

Ab Initio Study of Alkaline-Earth Halide Scintillators Doped with Eu^{2+} Ions

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Abstract—The results from ab initio quantum chemical calculations for inorganic scintillators BaBrI:Eu^{2+} and BaClI:Eu^{2+} are presented. The calculations were performed using the density functional theory and the VASP software package. Estimates are made for the band-gap width of the crystals, and for the locations of $4f$ - and $5d$ -levels of Eu^{2+} ions with respect to the valence and conduction bands, respectively, and the possibility of using a new material based on BaClI:Eu^{2+} as a scintillator is evaluated.

Keywords: ab initio quantum chemical calculations, inorganic scintillators, density functional theory, BaBrI:Eu^{2+} and BaClI:Eu^{2+} crystals, band-gap width

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INTRODUCTION

Along with Ce^{3+} and Pr^{3+} ions, Eu^{2+} ions are now the most popular activators of inorganic scintillators. The luminescence of such ions is due to allowed $4f^{(n-1)}5d^1 \rightarrow 4f^n5d^0$ transitions, but the duration of Eu^{2+} ion emission is quite long, compared to praseodymium and cerium ions: it is estimated to be 400–1500 ns for different matrices, which restricts the use of such activators as ultra-fast scintillators (in, e.g., medical tomographs).

In the world literature, however, there is now renewed interest in scintillation materials activated by europium ions, since high light yields and good energy resolution can be obtained using such materials as $\text{SrI}_2:\text{Eu}^{2+}$ and BaBrI:Eu^{2+} [1–3], and the decay time is sufficient for media activated by europium ions to be used in such fields as national security and the non-proliferation of nuclear weapons.

This work presents the results from calculating the positions of the $4f$ - and $5d$ -levels of europium ions in BaBrI:Eu^{2+} and BaClI:Eu^{2+} crystals. These calculations were performed by assuming that the $4f$ -level of impurity ions in an efficient scintillator should lie above the top of the valence band (the valence band maximum, or VBM) of the crystal, while the $5d$ -level should lie below the bottom of the conduction band (the conduction band minimum, or CBM). In other words, both the $4f$ - and $5d$ -levels of europium ions should lie in the band gap of the crystal (Fig. 1).

CRYSTAL CHARACTERISTICS

Information on the position of atoms in a BaBrI crystal and its symmetry was taken from the ICSD (Inorganic Crystal Structure) database [4]. Such data for BaClI are not available, however, so an X-ray diffraction analysis of a grown BaClI single crystal was performed to obtain crystallographic data.

We used BaCl_2 and BaI_2 mixed at a molar ratio of 1 : 1 to grow our BaClI crystals. The melting point of BaClI is 815°C. The crystals were grown from a melt using the vertical Bridgman method in vacuumed quartz ampoules. The temperature gradient ranged from 10 to 15°C/cm. The growth rate of the crystals was 1 mm/h. A number of BaClI crystals activated by rare-earth Eu^{2+} ions was grown in a wide range of concentrations (0.01 to 8%).

Fragments of BaClI crystals denoted as BCI-1 and BCI-4 were analyzed on an Bruker D8 VENTURE AXS X-ray diffractometer equipped with two radiation sources and a Photon 100 radiation detector of monochromatized MoK_α radiation that used a Bruker Cobranitrogen Cryostat attachment at 100 K. Three sets of 20 frames each were used to determine symmetry groups and unit cell parameters, while a complete data set was compiled by scanning through angles φ and ω with rotation of 0.3° and exposure of 2 s per frame, at a crystal-to-detector distance of 40 mm and electric parameters of 50 kV and 1 mA. The data collection strategy was optimized using the APEX2 software package [5], while the intensity of reflexes was

determined and corrected by allowing for Lorentz polarization with the SAINT code [6]. Semi-empirical corrections of absorption were made using the SADABS software package [7]. At this stage, it was established that the investigated samples crystallized in an orthorhombic system. Using the XPREP code helped determine the spatial group (*Pnma*) and calculate intensity statistics. Finally, the structure was refined via the least squares method using the CRYSTALS code [8]. The structure was preliminarily deciphered via charge flipping [9], while the spatial group was confirmed by analyzing a reconstruction of electron density.

The refined parameters were scale factors, the atomic coordinates of atoms, the population of positions, and atomic displacement factors. As a result of preliminarily deciphering the structure in the anisotropic approximation, the value of R was $\approx 4\%$ and 5% for BCI-1 and BCI-4, respectively. The calculated Fourier difference map showed considerable residual electron density. For the BCI-1 sample, the highest peaks ($\sim 2 \text{ e}^-/\text{\AA}^3$) were found at around $1.2\text{--}2.5 \text{ \AA}$ from the positions of Cl and I. For the BCI-1 sample, the highest peaks ($\sim 2\text{--}2.3 \text{ e}^-/\text{\AA}^3$) were observed at $2\text{--}2.4 \text{ \AA}$ from the positions of Ba and I. These peaks require further interpretation. The characteristics of the crystal and experimental data are given in Table 1.

Ba, Cl, and I atoms occupy fourfold special positions ($4c$) in the orthorhombic structure (space group *Pnma*) of the investigated compound, being located on a mirror plane perpendicular to the b axis. The position of each barium atom is coordinated by 9 anions with average interatomic distances of Ba–Cl ~ 3.15 and Ba–I $\sim 3.59 \text{ \AA}$ (Fig. 2).

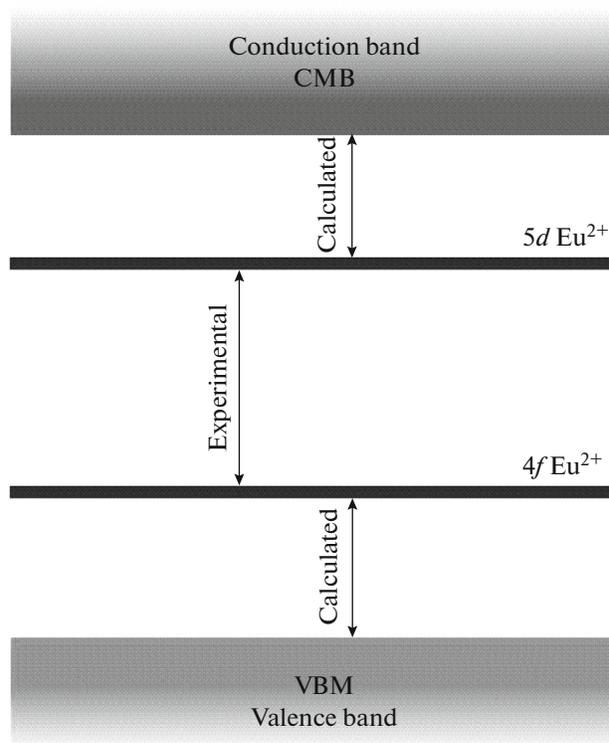


Fig. 1. Schematic representation of the band structure of scintillators activated by Eu^{2+} ions.

The localization of Eu ions and the refinement of the structure with allowance for the peaks of the residual electron density requires further detailed consideration and is now at the stage of implementation.

Table 1. Crystallographic characteristics, experimental data, and preliminary structural refinement for BCI-1 and BCI-4 samples

| Sample | BCI-1 | BCI-4 |
|---|--------------------------------|--------------------------------|
| Crystal system, space group | Orthorhombic, <i>Pnma</i> | |
| $a, \text{\AA}$ | 8.4829(5) | 8.4598(6) |
| $b, \text{\AA}$ | 4.9517(3) | 4.9331(4) |
| $c, \text{\AA}$ | 9.6139(5) | 9.5937(7) |
| $V, \text{\AA}^3$ | 403.83(4) | 400.37(5) |
| Z | 4 | 4 |
| $D_x, \text{g cm}^{-3}$ | 5.23 | 4.94 |
| Crystal size, mm | $0.42 \times 0.39 \times 0.02$ | $0.16 \times 0.12 \times 0.11$ |
| T, K | 100 | |
| Diffractometer | AXSD8 VENTURE Bruker | |
| Type of radiation; wavelength, \AA | $\text{MoK}\alpha_1; 0.71073$ | |
| Scan type | ω, φ | |
| T_{\min}, T_{\max} | 0.1784, 1.000 | 0.5714, 1.000 |
| $\theta_{\min}\text{--}\theta_{\max}, \text{deg}$ | 3.203–30.538 | 3.211–30.506 |
| Method of refining | LST on F | |

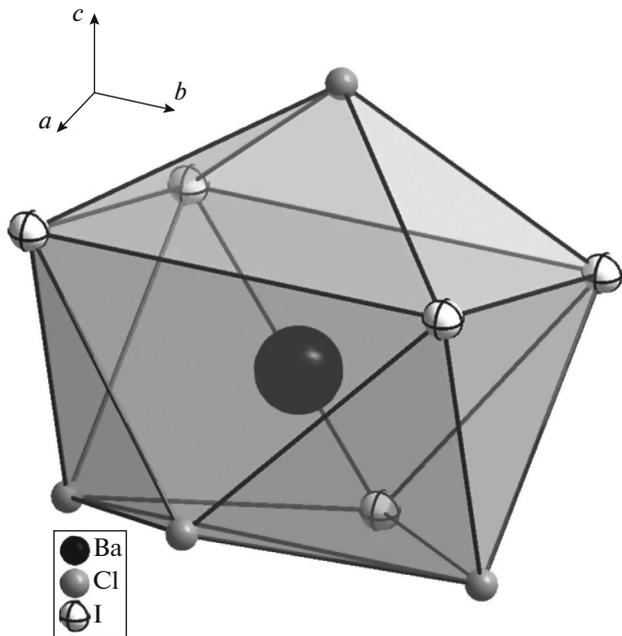


Fig. 2. Arrangement of Cl and I atoms around the Ba atom: a coordination polyhedron.

QUANTUM-CHEMICAL CALCULATIONS

Our *ab initio* calculations for BaBrI and BaClI crystals doped with Eu^{2+} were performed using the density functional theory and the VASP software complex [10] on the Akademik V.A. Fock [11] and Akademik V. M. Matrosov [12] computer clusters. A $2 \times 2 \times 1$ supercell consisting of 48 atoms was constructed, in which one Ba atom was replaced with a Eu atom. The positions of the atoms and the symmetry of the crystal for BaBrI were taken from the ICSD base [4], while we used XRD structural analysis data obtained for a BCl-1 sample when it came to the BaClI crystal. It should be noted that our calculations focused on the band structure of the BaBrI: Eu^{2+} crystal for a reason, since both experimental [13, 14] and calculated data [15] are available from the literature only for this crystal. We were therefore able to compare the results from our calculations and the published data.

Our spin polarization calculations were performed in a gradient approximation using the PBE exchange correlation potential [16]. Integration over the Brillouin zone was done along a Γ -centered grid of 8 k -points in the irreducible part of the Brillouin zone. The geometry was optimized with conservation of the shape and volume of the cell. Convergence was considered to be achieved if the difference between the total energies of the two iterations did not exceed 10^{-6} eV.

The ground state of Eu^{2+} ions with the $[\text{Xe}]4f^7$ configuration is characterized by half-filled f -shells. The authors of [15, 17] showed that a better description of $4f$ electrons requires the introduction of single-center Hubbard corrections into Coulomb and exchange

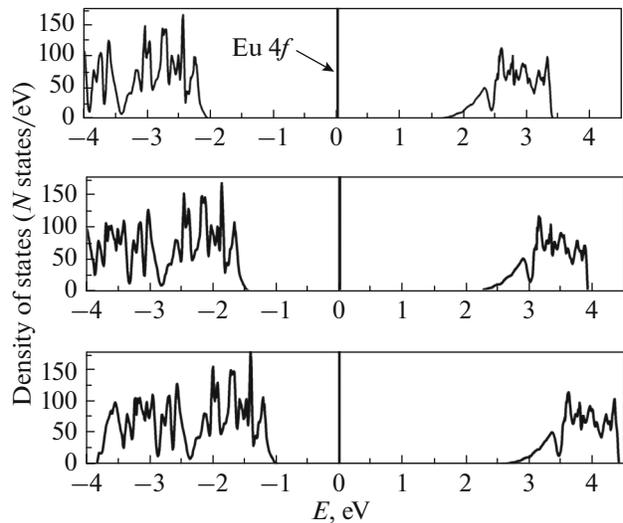


Fig. 3. Total densities of states for BaBrI: Eu^{2+} crystal at different values of parameter U_{ef} : (a) $U_{\text{ef}} = 1.0$; (b) $U_{\text{ef}} = 2.5$; (c) $U_{\text{ef}} = 3.5$. Only spin up states are presented. The Fermi level is normalized to 0.

interactions. Dudarev's PBE + U approximation [18] was therefore used to correct the position of the $4f$ level [18], where the difference $U_{\text{ef}} = (U - J)$ rather than individual parameters U and J is substantial. Data on activated Eu^{2+} ions found in the literature show that U_{ef} for Eu^{2+} should be ≥ 4 [19, 20]. However, it was shown in [15] that the $4f$ -levels of Eu^{2+} ions are best described by U_{ef} values ranging from 2.2 to 2.5. We performed a number of calculations for BaBrI: Eu^{2+} crystals to refine the U_{ef} parameter for our crystals (Fig. 3). The results from our calculations coincided almost completely with those obtained by the authors of [15]. The value of U_{ef} was set at 2.5, which yielded a $4f$ -VBM value of 1.4 eV (Table 2). We used the same value of U_{ef} in our calculations for BaClI: Eu^{2+} crystals. The value of the $4f \rightarrow 5d$ transition for the BaClI: Eu^{2+} crystals was estimated by assuming that this value was approximately the same as in the series of BaFI–BaClI–BaBrI crystals.

Calculations for the band-gap width of BaBrI and BaClI crystals were performed by means of both PBE and G_0W_0 approximation [21, 22]. It is known that using a density functional with the PBE potential in calculations for semiconductors and dielectrics leads to delocalized electronic states and thus to underestimated values of the band gap energy [23]. However, the use of such means as G_0W_0 yields a band gap value for ionic crystals that is comparable to experimental data [15, 17, 23], which was also confirmed by our calculations (Table 1).

The energy of the $4f \rightarrow 5d$ -transition in Eu^{2+} ions was obtained experimentally for a BaBrI crystal only.

Table 2. Results from calculating the band gap and the positions of the $4f$ - and $5d$ -levels of a Eu^{2+} ion with respect to the valence band maximum (VBM) and the conduction band minimum (CBM), respectively; all energies are given in eV

| Crystal | Band gap, eV | | Eu, $4f$ -VBM | $4f \rightarrow 5d\text{Eu}^{2+}$ | Eu, $5d$ -CMB |
|---------|--------------|----------|------------------|-----------------------------------|------------------|
| | PBE | G_0W_0 | | | |
| BaBrI | 3.49 | 5.34 | 1.4 | 3.19 | ~ 0.75 |
| BaClI | 3.71 | 5.57 | 1.5 | 3.23 | ~ 0.84 |

For the BaClI crystal, we used a value of 3.17 eV as the average between those of 3.22 and 3.12 eV obtained for BaBrI: Eu^{2+} crystals [24] and BaBrI: Eu^{2+} crystals [3], respectively, assuming that the energy of this transition for europium ions remains constant in the series of BaBrI–BaClI–BaBrI crystals. Knowing the width of the crystal band gap, the position of the $4f$ level of Eu^{2+} ions with respect to the valence band, and the energy of the $4f \rightarrow 5d$ transition, we could estimate the position of the $5d$ level of europium ions with respect to the bottom of the conduction band (the $5d$ conduction band minimum). The results from such an estimate are presented in Table 2.

For a material to luminesce so it can be used as a scintillator, it is generally necessary that the $4f$ - and $5d$ -levels of impurity ions lie in the band gap of the crystal. This was confirmed for BaBrI and BaClI crystals activated by europium ions. It should be noted that the position of the $5d$ level was calculated without allowing for lattice relaxation; however, it was shown in [25] that lattice relaxation can lead to a slight shift of levels on the order of ~ 0.1 eV. Ab initio quantum-chemical calculations were thus used to show that BaClI: Eu^{2+} crystal could be a new scintillation material.

CONCLUSIONS

A comprehensive study on the band structure of BaBrI and BaClI crystals activated by Eu^{2+} ions was performed using ab initio quantum-chemical calculations. Preliminary diffraction data for new BaClI: Eu^{2+} crystals were presented. It was shown that the $4f$ - and $5d$ -levels of europium ions lie in the band gaps of the crystals. We would therefore expect BaClI: Eu^{2+} crystals to have scintillation properties.

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