly shifted to lower energies (see Fig. 4). The V_k and F_H centers were completely converted back to oxygen-vacancy centers if the crystals were irradiated into the V_k band at 80 K. When a crystal was heated, the V_k band disappeared above 160 K and about half of the $F(Br^-)$ band also decayed (see Fig. 4). This means that some of the moving V_k centers are trapped by some defects and cannot reach the F_H centers. Perhaps these V_k centers were trapped by oxygen-vacancy centers as observed earlier in CaF_2 [24].

Above 200 K the reaction of dissociation of oxygen-vacancy centers begins to play a main role in the coloration of CaF_2 crystals [23]. In these X-ray coloration takes place by means of the same reactions as photochemical coloration [25]. The increase of X-ray [26] and photochemical coloration of oxygen-doped BaFCl in the 180–300 K range (see Fig. 6) as well as the parallel creation of O^- ions and F centers in BaFBr by X-irradiation [2] show that the dissociation of oxygen-vacancy centers is the main reason for X-ray coloration at room temperature.

The mechanism of photostimulated luminescence of barium fluorohalides doped with Eu^{2+} has been recognized as follows [1, 13]. F center creation as well as transformation of part of the Eu^{2+} to Eu^{3+} were observed under X-irradiation. Under exposure to visible light, the trapped electrons are released and recombine with Eu^{3+} ions, producing characteristic Eu^{2+} emission. Obviously, there are some defects in the crystals other than Eu^{2+} that can stimulate F center production by X-irradiation. The oxygen-vacancy centers are examples. Perhaps, the oxygen impurity is necessary for a good photostimulated luminescence yield from Eu^{2+} -doped BaFBr (also see [3]). Other defects that can enhance X-ray coloration of BaFBr include hydrogen-containing ones [27]. Additional investigations are required to solve this question.

5. CONCLUSION

1. Oxygen ions enter the BaFCl and BaFBr crystals as oxygen-vacancy centers. The main properties of the oxygen-vacancy centers in BaFCl and BaFBr

are similar to those in alkali halide and alkaline earth fluoride crystals.

2. Two types of oxygen-vacancy centers in barium fluorohalide were found. The first type of center consists of oxygen substituting at an F^- site and a neighboring Cl^- or Br^- vacancy. The second type of oxygen-vacancy center seems to be completely in the Cl or Br sublattice.

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