







ENERGY STRUCTURE OF CeCl₂Br AND CeClBr₂ CRYSTALS

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Band-energy structures of CeCl₂Br and CeClBr₂ crystals have been calculated using the projected augmented wave method (PAW) and the hybrid exchange-correlation functional PBE0. A valence band is formed by mixed 3*p* Cl and 4*p* Br states. There is an energy gap between the 5*d* states of Ce at the bottom of the conduction band, where subbands 5*d*1 and 5*d*2 have different effective electron masses of 2.3*m*₀ and 0.06*m*₀. 4*f* Ce states are located in the middle of the band gap. The calculated band gap values for CeCl₂Br and CeClBr₂ crystals are 4.5 eV and 4.0 eV, respectively.

Key words: scintillator, band structure, projected augmented wave method, band gap.

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I. INTRODUCTION

Inorganic scintillators like lanthanide fluoride crystals are intensively studied by scientists around the world due to their high light yield and fast decay kinetics [1, 2]. Nowadays, researchers focus on finding new compounds that eliminate the shortcomings important for practical usage.

In recent years, many works have been published on the study of crystals of the CeX₃ type (where X = F, Cl, Br, I) [3, 4] and LaF₃:Ln (Ln = Ce – Lu) [5, 6, 7]. One of the most popular crystals of this series is CeBr₃, which demonstrates unique scintillation properties. Unfortunately, the crystal has significant hygroscopicity [8], which severely limits the scope of its practical use. In [9], it has been demonstrated that mixing halogens in CeCl_{3-x}Br_x structures, despite a slight decrease in the light yield, significantly improved hygroscopic properties of such crystals. A detailed analysis of this approach will open the possibility of designing scintillators that will satisfy various applied scenarios. This method has already been successfully used to improve the scintillation properties of some crystals, including LaBr_{3-x}I_x: Ce [10] and CeBr_{3-x}I_x [11, 12]. In the current work, we present theoretical studies of CeCl₂Br and CeClBr₂ crystals, supplementing previously obtained information about CeCl₃ and CeBr₃ crystals [4] and interpret the results of experimental studies of the work [9].

The CeCl₃ crystal has a significant luminescence yield — 46 000 photons/MeV [13]. Also, good temperature stability of the decay time is expected since there are no transitions from the 5*d* Ce states to the bottom of the conduction band, which cause the noted drawback in the structurally and chemically similar LaCl₃:Ce [14]. Peaks with energies of 3.7 eV and 3.4 eV are observed in the emission spectra of the crystal at excitation energies of 4 eV and 5.4 eV [15].

Among all cerium fluoride crystals, the CeBr₃ crystal has the highest luminescence output value (68 000 photons/MeV) [16]. The luminescence spectrum

of this crystal is characterised by a typical doublet of the 4*f* Ce states at the energies of 3.35 eV and 3.17 eV [17]. The CeBr₃ crystal, having worse luminescent properties than LaF₃:Br, has a significantly lower value of background radioactivity [18], which is crucial for precision sensors.

II. MODELLING AND CALCULATIONS

Theoretical calculations have been made within the density functional theory (DFT) framework using the augmented projected wave (PAW) method [19], which allows taking into account the fast oscillations of the electron wave functions near the core, using limited computational resources. All above approaches are implemented in the open-source software Abinit [20, 21], which has been chosen for this study. To describe the exchange-correlation interaction of electrons, the PBE0 hybrid functional has been used, which is a typical choice for strongly localised systems like CeX₃ [3, 4]. Computer models of CeCl₂Br and CeClBr₂ crystal lattices have been used as input parameters for the calculations. Table 1 presents their parameters obtained using X-ray diffraction in [9]. In the study, the crystals have a hexagonal P3c1 structure [9]. The geometry optimization of lattices with the fixation of their volume has been made before the calculations.

Crystal	$\alpha = \beta$ (Å)	c (Å)	Volume (Å ³)
CeCl ₂ Br	7.65	4.37	221.47
CeClBr ₂	7.80	4.41	232.25

Table 1. Lattice parameters of CeCl₂Br and CeClBr₂ crystals [9]

All calculations have been performed on a 10 × 10 × 10 Monkhorst–Pack grid. The wave functions have been described by plane waves with a cut-off energy of



48 Hartrees (108 Hartrees within the PAW sphere). For a detailed analysis of the dispersion of the conduction band bottom states, 200 have been considered.

III. RESULTS AND DISCUSSION

Figure 1 shows the partial densities of states of CeCl_2Br (a) and CeClBr_2 (b) crystals. In both crystals, the top of the valence band is constructed by the

overlapped $4p$ Br and $3p$ Cl states. There is a typical high intensive peak $4f$ Ce in the middle of the band gap. The bottom of the conduction band is formed by the $5d$ Ce levels. The obtained band energy structure is similar to CeX_3 crystals [3, 4], and the peculiarity caused by using mixed halides is manifested only in the change of the valence band structure.

Differences in the total densities of states of the studied crystals are visually weakly noticeable (Fig. 2). In both cases, the width is 3.5 eV for the top of the valence band and 0.5 eV — for $4f$ Ce.

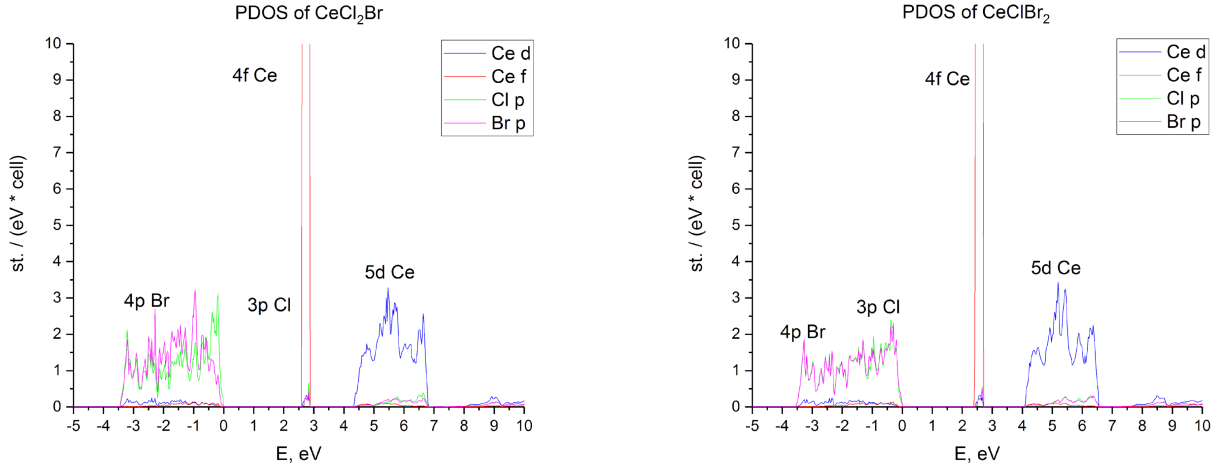


Fig. 1. Partial density of states (PDOS) of CeCl_2Br (a) and CeClBr_2 (b) crystals

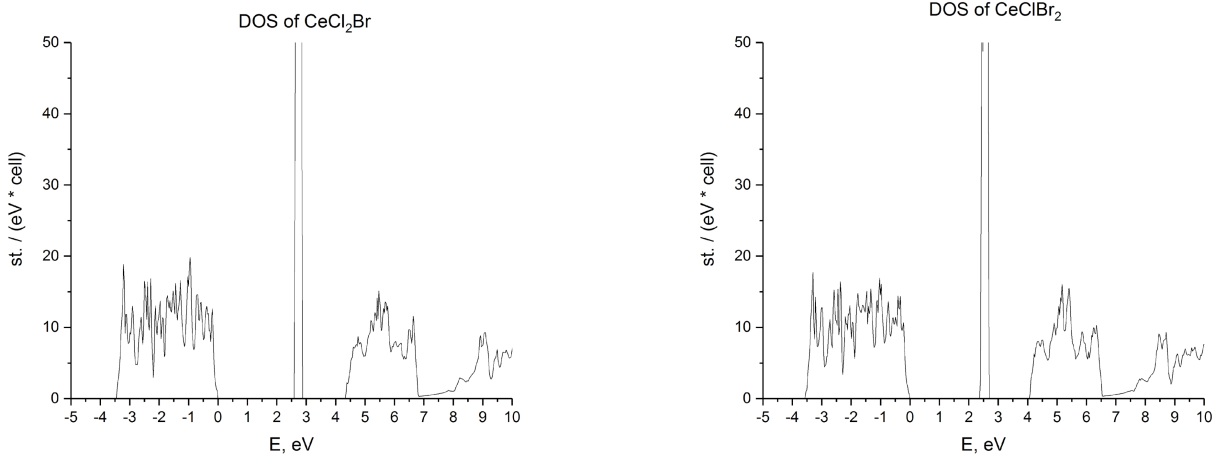


Fig. 2. Total density of states (DOS) of CeCl_2Br (a) and CeClBr_2 (b) crystals

Fig. 3 presents the calculated band structures of CeCl_2Br (a) and CeClBr_2 (b) crystals. The minimum value of the band gap (E_g) is at the proximity of Γ point and is equal to 4.5 eV and 4 eV for CeCl_2Br and CeClBr_2 , respectively. Based on the results of the work [4], it is expected that when the concentration of bromide ions increases, a decrease in the band gap occurs. The dispersion of states of the bottom of the conduction band

in both crystals is almost the same. In the case of the CeCl_2Br crystal, the position of the $4f$ Ce states is shifted to the higher energies region by 0.5 eV compared to CeClBr_2 . Based on the above information, it can be concluded that the change in the concentration of bromine ions in the $\text{CeCl}_{3-x}\text{Br}_x$ structure opens up the possibility of controlling the amount of light output of luminescence, which is inversely proportional to the value of

the band gap of crystals [22].

As previously shown in works [3, 4], the lower part of the conduction band of CeX₃ crystals ($X = \text{F, Cl, Br}$) has a peculiarity in the form of an energy gap between states characterised by radically different effective masses. Fig. 3 highlights the subbands 5d1 and 5d2 of

the conduction band of CeCl₂Br and CeClBr₂ crystals. The effective masses for both crystals are the same and are $2.3m_0$ for the 5d1 subband, and $0.06m_0$ for 5d2 (m_0 is the mass of a free electron). Such value of the effective mass of electrons in the 5d2 states facilitates the formation of the Frenkel exciton [3, 4].

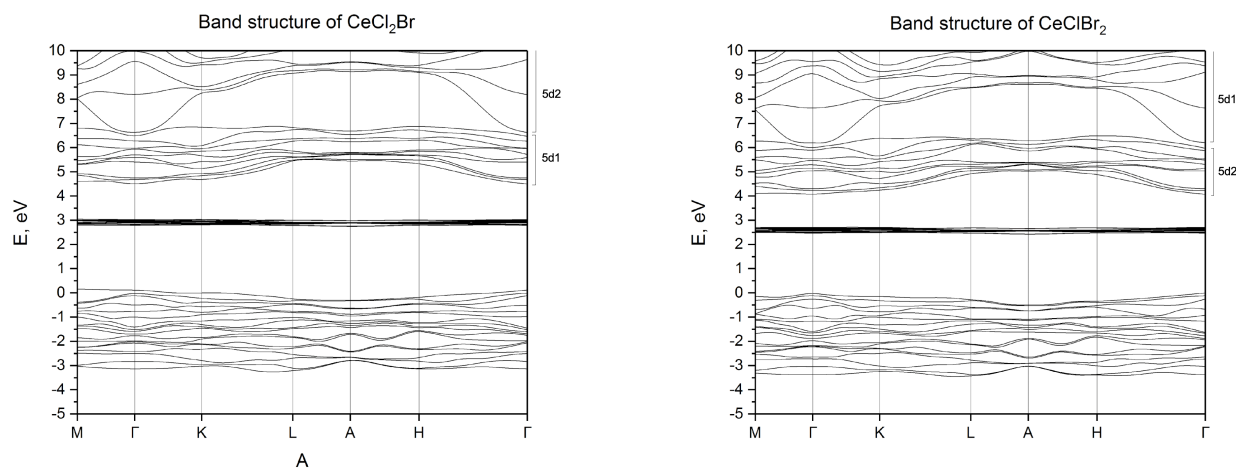


Fig. 3. Electron energy band structure of CeCl₂Br (a) and CeClBr₂ (b) crystals

IV. CONCLUSIONS

1. The augmented projected waves (PAW) method, in conjunction with the hybrid functional of exchange-correlation interaction (PBE0), allows conducting theoretical studies of the electronic energy structure of cerium crystals with mixed halogens like CeCl₂Br and CeClBr₂.
2. The top of the valence band of both crystals is constructed by the 3p and 4p states of the Cl and Br ions, and the bottom of the conduction band is formed by the 5d states of cerium. Also, there are 4 states of Ce in the middle of the band gap. In the case of CeCl₂Br crystal, the position of 4f Ce states is 0.5 eV higher than in CeClBr₂. The calculated band gap is 4.5 eV and 4 eV for CeCl₂Br and CeClBr₂, respectively.
3. The lower part of the conduction band of the studied crystals has a feature in the form of an energy gap between the 5d states of Ce, which are characterized by different values of effective electron masses. Also, the effective masses for the 5d1 and 5d2 subbands of Ce are $2.3m_0$ and $0.06m_0$, respectively. Such high values of effective electronic masses facilitate the formation of Frenkel excitons, which positively affects the scintillation properties of crystals.
4. The change in the concentration of bromine ions in the CeCl_{3-x}Br_x structure opens up the possibility of controlling the value of the luminescence light yield as a value inversely proportional to the gap width.

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- [1] B. Milbrath, A. J. Peurrung, M. Bliss, W. J. Weber, *J. Mater. Res.* **23**, 2561 (2008); <https://doi.org/10.1557/JMR.2008.0319>.
- [2] C. Dujardin *et al.*, *IEEE Trans. Nucl. Sci.* **65**, 1977 (2018); <https://doi.org/10.1109/TNS.2018.2840160>.
- [3] O. Kochan *et al.*, *Materials* **14**, 4243 (2021); <https://doi.org/10.3390/ma14154243>.
- [4] Ya. Chornodolskyy *et al.*, *J. Lumin.* **237**, 118147 (2021); <https://doi.org/10.1016/j.jlumin.2021.118147>.
- [5] V. O. Karnaushenko, Ya. M. Chornodolskyy, V. V. Vistovskyy, S. V. Syrotyuk, A. S. Voloshinovskii, *J. Phys. Stud.* **24**, 4703 (2020); <https://doi.org/10.30970/jps.24.4703>.
- [6] V. Karnaushenko, Ya. Chornodolskyy, V. Vistovskyy, S. Syrotyuk, A. Voloshinovskii, *Visn. Lviv. Univ. Ser. Phys.* **57**, 122 (2020); <https://doi.org/10.30970/vph.57.2020.122>.
- [7] Ya. Chornodolskyy *et al.*, *Materials* **15**, 7937 (2022); <https://doi.org/10.3390/ma15227937>.
- [8] T.-S. Sun, F.-L. Wang, Y.-M. Xiao, *Thermochim. Acta*,

- 311**, 21 (1998). [https://doi.org/10.1016/S0040-6031\(97\)00406-1](https://doi.org/10.1016/S0040-6031(97)00406-1).
- [9] H. Wei, V. Martin, A. Lindsey, M. Zhuravleva, Ch. L. Melcher, J. Lumin. **156**, 175 (2014); <https://doi.org/10.1016/j.jlumin.2014.08.015>.
- [10] M. Birowosuto, P. Dorenbos; K. W. Krämer, H. U. Güdel, J. Appl. Phys. **103**, 103517 (2008); <https://doi.org/10.1063/1.2930884>.
- [11] M. Loyd *et al.*, J. Cryst. Growth. **531**, 125365 (2020); <https://doi.org/10.1016/j.jcrysgro.2019.125365>.
- [12] K. Przystupa *et al.*, Materials, **16**, 5085 (2023); <https://doi.org/10.3390/ma16145085>.
- [13] E. V. D. van Loef, P. Dorenbos; C. W. E. van Eijk; K. Krämer; H. U. Güdel, Appl. Phys. Lett. **77**, 1467 (2000); <https://doi.org/10.1063/1.1308053>.
- [14] G. Ren *et al.*, Nucl. Instrum. Methods. Phys. Res. A **579**, 11 (2007); <https://doi.org/10.1016/j.nima.2007.04.003>.
- [15] J. Andriessen *et al.*, Opt. Commun. **178**, 355 (2000); [https://doi.org/10.1016/S0030-4018\(00\)00665-9](https://doi.org/10.1016/S0030-4018(00)00665-9).
- [16] K. S. Shah *et al.*, IEEE Symp. Conf. Record Nucl. Sci. **7** (2004); <https://doi.org/10.1109/NSSMIC.2004.1466835>.
- [17] F. G. A. Quarati *et al.*, Nucl. Instrum. Methods. Phys. Res. A **729**, 596 (2013); <https://doi.org/10.1016/j.nima.2013.08.005>.
- [18] A. F. Iyudin *et al.*, Instrum. Exp. Tech. **52**, 774 (2009); <https://doi.org/10.1134/S0020441209060037>.
- [19] P. Blochl, Phys. Rev. B **50**, 17953 (1994); <https://doi.org/10.1103/PhysRevB.50.17953>.
- [20] X. Gonze *et al.*, Comp. Phys. Commun. **205**, 106 (2016); <https://doi.org/10.1016/j.cpc.2016.04.003>.
- [21] V. Tognetti, P. Cortona, C. Adamo, J. Chem. Phys. **128**, 034101 (2008); <https://doi.org/10.1063/1.2816137>.
- [22] M. Birowosuto, P. Dorenbos, Phys. Status Solidi A **206**, 9 (2009); <https://doi.org/10.1002/pssa.200723669>.

ЕНЕРГЕТИЧНА СТРУКТУРА КРИСТАЛІВ CeCl_2Br ТА CeClBr_2

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На сьогодні неорганічні скінтілятори на основі фторидних кристалів лантанідів інтенсивно досліджують учені всього світу, оскільки вони мають високе значення світловиходу та швидку компоненту кінетики загасання. Все частіше постає питання пошуку нових сполук, які нівелюють важливі для практичного використання недоліки. Останніми роками опубліковано низку праць із дослідження кристалів типу CeX_3 (де $X = \text{F}, \text{Cl}, \text{Br}, \text{I}$) та $\text{LaF}_3:\text{Ln}$ ($\text{Ln} = \text{Ce} - \text{Lu}$). Унаслідок своїх унікальних скінтіляційних властивостей кристал CeBr_3 має значну гігроскопічність, що сильно обмежує сферу його практичного використання. В останніх публікаціях, присвячених цій темі, продемонстровано, що змішування галогенів у структурах $\text{CeCl}_{3-x}\text{Br}_x$, попри незначне зменшення величини світловиходу, дає змогу суттєво поліпшити гігроскопічні властивості. Детальніше дослідження такого підходу дасть змогу проектувати скінтілятори, що задовольнятимуть різноманітні сценарії їх використання. У цій праці ми представляємо теоретичні дослідження кристалів CeCl_2Br та CeClBr_2 , що доповнюють раніше отримані відомості про кристали CeCl_3 та CeBr_3 та інтерпретують результати експериментальних досліджень роботи. Зокрема, розраховано зонно-енергетичну структуру кристалів CeCl_2Br та CeClBr_2 за допомогою методу приєднаних проєкційних хвиль PAW та гібридного функціоналу обмінно-кореляційної взаємодії PBE0. Установлено, що валентна зона кристалів формується $3p$ -станами Cl та $4p$ -станами Br, а в нижній частині зони провідності утворюється енергетична щілина між $5d$ -станами Ce, де формуються дві підзони $5d1$ та $5d2$ з різними ефективними масами електронів $2.3m_0$ та $0.06m_0$ відповідно. Показано, що $4f$ -стани Ce розміщені в середині забороненої зони. Одержані значення ширини забороненої зони для кристалів CeCl_2Br та CeClBr_2 становлять 4.5 eV і 4.0 eV відповідно.

Ключові слова: скінтілятор, зонна структура, метод приєднаних проєкційних хвиль, ширина забороненої зони.