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T.M. Muzyka¹, V.O. Karnaushenko¹, S.O. Ihnatsevych¹, Ya.M. Chornodolskyi¹,
S.V. Syrotyuk², A.S. Voloshinovskii¹

Theoretical Study of the Effect of Vacancy Defects on the Energy Structure of CsPbCl₃:Ce Crystals

¹Ivan Franko National University of Lviv, Lviv, Ukraine, yaroslav.chornodolskyi@lmu.edu.ua;

²Lviv Polytechnic National University, Lviv, Ukraine

The study of the energy structure of perovskites is of critical importance for enhancing the stability and efficiency of next-generation light-emitting diodes and solar cells. In this work, a comparative analysis of CsPbCl₃:Ce crystals with two charge compensation mechanisms a single Cl vacancy and a double Cl–Pb vacancy was performed using density functional theory (DFT) as implemented in the ABINIT software package. It was established that the valence band of both structures is formed by Cl 3*p* states, while the conduction band minimum is determined by Pb 6*p* and Ce 5*d* states, with a typical localization of Ce 4*f* states. The primary finding is a substantial energy shift of the Ce 4*f* states relative to the valence band from 3.7 eV to 2 eV upon the introduction of an additional lead vacancy, indicating high sensitivity of impurity levels to the local crystal field. The results of the study confirm the defect tolerance of the material and establish a theoretical framework for the targeted design of optoelectronic devices with tailored luminescence characteristics.

Keywords: band structure, density of states, projector augmented-wave method, perovskites, luminescence, vacancy.

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Introduction

Inorganic lead-based halide perovskites CsPbX₃ (X = Cl, Br, I) are currently in the center of attention of the scientific community due to their unique optoelectronic properties [1,2]. These materials are characterized by a wide tunable band gap, a high luminescence quantum yield, and a large absorption cross-section, which makes them promising candidates for the development of high-efficiency light-emitting diodes (LEDs), next-generation solar cells, scintillators, and luminescent solar concentrators [3–6]. Of particular interest is the doping of perovskite matrices with lanthanide ions (Ln³⁺), specifically cerium (Ce³⁺), which allows not only for tuning the spectral characteristics from the ultraviolet to the visible range, but also for substantially enhancing the physicochemical stability of the materials as well as their photoelectric conversion efficiency [7–10].

Despite their significant potential for applications, the widespread commercial deployment of CsPbX₃ based devices are hindered by their intrinsic instability under moisture, heat, and prolonged photo-irradiation, which originates from the low formation energy of the soft ionic lattice [11,12]. The introduction of heterovalent impurities, such as Ce³⁺, at Pb²⁺ sites inevitably leads to a charge imbalance, which requires the formation of compensating vacancy defects [13–15]. Understanding the interaction between impurity atoms and vacancies is critical for stabilizing the crystalline phase, as the identification of structural imperfections and their impact on the electronic landscape in bulk crystals remains one of the most challenging problems in modern semiconductor physics [16, 17].

This work is devoted to a theoretical investigation of the energy structure of CsPbCl₃:Ce crystals, considering various types of vacancy defects. Within the framework of density functional theory (DFT) using the ABINIT

software package, supercells corresponding to two distinct charge compensation mechanisms were modeled [18]. The first case considers the substitution of a lead atom by a cerium atom accompanied by the formation of a single chlorine vacancy, whereas the second case addresses the formation of a double defect featuring an additional vacancy in the lead sublattice. The obtained results regarding the electronic density of states and band structure allow for a detailed analysis of the impact of local lattice distortions on the physical properties of the doped perovskite, which is an essential step toward the targeted design of novel functional materials.

I. Theoretical Framework

To correctly describe the electronic structure of the investigated crystal systems, the projector augmented-wave (PAW) approach was chosen [19], which combines the advantages of pseudopotential and full-potential methods. Within the PAW formalism, the electronic wave function is represented as a smooth part, effectively described on a plane-wave basis, and localized corrections in the atomic spheres, where its full nodal structure is restored. This approach enables accurate accounting of the rapid oscillations of core wave functions without requiring a significant increase in the basis set size. This is particularly crucial for systems containing heavy elements, specifically lanthanides, where electronic states exhibit complex spatial localization and strong nuclear interactions. Thus, PAW provides high accuracy while maintaining computational efficiency, which is critical for modeling defect-containing crystals with a large number of atoms per unit cell.

Additionally, the PBE0 hybrid functional was utilized to describe the exchange-correlation interaction [20], incorporating a fraction of exact Hartree-Fock exchange for d (f) electronic states. This approach significantly improves the description of energy bands and localized electronic states compared to the standard LDA and GGA approximations. This is fundamentally important for the correct representation of the electronic structure of impurity centers, particularly the cerium $4f$ orbitals, which are characterized by a high degree of localization and strong electronic correlation. Owing to the inclusion of the exact Hartree-Fock exchange potential, the PBE0 hybrid functional partially eliminates the self-interaction of d (f) electrons, yielding better agreement between theoretical and experimental band gap values. In combination with PAW, this ensures a consistent and physically sound description of the electronic properties of defect-containing crystal structures, which is necessary for the subsequent analysis of the density of states and band structure.

In the framework of this study, two modified crystal unit cells were modeled based on the pristine lead chloride structure, taking into account defects and impurity atoms. In the first case, a lead atom was substituted by a cerium atom, leading to the formation of a single vacancy in the chlorine sublattice to ensure the charge neutrality of the system; no vacancy is formed in the lead sublattice in this scenario. In the second case, in addition to an analogous chlorine vacancy, a vacancy in the lead sublattice is

additionally formed, corresponding to an alternative charge compensation mechanism and allowing for the investigation of the double-defect impact on the electronic structure. The geometries of both unit cells were fully optimized prior to calculations by minimizing the atomic forces using appropriate convergence criteria.

The calculations were performed within the framework of density functional theory using the ABINIT software package [18]. To describe the exchange-correlation interaction, the local density approximation was applied, and the electronic wave functions were expanded in a plane-wave basis set with a maximum kinetic energy cutoff of 15.0 Ha, which corresponds to a $120 \times 80 \times 80$ fast Fourier transform (FFT) grid. Typically, the implementation of the FFT for the electronic density and potential components in a crystal requires a finer grid. For this purpose, we employed a twice denser grid of $240 \times 160 \times 160$, generated by the ABINIT program with a kinetic energy cutoff of 60.0 Ha. Geometry optimization was carried out in two steps. In the first step, the lattice constants of the supercell were optimized. The second step consisted of optimizing the individual atomic coordinates of the superlattice. The resulting optimized structures served as input data for subsequent calculations of the electronic density of states and band structure to perform a comparative analysis of the effects of various defect types on the electronic structure parameters of the materials.

II. Results and Discussion

The energy structure calculation results for CsPbCl₃:Ce crystals with varying degrees of vacancy defectiveness demonstrate a significant impact of vacancies on the localization of impurity states. Figure 1 presents the partial and total densities of states for the case of a single chlorine vacancy, which ensures charge neutrality upon the substitution of Pb²⁺ by Ce³⁺. The main contribution to the valence band formation in such a crystal arises from the Cl $3p$ states (energy range from -4 eV to 0 eV). The lower part of the conduction band is predominantly determined by Pb $6p$ and Ce $5d$ states. A characteristic feature of this structure is the presence of narrow, intense peaks of Ce $4f$ states located in the energy region of the lower conduction band, at approximately 3.7 eV above the valence band maximum, as clearly reflected in the density of states plots. The band structure (Fig. 3, left) confirms this result through the presence of flat, non-dispersive bands in the specified energy range, indicating a high degree of localization of the cerium $4f$ electrons.

The introduction of an additional vacancy in the lead sublattice substantially transforms the electronic spectrum of the crystal, as becomes evident when comparing the calculation results. According to the density of states plots (Fig. 2) for the system with two vacancies, the energy position of the impurity Ce $4f$ states shifts downward toward the valence band (to approximately the 2 eV level), indicating a significant change in the crystal field surrounding the lanthanide ion. The additional lead vacancy acts as a strong perturbation to the lattice potential, leading to a narrowing of the effective band gap and a modification of the band dispersion near the Fermi

level, which is clearly visible in the corresponding band structure plots (Fig. 3).

The physical nature of these changes lies in the features of heterovalent doping of perovskite matrices with Ln^{3+} ions. Since the substitution of divalent lead by trivalent cerium leads to a charge imbalance, the formation of vacancies is critically necessary to maintain the electroneutrality of the system. This agrees with reports that inorganic halide perovskites possess high tolerance to point defects, which often form levels inside the band gap without destroying the integrity of the crystal structure [21]. The effect of vacancies on the energy position of the

Ce 4f levels is crucial for the optoelectronic properties, as the specific alignment of these levels relative to the band edges determines the luminescence efficiency and energy transfer processes from the host matrix to the activating centers.

A comparative analysis shows that the charge compensation mechanism via a double vacancy creates a more complex electronic structure, which may contribute to additional stabilization of the crystalline phase. Doping with lanthanides can increase the formation energy of the soft ionic perovskite lattice and suppressing non-radiative recombination centers through the modification of the

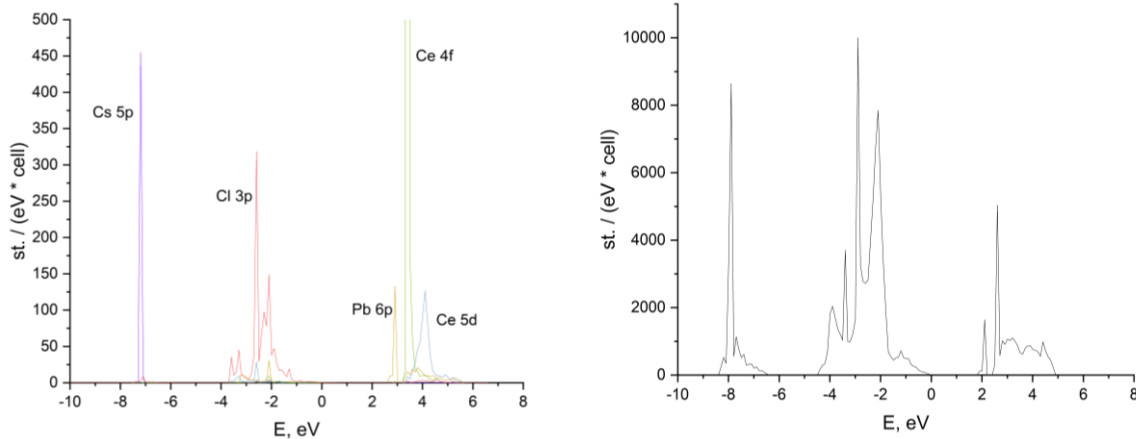


Fig. 1. Partial (left) and total (right) densities of states of a CsPbCl_3 : Ce crystal with a Cl vacancy.

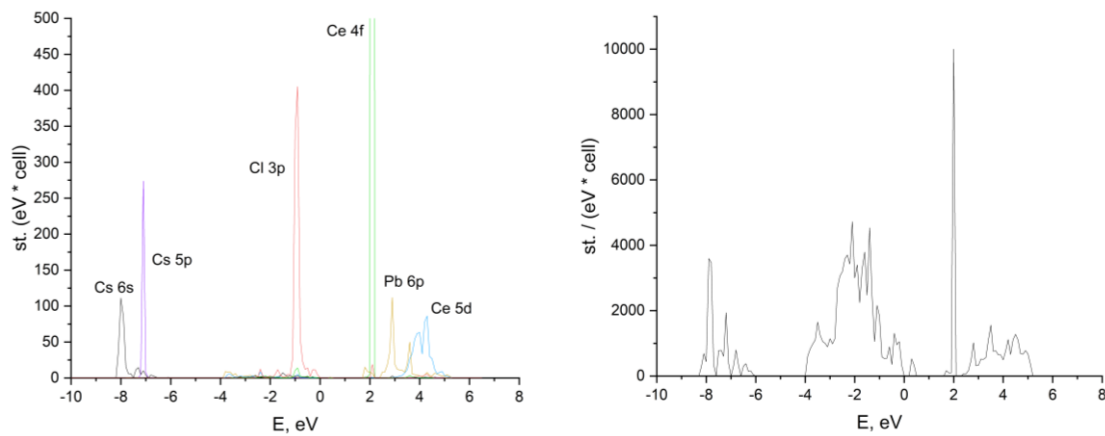


Fig. 2. Partial (left) and total (right) densities of states of a CsPbCl_3 : Ce crystal with Cl and Pb vacancies.

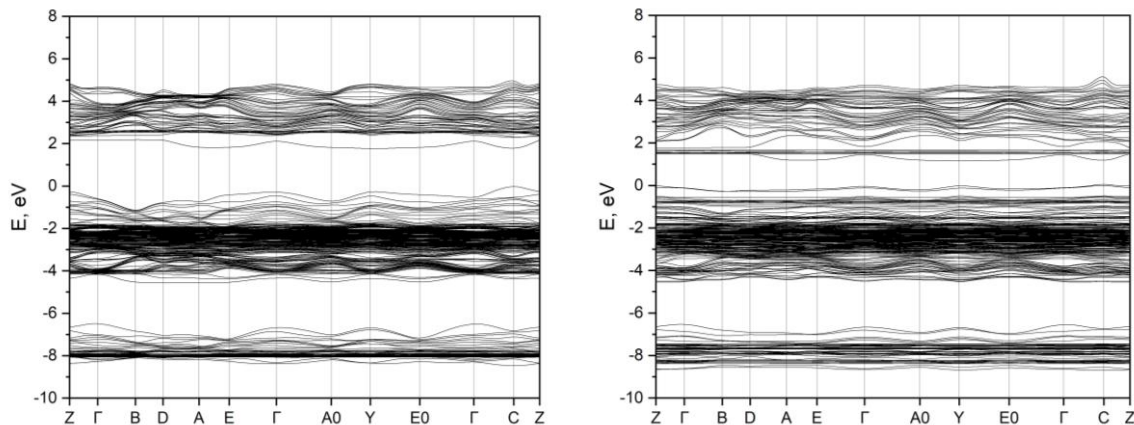


Fig. 3. Electronic energy band structure of CsPbCl_3 : Ce crystals with a single vacancy (left) and a double vacancy (right).

defect-state profile [21]. The obtained theoretical data regarding the shift of the Ce 4*f* levels enable a more accurate prediction of the spectral characteristics of CsPbCl₃:Ce for the development of novel functional materials, such as light-emitting diodes with tunable color output and high-efficiency scintillators.

Conclusions

Based on density functional theory (DFT) using the Abinit software package, two charge compensation mechanisms (a Cl vacancy and a double Cl and Pb vacancy) upon cerium doping of CsPbCl₃:Ce were successfully modeled, allowing for the determination of the stability of defect configurations and their impact on the ionic lattice. It was established that the energy structure of both crystals is determined by the dominance of Cl 3*p* states in the valence band and Pb 6*p* and Ce 5*d* states in the conduction band; however, the presence of vacancies leads to the formation of narrow, highly localized Ce 4*f* levels inside the band gap and the conduction band.

The most crucial result of this study is the revealed significant energy shift of the Ce 4*f* states relative to the

valence band maximum, from the 3.7 eV level down to 2 eV upon the introduction of an additional lead vacancy, indicating a critical dependence of the energy structure on the local environment and the crystal field. The results confirm the concept of high defect tolerance of the perovskite matrix and open a pathway toward controlling luminescence characteristics and energy transfer processes via the targeted creation of vacancy defects in novel optoelectronic materials.

Muzyka T.M. – PhD student;
Karnaushenko V.O. – PhD;
Ihnatsevych S.O. – Junior Research Fellow
 Department of General Physics;
Chornodolskyy Ya.M. – Candidate of Physical and Mathematical Sciences, Associate Professor of the Department of General Physics;
Syrotyuk S.V. – Candidate of Physical and Mathematical Sciences, Associate Professor, Department of Computerized Automation Systems;
Voloshinovskii A.S. – Doctor of Physical and Mathematical Sciences, Professor, Head of the Department of Experimental Physics.

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Т.М. Музика¹, В.О. Карнаушенко¹, С.О. Ігнацевич¹, Я.М. Чорнодольський¹,
С.В. Сиротюк², А.С. Волошиновський¹

Теоретичне дослідження впливу вакансійних дефектів на енергетичну структуру кристалів CsPbCl₃:Ce

¹Львівський національний університет імені Івана Франка, Львів, Україна, yaroslav.chornodolskyy@lnu.edu.ua;

²Національний університет "Львівська політехніка", Львів, Україна

Дослідження енергетичної структури перовскітів є критично важливим для підвищення стабільності та ефективності світлодіодів і сонячних елементів нового покоління. У даній роботі методом DFT, втіленим у програмному пакеті ABINIT, проведено порівняльний аналіз кристалів CsPbCl₃:Ce із двома механізмами зарядової компенсації: одиночною вакансією Cl та подвійною вакансією Cl та Pb. Встановлено, що валентна зона обох структур формується 3p станами Cl, а дно зони провідності – 6p станами Pb та 5d станами Ce, із характерною локалізацією 4f станами Ce. Основним результатом є виявлений суттєвий енергетичний зсув відносно валентної зони 4f станів Ce, з 3,7 еВ до 2 еВ, при введенні додаткової вакансії свинцю, що свідчить про високу чутливість домішкових рівнів до локального кристалічного поля. Результати дослідження підтверджують дефектну толерантність матеріалу та закладають теоретичне підґрунтя для цілеспрямованого проектування оптоелектронних пристроїв із керованими характеристиками люмінесценції.

Ключові слова: зонна структура, густина станів, метод приєднаних проекційних хвиль, перовскіти, люмінесценція, вакансія.