F-Centers in BaBrI Single Crystal

Roman Shendrik [iD], Nikolay Popov [iD], and Alexandra Myasnikova

Abstract— In this article, we demonstrate the results of experimental and theoretical studies of F-centers in BaBrI single crystals. We have observed two types of F-centers related to an electron trapped in the iodine or bromine vacancy site. It was found that absorption bands due to F-centers can be induced either by radiation or additive coloration. The excitonic mechanism of F-center production was established and demonstrated. Optical properties of the F-centers in a monoclinic symmetry environment have been calculated by means of the embedded cluster method.

Index Terms— Ab initio, density functional theory, embedded cluster, F-center, mixed alkali-earth halides, scintillator.

I. INTRODUCTION

MIXED alkali-earth halides are promising scintillator materials [1]–[6]. Several experiments have been reported in recent years that demonstrated the studies of color centers in BaBrI [7] and BaBrCl [8], [9] single crystals. The room temperature crystalline phase of BaBrI as well as BaClBr, $BaBr_2$, and $BaCl_2$ reveals the orthorhombic system. This fact is important because the color centers in these crystals could possess characteristic properties which are different from those known in cubic alkaline-earth fluorides.

The first detailed study of color centers in $BaBr_2$ and $BaCl_2$ orthorhombic crystals was performed by Houlier [10]–[12]. The authors could not obtain color centers by irradiation at room and liquid nitrogen temperature (LNT). However, they were able to induce the color centers after annealing in barium vapor atmosphere (so-called, an additive coloration) as well as under the electrolytic coloration.

Anion vacancies with a trapped electron (F-centers) in pure BaBrCl crystals were observed after X-ray irradiation [8] or under multiphoton laser irradiation [9]. In our recent study, we found an intensive absorption in the red spectral region in undoped BaBrI crystals after X-ray irradiation. Our preliminary estimations pointed out that these bands are attributed to the absorption of F-centers in BaBrI [7]. Furthermore, it was shown in [8] that X-ray irradiation of BaBrCl crystals induces the absorption bands at about 1.7 and 2.0 eV. The first band was attributed to F(Cl) centers,

whereas another one corresponded to F(Br) centers [9]. In this article, we demonstrate a detailed study of F-centers in BaBrI crystals using both experimental and theoretical approaches.

II. EXPERIMENTAL TECHNIQUE

Nominally pure BaBrI single crystals were grown by Bridgman technique in sealed quartz ampoules as reported elsewhere [2], [6], [13]. The crystal plates are cut off in the plane perpendicular to the crystallographic *b*-axis. A typical sample thickness was about 1.5 mm.

We can expect the coexistence of two types of F-centers in BaBrI crystals. In order to change a ratio between different types of F-centers, we applied the Czochralski growth method [14]. The conventional growth setup with the graphite thermal screens and the resistivity heater was utilized. The crystals were grown in argon atmosphere in the glassy carbon crucible. The BaBrI seeds were utilized for all growth experiments. The crystal pulling rate was 0.5 mm/h and the rotation rate was 5 rpm. Changing the ratio of $BaBr_2/BaI_2$ in the mixture, the undoped crystal having the excess of F(I) centers can be grown. We denoted such sample as nonstochiometric crystal BaBrI-Br.

Optical absorption spectra were measured using a Perkin-Elmer Lambda 950 spectrometer. The crystals are hygroscopic and therefore all measurements must be carried out putting the samples into the vacuum chamber.

The undoped BaBrI crystals were irradiated by the X-ray tube with Pd anode (40 kV, 20 mA) as well as by the low-pressure Hg-lamp ($\lambda = 185$ nm) for 20 min. The induced color of the crystals was the same. To measure the efficiency of F-centers creation, the samples were placed into evacuated closed-cycle cryostat, equipped with a cryocooler Janis Research CCS-100/204N, and then they were irradiated for 15 min at different temperatures.

Procedure for the additive coloration of the alkaline and alkaline-earth halides was first described in [15]. The F-centers may be induced in the alkali-earth halides by heating them in the presence of alkali-earth metal vapor and the subsequent cooling of the crystals rapidly to room temperature (i.e., quenching). Additive coloring of crystals in metal vapors begins with the addition of a metal ion into the crystal to the cation site and the subsequent migration of the anion vacancies and electrons into the lattice [16]. This method was used for coloration of alkaline halide [15] and alkaline-earth fluoride crystals [11], [17]. Van Doorn proposed the method of controlled coloration by adjusting the pressure of the buffer gas introduced into the ampoule, which was called the "heating pipe" method [18]–[20]. In this article, we used a modified Van Doorn method described in [21].

The additive coloration of crystals was performed in a stainless steel autoclave at 670 °C in vacuum 10^{-3} Torr. The crystal samples and metal calcium granules were placed in two open containers, 1 cm apart. The evacuated autoclave was lowered into a furnace. After the heating to the required temperature, the autoclave with the samples was kept in the furnace for 2 h, with subsequent cooling. As a result of coloration, the surface of the samples became opaque. Therefore, the samples should be polished. After coloration, hollow white spheres remained in the calcium container. It means that the metal calcium evaporated during the coloration and a surface oxide film remained.

The temperature dependence of calcium vapor pressure is described by the empirical formula :

$$\log(p(\text{Torr})) = 7.79 - 8524/T \qquad (1)$$

where T is the temperature in K [22], [23]. The calcium vapor pressure at 670 °C is $5.6 \cdot 10^{-2}$ Torr.

The additively colored crystals have a deep blue color similar to the irradiated samples. The coloration of irradiated samples mainly occurs near the surface of the crystals. On the other hand, the additively stained samples have a uniform color over the whole crystals' volume. Both electron and hole color centers were detected in irradiated crystals which were formed as the result of a nonradiative relaxation of excitons. However, only electron trapped centers were observed in additively colored crystals [24]. Therefore, the additive coloration cannot be bleached by a heat treatment of the crystals.

III. COMPUTATION DETAILS

The calculations of the electronic and spatial structure of F-centers consist of two parts. First, the spatial structure of the defect's nearest environment was estimated using the periodic density functional calculations. Then, the displacements of the defect's nearest environment from the periodic calculations were projected to the embedded cluster model and the excited defect states and absorption spectrum of the F-center in BaBrI crystal were calculated.

A. Periodic Calculations

The calculations were carried out with CP2K package [25] at the hybrid density functional level of theory (DFT) with Heyd–Scuseria–Ernzerhof (HSE06) functional [26] using the mixed Gaussian and plane-wave approach [27]. Gaussian triple-ζ basis sets from MOLOPT [28] family were used for the description of the electronic states of Ba^{2+}, Br^-, and I^- ions. To reduce computational time using the highly contracted basis sets, we applied the auxiliary density matrix method [29]. The potentials of the Grodecker–Teter–Hutter (GTH) type were used for the description of the core electrons [30]–[32]. The search of the ground state of the electronic subsystem was performed using the orbital transformations (OT) method [33].

All calculations were performed at -point. The threshold for inclusion of plane waves in the auxiliary basis set by the energy was 700 Ry. The forces convergence criterion during the geometry optimization process was
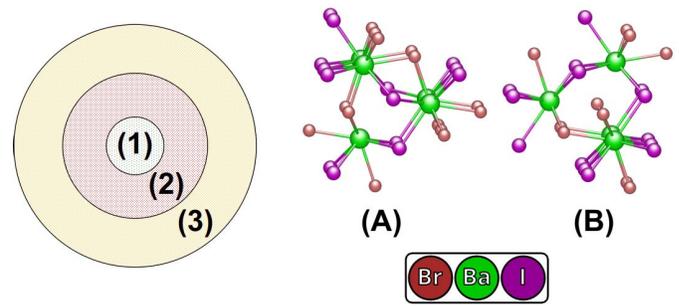

Fig. 1. Schematic representation of embedded cluster approach: (1)—quantum cluster, (2)—interface layer, (3)—point charges layer. On the right side of the figure, selected quantum clusters are shown: (A)—Ba $_5$Br$_{14}$I$_{14}$ (F(I)-center) and (B)—Ba $_4$Br$_{10}$I$_{14}$ (F(Br)-center).

10^{-4} Bohr^{-1} × Hartree. Optimization of geometry was performed using the limited Broyden–Fletcher–Goldfarb–Shanno (BGFS) method [34].

To simulate F-centers in BaBrI crystal, the supercell consisting of 192 atoms (Ba $_{64}$Br$_{64}$I$_{64}$) was used. The number of atoms was chosen as a compromise between the accuracy of the calculations and the computational time for large cells. The supercell was generated by the repetition of 4 × 2 × 2 unit cell. For the simulation of F-center, one of the Br$^-$/I$^-$ anions was removed. Cell charge and total spin were set to 0 and 1/2 values, respectively, and geometry was optimized.

B. Embedded Cluster Calculations

Using the displacements of the F-center's nearest neighbors from periodic calculations, the defect-centered embedded cluster has been constructed [35]. B3LYP [36] hybrid functional was utilized in time-dependent density functional theory calculations [37] to study the excited states of the F-centers. The RIJONX [38] approximation with Coulomb-fitting basis set [39] was used to speed up the computation. Calculations in this part were performed with Orca quantum chemistry package [40], [41]. The displacements projecting approach demonstrates high performance for the calculation of the electronic structure of Sm $^{2+}$-centers in LaF $_3$ [42].

In the embedded cluster approach, the model space is split into three layers, as shown in Fig. 1. There are (1) quantum cluster; (2) interface layer; and (3) point charges layer. In the first layer, all atoms of the quantum cluster are considered quantum-mechanically. Electronic states in the quantum cluster were described with correlation-consistent cc-PV-pp [43], [44] triple-ζ basis set with relativistic effective core potential [43], [45]. We expanded the barium basis set with additional diffuse exponents for a better description of F-center's excited states. We did not use any basis set for vacancies (basis set on ghost atom). It was found in [46] that d-functions of the surrounding cations led to a correct description of the F-center. F(Br) and F(I) centers were simulated with Ba $_4$Br$_{10}$I$_{14}$ and Ba $_5$Br$_{14}$I$_{14}$ quantum clusters, respectively (Fig. 1). Neighboring distance for Ba–Br equals 3.46 Å and for Ba–I equals 3.85 Å.

The next layer (2) consists of two types of entities: anions represented as point charges (-1) and barium ions modeled
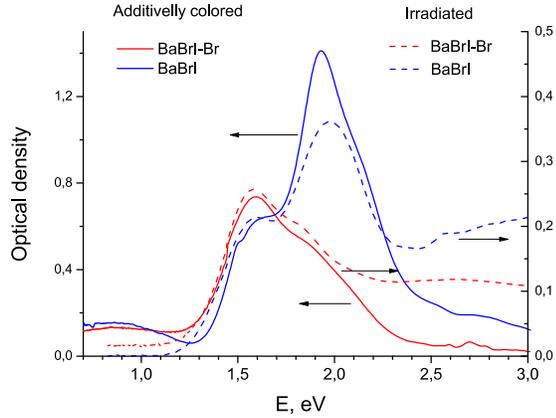
Fig. 2. Optical absorption spectra of additively colored BaBrI (blue solid curve) and BaBrI-Br (red solid curve) and irradiated BaBrI (blue dashed curve) and BaBrI-Br (red dashed curve).

using SDD effective core potential [47]. The last layer (3) consists of point charges.

IV. RESULTS AND DISCUSSION

Additive coloration and UV coloration lead to very similar optical absorption spectra (Fig. 2). In stoichiometric BaBrI, two absorption bands are observed: the high-intensity band at ∼1.95 eV and the less intensive one at ∼1.55 eV. The pedestal at energy higher than 2.5 eV in the spectra of UV irradiated samples can be attributed to the formation of complex hole centers [7], [48], [49].

The absorption spectra of additively colored and UV irradiated BaBrI-Br differ from the corresponding spectra for BaBrI. The strong absorption band in the region of 1.55 eV is dominant in the spectra for the BaBrI-Br crystals.

In both additive colored samples, a weak absorption band at about 0.9 eV was observed. The intensity of this band depends on the autoclave cooling rate after additive coloration. A slow cooling down rate (at about 100 °C/hour) leads to the increased intensity of this band. On the other hand, a quenching rate decreases the intensity of this band. In alkali-earth fluorides and alkali halide crystals, similar bands were explained as F-center aggregates such as M- and more complex centers [17], [20], [48], [50]–[54].

In our previous article [7], we assumed that the absorption bands at 1.95 and 1.55 eV in the irradiated BaBrI could be attributed to F-centers. Taking into account that the crystal has two types of halogen ions, two different types of F centers can exist. In other words, iodine F(I) and bromine F(Br) electron-trapped vacancies are expected. Thus, the observed absorption bands have been explained by the transitions from ground 1s-like state to the triply degenerated p-states of F-centers. This model is confirmed by Mollwo–Ivey law. Namely, the positions of the most intense absorption band for F(I) and F(Br) centers are in good agreement with Mollwo–Ivey law [55]: 1.98 eV for F(Br) and 1.55 eV for F(I) centers, when the distance between Ba–Br or Ba–I ions was taken as lattice parameter.

The ground states of F(Br) and F(I) are located at 1.72 and 1.50 eV below the bottom of the conduction band, respectively. The absolute displacements of F-center's nearest

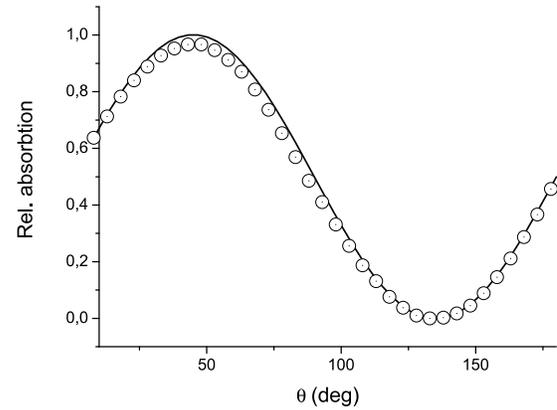| State Energy[eV]	Osc. strength	Trans. dipole moment[a.u.]		
		x	y	z
F-center(I)				
1.527	0.154	-2.001	0	0
1.590	0.165	0	-1.757	-1.014
1.914	0.100	0	0.616	-1.300
F-center(Br)				
1.600	0.151	0	-1.099	-1.587
1.912	0.077	0	-1.100	0.633
1.957	0.112	-1.506	0	0

Fig. 3. Measured (circles) and calculated (solid line) angular dependencies of 1.6 eV absorption band in BaBrI-Br crystal.

environment do not exceed 0.033 Å for F(Br) and 0.011 Å for F(I). The symmetry group of F(Br) and F(I) is monoclinic C_s. The same point group was observed for F-centers in $BaBr_2$ and $BaCl_2$ crystals [10]–[12].

Molecular orbitals of the ground and excited states are presented in Fig. 4. Transitions with high amplitudes (>0.95) are only shown. The ground state of F-centers has approximately an s-like wave function (A1 for F(Br) and B1 for F(I)). The excited states (A2–A4 for F(Br) and B2–B4 for F(I)) split into three states due to monoclinic group C_s. Excited states of the F-center are p-like orbitals. They do not preserve the shape of atomic p-orbitals but preserve axis orientation.

Energies of excited states, oscillator strengths for transitions from ground to excited state, and transition dipole moments for F(Br, I)-center are presented in Table I. According to the calculation of dipole moment in Table I, F(I) and F(Br) absorption should have dichroism. In stoichiometric BaBrI, we must consider the superposition of the contributions of all bands of F(I) and F(Br) centers to the absorption spectrum. In the nonstoichiometric crystal, we observed an excess of F(I) centers and optical absorption peak shifts to low energy region. In Fig. 3, circles indicate the intensity of the absorption band at 1.55 eV depending on the polarizer angle. The solid line is calculated dichroism of 1.55 eV based on Table I. The calculated and experimental data are consistent. Therefore, we can conclude that in the absorption spectrum of F(Br) centers the most intense band is located at about 1.95 eV and the less intensive band is located at about 1.6 eV. For F(I)
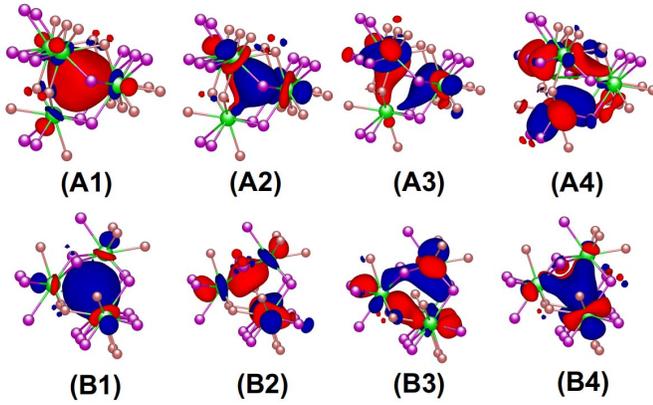
where k_B is Boltzmann's constant, l_0 is the average range of the replacement sequence at 7 K, r_0 is a critical distance of annihilation F–H pair, and E is the activation energy of F–H pair separation. The comparison of the experimental F-centers production efficiency with the estimation using (2) at low temperatures is shown in Fig. 5, solid line. It is clearly seen that (2) reasonably well explains the production yield for the temperature range between 10 and 290 K. The parameters l_0/r_0, l_1/r_0, and E could be found. The best fit curve was obtained if the parameters are $l_0/r_0 = 0.52$, $l_1/r_0 = 500$ and $E = 0.043$ eV as shown in Fig. 5. Thus, the separation barrier of the F–H pair is about 0.043 eV, which is close to the known value in alkali halide crystals [62], [63]. A lifetime of the state of $\sqrt{}$halogen in interstitial position τ_0 may be equal to $l_1/(10^{12} \overline{2} a)$, where a is a Ba–I distance. Using (2), the lifetime is about 10^{-9} s, which agrees well with the experimental data given in [9]. The ratio $l_1/l_0 \sim 10^3$ has the same order of magnitude as the corresponding value in alkali halides [63]. The decrease of F-centers production efficiency under UV irradiation at high temperatures can be attributed to the motion of complex hole centers (i.e., V_3) [64]–[66].

V. CONCLUSION

Two kinds of F-centers are identified in BaBrI single crystals. There are F(Br) and F(I) centers with C_s symmetry. They can be generated under UV, X-ray irradiation, or by means of the additive coloration technique. The *ab initio* calculation of the energies and the intensities of the optical absorption bands are performed. Based on the calculation, we suppose that the absorption bands are due to transition from the 1s-like ground state to the split by the crystal field p-like states of F-center. It was established that the excitonic mechanism of the defect formation takes place in BaBrI crystals.

Fig. 4. Molecular orbitals of ground and excited states of F(Br,I) in BaBrI crystal. F(I): A1—ground state, A2–A4—excited states(px, py, pz—like). F(Br): B1—ground state, B2–B4—excited states.
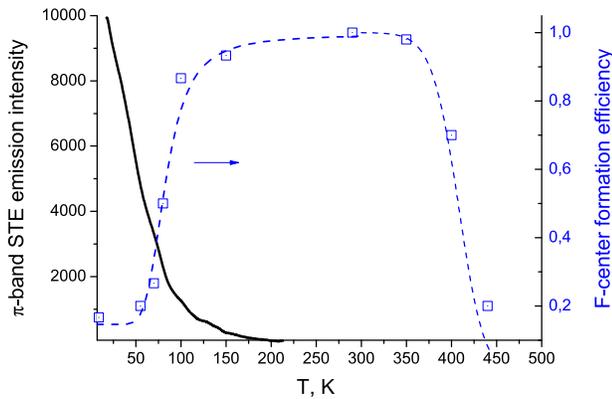

Fig. 5. Temperature dependence of STE emission (solid curve) and F-centers formation efficiency (squares).

centers, a lower energy band at about 1.55 eV becomes the most intense and less intensive bands at about 1.9 eV take place.

As shown in Fig. 5, the efficiency of F-centers production decreases during cooling at temperatures below 100 K, where the intensity of self-trapped exciton (STE) band emission increases [2], [3]. This anticorrelation behavior is similar to the alkali halides crystals observed before [56]. Therefore, the excitonic mechanism of the defect formation in BaBrI crystals is evident. After the irradiation, a free anion exciton decays into F–H pairs by analogy with alkali halide crystals [57]–[60].

The increase of F-centers production efficiency could be explained using the model promoted by Sonder [61], Saidoh *et al.* [62], and Itoh [63]. It was pointed out in this model that the increase of defects production efficiency is driven by the probability of the formation of stable interstitial halogen and anion vacancy pairs. The average range of the replacement sequences increases with temperature. In [62], it was pointed out that if the range of a dynamic sequence exceeds a critical value of r_0, a stable Frenkel defects pair is formed. In this model, the escape probability of a replacement sequence from a vacancy can be described by the following equation:

$$p = \exp(-r_0/l) = \exp \frac{r_0}{l_0 + l_1 \exp(-E/k_B T)} \quad (2)$$

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