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AB INITIO CALCULATIONS OF BAND GAPS OF $CsPbI_3$ AND $RbPbI_3$ HALYDE PEROVSKITES

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Key words: DFT, perovskites, VASP, zone structure.

Abstract. We have performed first principles density functional calculations of $CsPbI_3$ and $RbPbI_3$ halyde perovskites. Lead halide perovskites have attracted great interest because of rapid improvements in the efficiency of photovoltaics based on these materials. To predict new related functional materials, a good understanding of the correlations between crystal chemistry, electronic structure properties is required. Used approach is density functional calculations with the Perdew, Burke, and Ernzerhof method of Generalized Gradiend Approximation (PBE-GGA) and the projector-augmented-wave method as implemented in VASP. Their characteristics in cubic phases were determined along with calculation of the forbidden band widths. For cubic phases of the $CSPbI_3$ and $RbPbI_3$ - type perovskites crystalline structures forbidden band widths are 1,45 eV and 1,78 eV respectively. The calculated parameters are found to agree well with the experimental data.

INTRODUCTION

Current development of computer technologies allows to set up computational experiments and make them an integral part of modern research.

Researchers therefore have got practical capabilities for simulation of both ideal crystals and structurally imperfect real crystals and artificial compounds [1].

Interest to study such compounds is related to their potential practical applications in, for instance, solar power generation [2].

ABM_3-type perovskites are intensively studied due to their various promising electronic, electro-mechanic and conductive properties for numerous and diverse applications [3]. One of the important application areas for these perovskites is laser systems: a large cation A in the perovskite structure can be Nd (III) and Sm (III), which are the main laser ions [4].

Since the particular attention is paid to solar power generation, we have to mention works performed in Oxford University where thin film solar cell has been created with light absorption for 15 % better than that of the best silicon-based cells [5]. This thin film solar cell of the new generation has been created based on an organo-metallic crystalline semiconductor material called perovskite. It is reported that the new cells have simple design and can be easily large-scale produced employing available precipitation process currently used in production of silicon solar cells. Group of the University of Oxford [5] created a thin film solar cell based on a new class of perovskite compounds.

The first study of ABM_3-type perovskites performed within the density functional theory by Muller on the $CsPbI_3$ [6]. After that, many works further developed the computational methods up high levels of precision. There are extensive analytical works devoted to specific materials and compounds [7]. As an example we can refer to calculations [3] where structure and optoelectronic properties of $CsPbM_3$ (M=Cl, Br, I) perovskites were determined. The structure and electronic properties were calculated with Wien2 software code employing the method FP-LAWP (full potential linearized augmented plane wave method).

In the present paper we calculated structure and electric properties of $CSPbI_3$, $RbPbI_3$ perovskites in cubic phase. The calculations were performed with VASP software employing the method GGA-PBE.

Objective of the present work is to test the calculation methods and compare the results on $CSPbI_3$, $RbPbI_3$ perovskite structures in cubic phases with the previously obtained data with using different methods [2, 3, 6].

CALCULATION

Perovskite is usually crystallized in rhombic crystal system (pseudocubic). So, in the pseudoisometric coordination structure of $TiCaO_{12}$ perovskite, each Ca atom is surrounded by 12 oxygen atoms occupying a cuboctahedron vertexes, and Ti atom is in the octahedral coordination. There is a characteristic hatching on the pseudocubic faces parallel to the edges [8].

Our calculations and ABM_3 numerical simulations showed that the crystalline structures of the perovskites $CsPbI_3$ have the following characteristic varieties (phases): cubic phase (Fig. 1), tetragonal (Fig. 2.a) and orthorhombic phase (Fig.2.b).

These phases demonstrate different characteristics - width of the energy gap and lattice parameters.

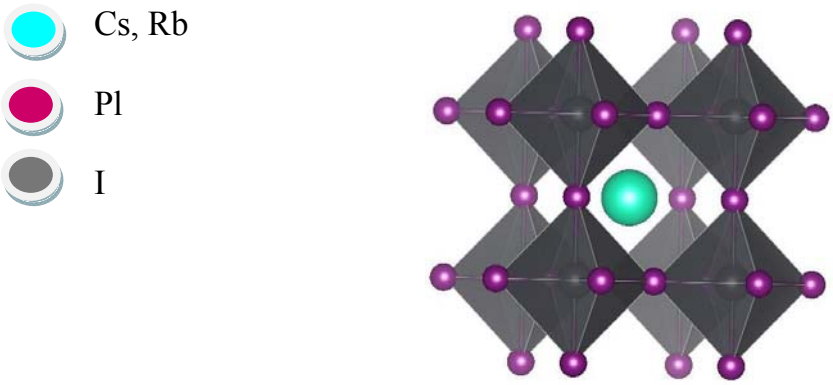
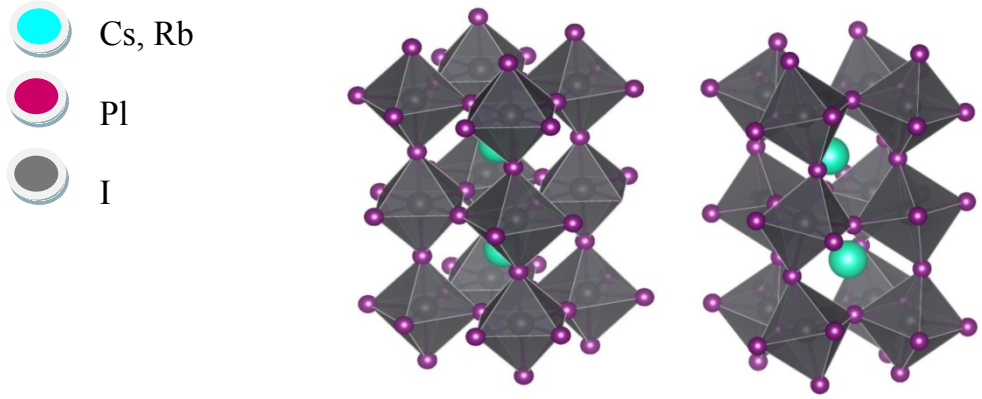


Figure 1 – Pm-3m crystal structure of the C_SPbI_3, $RbPbI_3$ perovskites (visualized in VESTA software)

Due to peculiarities of their structure, perovskites can reveal ferroelectric, ferromagnetic and superconducting properties [4]. In perovskite structure A-atom represents a large sessile cation. The B atom has smaller size and can move. Perovskite can be in cubic or in non-cubic phase. Non-cubic phases are achieved by a shift of atoms or by octahedral tilt.



a) tetragonal phase SG 123 b) orthorhombic phase SG 62

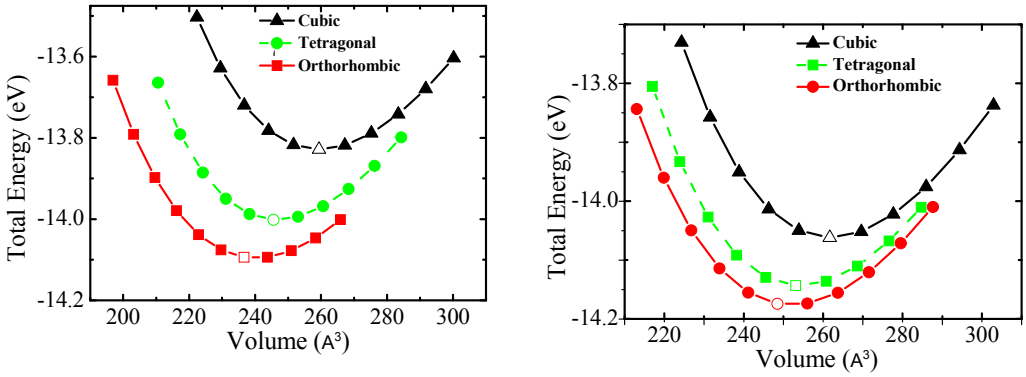
Figure 2 – P4/mmm tetragonal structure and $Pmc2_1$ orthorhombic structure of $CsPbI_3$ and $RbPbI_3$ perovskites

The pseudopotentials method in the software package VASP was applied in this work for optimization of the lattice geometry and obtaining the equation of state (EOS). The method GGA-PBE was used for the perovskite $CSPbI_3$ in cubic phase [9]. We considered the following valence electron configuration: $5s^25p^66s^1$ for Ce, $4s^24p^65s^1$ for Rb, $5d^{10}6s^26p^2$ for Pb, and $5s^25p^5$ for I. The electronic wave

functions were expanded with plane waves up to a kinetic-energy cutoff of 400 eV except for structural optimization, where a kinetic energy cutoff of 520 eV has been applied to reduce the effects of Pulay stress. The momentum space integrations were performed using a 5 × 4 × 4 Γ-centered Monkhorst-Pack *k*-mesh [29].

RESULTS AND DISCUSSION

The total energy vs volume with a given space group for one perovskite formula unit cell is calculated to show the equation of state diagram, and at each given volume, the cell shape and internal atomic coordinate was fully optimized. Calculated EOS of the optimized $CSPbI_3$ and $RbPbI_3$ perovskite structures are presented at Fig.3. The structure demonstrates that that most stable phase in $CsPbI_3$ and $RbPbI_3$ is orhorhombic.



a) $CSPbI_3$ b) $RbPbI_3$

Figure 3 – Total energy vs volume of the $CSPbI_3$ and $RbPbI_3$ perovskite structures

Calculated zone-energy structures of $CSPbI_3$ and $RbPbI_3$ perovskites in cubic phase are presented at Fig.4. and Fig.5 The structure demonstrates direct transition. The valence band maximum and the conduction zone minimum are located in the G point of the Brillouin zone

The top of the valence band at 1.1056 eV is located in the point 0 0 0. The minimum of the conduction zone 2,5710 eV is located at 0 0 0 in reverse coordinates. Direct transitions are therefore permitted and an electron can emit photon directly. The energy gap width (E_G) was found to be - 1.11 eV.

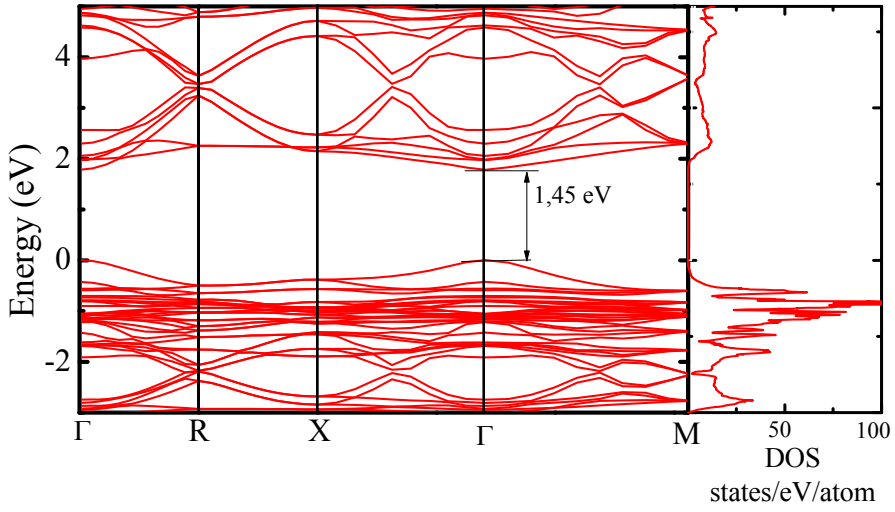


Figure 4 – Band structure of the Pm-3m cubic phase of the C_SPbI_3 perovskite

Calculation outcomes are presented in Table below along with data of other scientists.

Lattice parameters, energy gap width

Structure(authors)	Cryst. Group	Lattice parameter (Å)	Energy gap width, E_g(eV)
$CsPbI_3$(This work)	221	6.34	1.46
$RbPbI_3$ (This work)	221	4.14	1.78
$CsPbI_3$(Murtaza) [3]	221	6.18	1.3
$CsPbI_3$(Other exp.) [10]	221	6.29	1.1

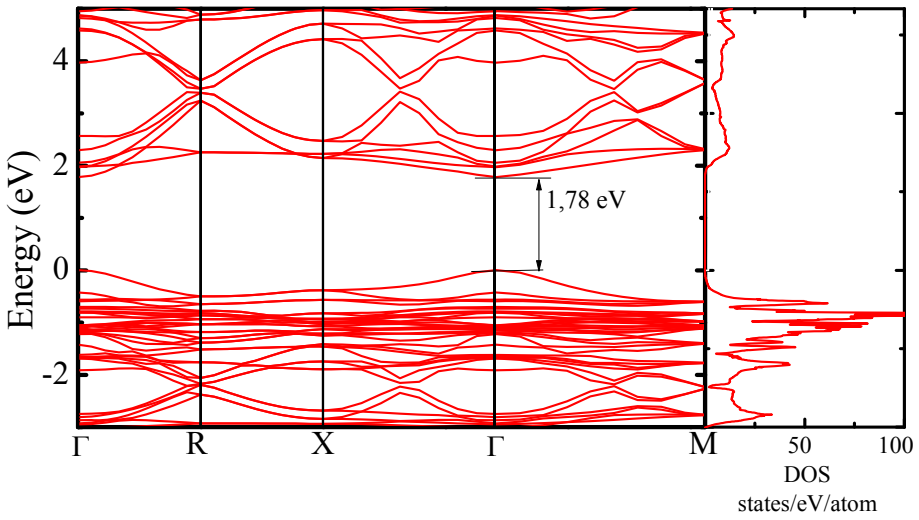


Figure 5 – Band structure of the Pm-3m cubic phase of the $RbPbI_3$ perovskite

The top of the valence band at 1.245 eV is located in the point 0 0 0. The minimum of the conduction zone 3,0292 eV is located at 0 0 0 in reverse coordinates. Direct transitions are therefore permitted and an electron can emit photon directly. The energy gap width (E_G) was found to be – 1.7842 eV.

CONCLUSION

In summary we examined the structural and electronic properties of $CSPbI_3$ and ¸ $RbPbI_3$ perovskites. The method used for simulations and calculations describes quite well the structure properties of the $CSPbI_3$ and ¸ $RbPbI_3$ perovskites and provides satisfactory results for the energy gap width. It was determined that the structure of $CsPbI_3$ in cubic phase has the energy gap width is 1.465 eV. With of forbidden zone in $RbPbI_3$ is 1.7842 eV.

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$CsPbI_3$ И $RbPbI_3$ ГАЛОГЕНИД ПЕРОВСКИТТЕРДІҢ ТЫЙЫМ САЛЫНҒАН ЗОНА ЕНІН AB INITIO ЕСЕПТЕУ

Б. К. Абдыкадыров, Н. Ж. Такибаев

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Тірек сөздер: тығыздық функционал теориясы, VASP, электронды зоналық құрылым.

Аннотация. $CsPbI_3$ и $RbPbI_3$ галогенид перовскиттер бірінші принциптерден тығыздық функционалы негізінде зерттелді. Бұл материалдарды зерттеу осы материалдардың күн энергетикасында кең қолданылу мүмкіндігімен байланысты. Материалдардың жаңа функционалдық қасиеттерін болжау үшін олардың электрондық қасиеттері мен кристаллохимияны зерттеу маңызды. Есептеу VASP бағдарламасында жасалған. Perdew, Burke, и Ernzerhof тәсілі, градиентті жалпылама жуықтау әдісі қолданылған. $CsPbI_3$ и $RbPbI_3$ галогенид перовскиттер құрылымдық қасиеттері анықталып, электрондық қасиеттері есептелген. $CsPbI_3$ и $RbPbI_3$ перовскиттердің есептелген тыйым салынған зона ені сәйкесінше 1,45 и 1,78 eV. Есептеу барысында алынған нәтиже эксперименталды мәліметке сәйкес келеді.

AB INITIO РАССЧЕТЫ ШИРИНЫ ЗАПРЕЩЕННОЙ ЗОНЫ ГАЛОГЕНИД ПЕРОВСКИТОВ $CsPbI_3$ И $RbPbI_3$

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Ключевые слова: теория Функционала Плотности, VASP, электронная зонная структура.

Аннотация. Были проведены рассчеты из первых принципов галогенид перовскитов $CsPbI_3$ и $RbPbI_3$. Интерес к изучению таких соединений связан с их возможными практическими применениями, в частности, для использования в солнечной энергетике. Для предсказания новых функциональных свойств материалов необходимы исследования электронных свойств и кристаллохимии. Рассчет произведен в программе VASP. Использованный подход Perdew, Burke, и Ernzerhof и метод Обобщенного Градиентного Приближения (PBE-GGA) и метод метод проекцированных дополненных плоских волн. Определены структурные свойства галогенид перовскитов $CsPbI_3$ и $RbPbI_3$ и рассчитаны их электронные свойства. Значение ширины запрещенной зоны для перовскитов $CSPbI_3$ и $RbPbI_3$ в кубической фазе 1,45 eV и 1,78 eV соответственно. Полученные результаты согласуются с экспериментальными данными.

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