

The First-Principle Calculation of F-Centers in BaXY Crystals (X, Y - F, Cl, Br, I)

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Abstract. This paper presents the results of *ab initio* calculations of F centers in a number of crystals of mixed barium halides. The calculations were performed using the density functional method and the PBE0 hybrid functional. On the basis of the calculation results, layout of the location of the main levels of F centers in the band gap of the crystals under study was made.

INTRODUCTION

Interest in mixed barium halides reappeared after discovery of a high light yield of the BaFI: Eu²⁺ crystal [1], which was considered a good phosphor for computed tomography until 2010 [2]. The light yield of this crystal turned out to be higher than the light yield of the individual dihalide components (BaF₂ and BaI₂). Further studies were conducted on other mixed barium halides, the results of such studies are presented in Table 1. To date, complex alkaline earth metal halides (for example, BaBrI:Eu²⁺ [3], CsBa₂I₅:Eu²⁺ [4] and others) are the most effective scintillators with the best combination of high light output and proportionality. Payne et al. [5] demonstrated that the scintillation characteristics of crystals strongly depend on their crystal structure. In addition, Li et al. [6] suggested that the main reason for the better performance of complex halides compared to simple alkaline halides is the concentration and properties of deep electron traps in the crystal matrix. Diffusion, depth, concentration of traps, as well as the capture cross section, together determine the factor controlling both the disproportionality and the light output of the scintillator [7]. The elimination of deep traps can serve as a factor in reducing the disproportionality of halide scintillators, as well as increase the potential light output to very high values. Therefore, the study of intrinsic defects in the crystal structure of promising materials based on complex halides is a relevant task in the physics of scintillators.

On the other hand, the development of quantum chemistry methods in the field of periodic calculations in the last decade allows us to study the structural and optical properties of intrinsic defects in crystal structures (F centers, V_k centers, excitons). The relevance of such studies is connected both with the study of the position of electron and hole traps in the band gap of crystals, and with the study of the formation of self-trapped excitons (F-H pairs in halide crystals in most cases). Therefore, the *ab initio* calculation of F centers can be considered as the first step in the study of excitons.

At present, periodic calculations using the density functional method are carried out in the framework of the gradient approximation using the exchange-correlation potential PBE [8] or PBEsol [9]. It is known that use of the density functional with the PBE potential for calculations for semiconductors and dielectrics yield delocalized electronic states and, correspondingly, understated energy values of the band gap [10]. The most accurate methods such as GW0 [11], which give very good agreement with the experiment for halide crystals, are also gaining

popularity, but these methods require very large computational resources. Nevertheless, Rinke et al. [12] have presented the results of calculations of the optical spectra of F centers by the GW0 method together with the Bethe-Salpeter equation (BSE) approximation. In addition, studies of F centers have been carried out using hybrid functionals of the PBE0 type [13,14]. In this paper, we consider the applicability of the PBE0 hybrid functional for a number of crystals of mixed barium halides, and also evaluate the position of the levels of F centers in the band gap of crystals.

TABLE 1. Characterization of some scintillators based on certain barium halides (light yield data were taken from the scintillation properties database [15]).

Crystal	Light yield, photon / MeV (for nominally pure)	Light yield, photon / MeV (for 5% Eu activation)	Band gap, eV
BaF ₂	10000	no data	11 [16]
BaFCl	no data	no data	9.1 [17]
BaCl ₂	6000	52000	7.9 [18]
BaFBr	no data	27000	8.3 [19]
BaBrCl	no data	52000	7.3 [20]
BaBr ₂	19300	49000	6.8 [18]
BaFI	no data	55000	6.8 [21]
BaClI	no data	54000	6.3 [22]
BaBrI	no data	97000	5.5 [22]
BaI ₂	4600	38000	5 [18]

CALCULATION METHOD

An *ab initio* calculations for crystals of mixed barium halides were carried out in the framework of the density functional theory using the VASP software package [23] on the “Akademik V.M. Matrosov” computing cluster [24]. For calculations, a 2×2×2 supercell (96 atoms) was constructed in which an F center was formed in place of one of the lattice anions. The atomic positions and crystal symmetry were taken from the ICSD base [25].

The geometry optimization calculations were performed as part of the gradient approximation using the PBEsol exchange-correlation functional. Integration over the Brillouin zone was carried out over a G-centered grid of 8 k-points in the irreducible part of the Brillouin zone. The geometry optimization was carried out with preservation of the shape and volume of the cell. Convergence was considered achieved if the difference in the total energies between the two iterations did not exceed 10⁻⁶ eV.

The band gap calculations of alkaline-earth fluoride crystals were performed using the PBE0 hybrid functional, since it was demonstrated that this method gives fairly good comparability of the results with experimental data and does not require large computational resources [14,26]. The band gap was estimated as the energy difference between the highest occupied molecule orbital (HOMO) and the lowest unoccupied molecule orbital (LUMO).

To calculate the energy of formation of the F-center, we used the following expression [27]:

$$E_f = E_{def} - E_{perf} + U_x, \quad (1)$$

where E_{def} is the energy of the defective cell, E_{perf} is the energy of the defect-free cell and U_x is the chemical potential of the ion at the site of vacancy creation. To calculate the chemical potential, we used the calculated energy of the X₂ molecule:

$$U_x = \frac{1}{2}E(X_2). \quad (2)$$

The chemical potentials for the ions F, Cl, Br, and I, calculated by the formula (2), were equal to 1.86; 1.78; 1.49 and 1.32 eV, respectively. The results of calculations of the energy of formation of F centers using expression (1) are given in Table 2.

TABLE 2. The calculated energies of defect formation and the position of its level relative to the bottom of the conduction band, as well as the band gaps of defect-free crystals. For comparison, the experimental absorption energies of F centers in these crystals are presented.

Crystal	Type of F center	Formation energy of F center, eV	$E_{(F-CB)}$, eV	F center absorption energy (exp.), eV	Calculated band gap, eV
BaF ₂	F (F)	8.0	2.9	2.3 [28]	9.3
BaFCl	F(F)	8.7	2.3	2.9 [17]	7.2
	F(Cl)	6.8	1.9	2.2 [17]	
BaCl ₂	F(Cl)	4.6	2.1	2.5 [29]	6.8
BaFBr	F (F)	8.6	2.3	2.5 [17]	6.6
	F(Br)	6.4	2.1	2.1 [17]	
BaBrCl	F(Br)	4.0	1.9	2.3 [20]	6.2
	F(Cl)	4.1	2.0	1.8 [20]	
BaBr ₂	F(Br)	4.7	1.8	2.2 [29]	5.9
	F(F)	8.7	2.2	2.6 [21]	
BaFI	F(I)	6.0	1.8	2.0 [21]	5.4
	F(Cl)	3.6	1.7	no data	
BaClI	F(I)	3.0	1.6	no data	5.2
	F(Br)	3.5	1.6	2.0 [30]	
BaBrI	F(I)	3.3	1.4	1.5 [30]	5.0
	F(I)	3.3	1.2	no data	

RESULTS AND DISCUSSION

Geometry of the defect was optimized in crystals of BaXY crystals (where X, Y are F, Cl, Br, I) with use of the GGA-PBESol method. Figure 1 shows the charge density of the F center, according to which it can be argued that the optimization performed is sufficient to localize the electron to vacancies with the formation of an s -like state. The results of our calculations are presented in Table 2. The calculated values of the band gap turned out to be somewhat understated in comparison with the experimental data (Table 1), which was expected considering other works with calculations made using the PBE0 hybrid functional [26].

The energies of the formation of the F center decrease with increasing radius of the anion (anionic radii: F⁻ – 1.33 Å, Cl⁻ – 1.33 Å, Br⁻ – 1.33 Å, I⁻ – 1.33 Å). The highest energy of formation is observed for F centers at the site of the fluorine ion vacancy, which is in good agreement with other calculations [31]. For mixed barium halides of the BaFX type (X – Cl, Br, I), a significant difference was obtained between the energies of the formation of F centers depending on the anion (up to 2.7 eV for the BaFI crystal), while for the other studied mixed barium halides the largest difference was only 0.6 eV (BaClI, Table 2). Thus, we can say that a higher concentration of vacancies will be observed at sites of heavier lattice anions in crystals of the BaFX type (where X is Cl, Br, I). For the remaining mixed barium halides, there is no significant difference in the energies of the formation of F centers; therefore, the concentration of defects of both types will most likely be the same.

The ground state of the F center is a $1s$ -like orbital, its charge density is shown in Fig. 1. The excited $2s$ and $2p$ states usually lie in the band gap near the bottom of the conduction band. Therefore, the value of $E_{(F-CB)}$, which determines the distance between the bottom of the conduction band and the ground $1s$ state of the F center, should correlate with the absorption energy $1s \rightarrow 2p$ of the F centers. As one can see from Table 2, the values of $E_{(F-CB)}$ are comparable with the experimental values of the absorption of F centers for all of the crystals under study.

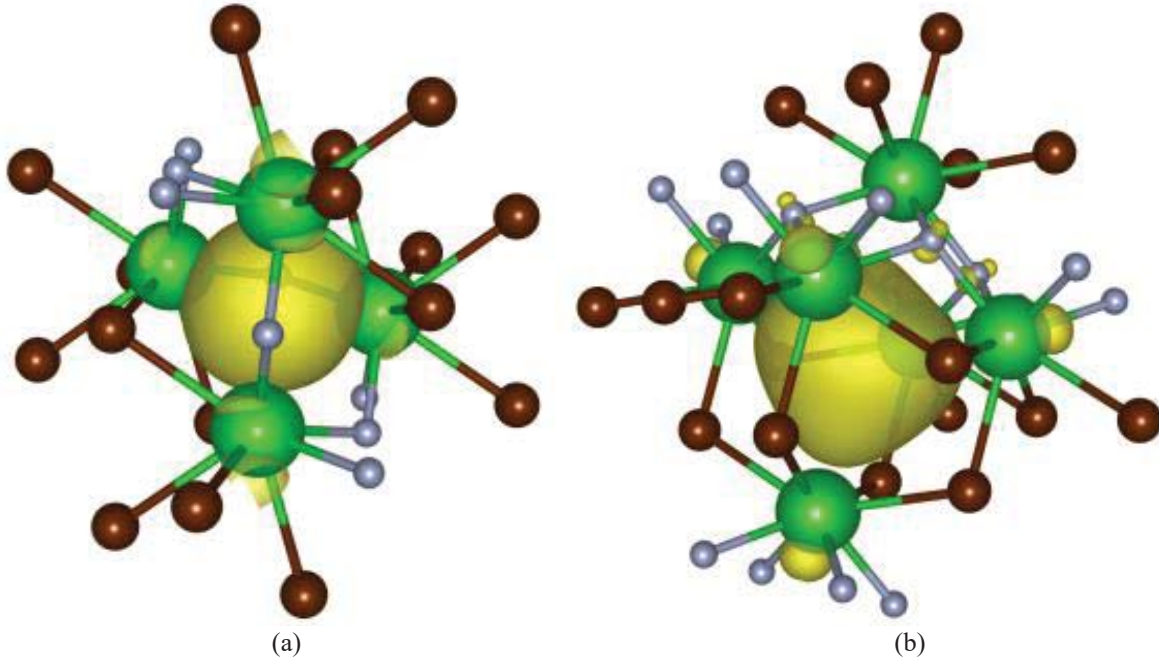


FIGURE 1. Image of the charge density of F center in BaFBr crystal: F center at the site of the vacancy of fluorine ion (a) and F center at the site of the vacancy of bromine ion (b)

On basis of the calculated data we made a schematic diagram of the position of the main levels of F centers in the band gap of crystals of mixed barium halides was constructed (Fig. 2). One can see from the diagram that the levels of F centers formed at the site of lighter anions are located lower in the conduction band. The experimental absorption energies for such ions are higher, which correlates well with our calculated data. In addition, it can be seen from Fig. 2 that the larger the band gap of the crystal, the lower the F-center levels are located relative to the bottom of the conduction band, therefore the electron traps become deeper which increases the time of energy transfer to the activator and delays the luminescence process. Correspondingly, all BaFX type crystals (X – Cl, Br, I), despite a large light yield, will show a long glow time due to the presence of deep electron traps in the form of F centers formed on fluorine ion vacancies.

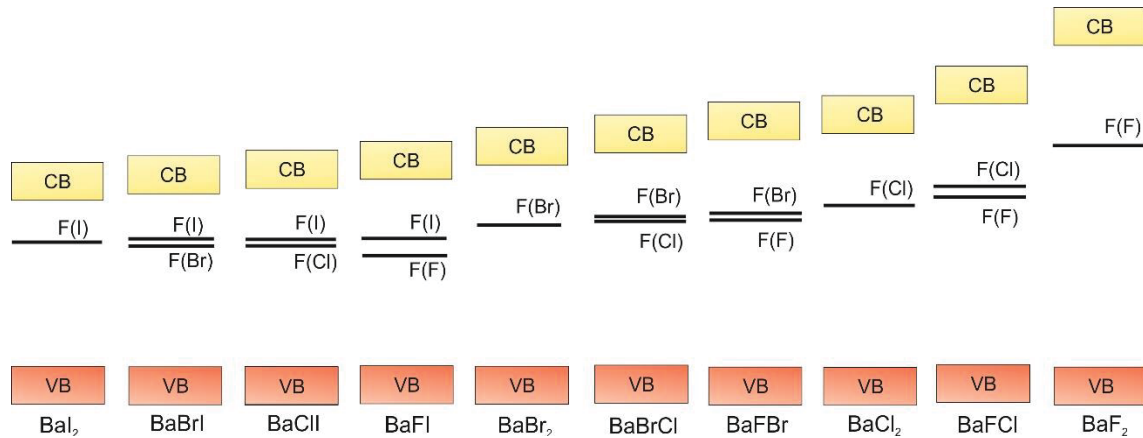


FIGURE 2. Schematic representation of the position of main levels of F centers in the band gap of crystals of mixed barium halides based on non-empirical calculations (CB – conduction band, VB – valence band)

CONCLUSION

The work presents studies of the band gap of crystals of mixed barium dihalides BaXY (where X, Y is F, Cl, Br, I), carried out by *ab initio* methods in the framework of the density functional method. The calculations were performed using the PBE0 hybrid functional, which turned out to be sufficient for the correct reproduction of the electronic structure of the crystals under study. A study of the position of the levels of F centers in the band gap of such crystals was conducted. It was shown that the levels of F centers formed at the site of lighter anions are located lower in the conduction band. In addition, F centers formed at the site of fluorine ions turned out to be the deepest electron traps, which explains the use of BaFX crystals (X – Cl, Br, I) as phosphors.

ACKNOWLEDGMENTS

This work was supported by the Russian Science Foundation (grant no. 18-72-10085). The study of F centers in barium dihalides (BaF₂, BaBr₂, BaI₂) was carried out within framework of Russian Academy of Science project no. 0350-2019-002 (AAAA-A17-117101170035-3). Authors are grateful to the Irkutsk Supercomputer Center of SB RAS for providing computational resources of the HPC-cluster “Akademik V.M. Matrosov”. Authors also acknowledge facilities of Information and Computing Center of Novosibirsk State University.

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