Ab initio Study of Optical and Bulk Properties of Cesium Lead Halide Perovskite Solid Solutions

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Abstract—The first principles calculations of band gaps and bulk moduli of cesium lead halide perovskite solid solutions, CsPb(I_{1-x}Cl_x)_3 and CsPb(I_{1-x}Br_x)_3, are performed at the level of general gradient approximation of the density functional theory. We use supercell approach for computational modeling of disordered systems, which gives a description of the properties of the structure basing on the average over a set of multiple configurations, namely distributions of different species over a given set of atomic positions. The calculations were performed with the CRYSTAL14 program package. The dependence of the band gap and bulk modulus on the content of iodine and the doping element (Br or Cl) is investigated over the whole range 0 ≤ x ≤ 1.

Keywords: cesium lead halide perovskite, solid solutions, band gaps, bulk moduli, first-principles calculations, density functional theory

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1. INTRODUCTION

The use of cesium lead halide perovskites, described by the structural formula CsPbX_3 (X = Cl, Br, I), as absorbers in solar batteries has several advantages and disadvantages compared to the hybrid organic-inorganic perovskites of the (MA)PbX_3 or (FA)PbX_3 type, where MA = CH_3NH_3, FA = HC(NH_2)_2. Structures like (MA)PbX_3 have a smaller value of the band gap and the absorption spectrum for them starts from the visible and infrared range, that is important since allows the maximal use of the entire spectrum of solar radiation [1]. On the other hand, such organometallic structures are optically and thermally unstable, which makes their practical use difficult. The compound CsPbI_3 has a band gap of 1.73 eV, which is even smaller than that of silicon, widely used as a solar absorber, while the band gaps for CsPbBr_3 and CsPbCl_3 are significantly larger, 2.36 and 3.0 eV [2, 3], accordingly. Thus, CsPbI_3 is a good candidate for the role of an absorber of solar radiation in the optical and infrared ranges. Recent experimental studies on chemical and optical properties of the CsPbI_3 compound have shown that partial replacement of iodine by chlorine or bromine stabilizes the structure and makes such a mixed compound thermodynamically more stable at room temperatures than the initially pure compound with iodine [3, 4]. It was also observed that the experimentally measured band gap of such a mixed compound does not increase much as compared to the pure compound CsPbI_3 at the small x < 0.2.

Here we present a theoretical study for the optical band gap and bulk modulus dependences in the CsPb(I_{1-x}Br_x)_3 and CsPb(I_{1-x}Cl_x)_3 cubic phases on the relative content of the iodine and the doping element (Br or Cl) performed at the level of first-principles quantum mechanical calculations within the Density Functional Theory (DFT) [5, 6]. The principal difference between doped compounds and pure ones is that their crystal structure is stoichiometrically disordered and additional models are necessary to perform DFT calculations of physical properties. At present, two methods are proposed for calculations of properties of disordered solid solutions: the supercell approach [7, 8] and the coherent potential approach implemented within a Green function method [9, 10]. The subject of presented study is a calculation in the supercell approach.

2. SUPERCELL APPROACH

Within the supercell approach, periodic conditions are imposed not on a primitive cell, as in ordered structures, but on a sufficiently large supercell obtained by scaling the primitive cell. The usual properties characterizing an ordered structure (cell parameters, spatial symmetry group, positions of nonequivalent atoms) in this case refer to the supercell. The size of the supercell should be chosen such that it corresponds to the content x and reproduces periodical
conditions on the large scale of the supercell. In an ideal crystal, each atomic position is strictly occupied by an atom of a certain type, and in a disordered structure, atomic positions are occupied by atoms of different kinds in a random way, as shown by diffraction measurements. The idea of the supercell method is that a disordered structure can be modeled as a statistical ensemble of ordered structures with all possible configurations of atomic positions. The statistical method for the theoretical simulation of disordered compounds is based on obtaining average values of physical quantities from a set of configurations of strictly ordered compounds, each of them corresponds to a particular choice for the occupation of atomic positions in the crystal lattice. Such an approach is justified when the atoms composing the ordered system are substituted with atoms of the other constituent in a random way. For a small number of configurations, averaging over all possible configurations of ordered compounds can be performed. In the case that the number of possible configurations is significant, a random sample is used for the average utilizing the direct Monte Carlo method. Symmetry properties play a key role in the choice of configurations. The entire set of configurations is represented as a collection of classes that contain symmetrically equivalent configurations. The choice of only symmetrically independent configurations (SIC), by which the averaging is performed, allows a significant reduction in the number of configurations during averaging. All symmetrically independent configurations can be selected and their multiplicity determined in each class. Then, averaging is implemented only by classes of independent configurations, in other words, only for the one representative of each class. If the number of independent configurations is large, even after taking into account symmetrically equivalent configurations, random sampling with weights proportional to the multiplicities in each symmetric class is carried out. This computational scheme is called the symmetric-adapted Monte Carlo method (SAMC), which makes it possible to calculate structural and electronic properties of a disordered structure starting from the average over a finite number of ordered structures [11, 12].

We consider the cubic phase of the compounds CsPb(I$_{1-x}$Cl$_x$)$_3$3 and CsPb(I$_{1-x}$Br$_x$)$_3$, where 0 < x < 1 in the general case. The primitive cell contains three positions of halogen atoms, which can be occupied by iodine or chlorine (bromine) in prescribed proportions, namely 0 : 3, 1 : 2, 2 : 1, 3 : 0. Obviously, the ordered structures obtained by multiplication of a primitive cell can not reproduce the properties of a disordered structure, since the positions of the atoms are strictly correlated on the scale of one cell. The minimal supercell that preserves the symmetry properties of a primitive cubic cell and is large enough to neglect correlations in the position of atoms is the 2x2x2 supercell, which contains 24 positions occupied by halogen atoms. If $n_i$ is the number of positions in the simulation cell occupied by iodine atoms, $n_{Ci}$ is the number of positions occupied by chlorine (bromine) atoms, the total number of configurations is determined by the number of combinations equal to

$$N_C = \frac{(n_i + n_{Ci})!}{n_i!n_{Ci}!}. \quad (1)$$

Taking into account the symmetry properties allows one to pick out symmetrically independent configurations, which number is much smaller than the total number of possible configurations. Table 1 shows the total number of configurations $N_C$ and the number of symmetrically independent $N_{SIC}$ configurations calculated in the SolidSolution program [11, 12], which is a part of the CRYSTAL14 [13] software package, for a 2x2x2 supercluster with various proportions between iodine and chlorine or bromine.

### 3. DETAILS OF CALCULATIONS

So, the parameters of the supercell are relaxed until the values at which the energy minimum of the given structure is reached with an accuracy of $2 \times 10^{-6}$ eV per supercell and the effective pressure in the cell does not
exceed $10^{-2}$ GPa. With the obtained relaxed parameters of the supercell, the self-consistent calculation of the band structure is carried out and the width of the band gap is guaranteed with an accuracy 0.05 eV.

The calculations were carried out with the BECKE exchange functional [14], which correctly takes into account the asymptotic of the exchange interaction at large distances and coincide with the standard correlation functional PBE [15]. The exchange functional BECKE effectively takes into account the contribution of the Hartree–Fock exchange interaction, although it is not a hybrid potential in the strict sense. As it was shown in [14], its use allows to reproduce the values of the band gap for a large number of dielectrics, which are usually obtained using hybrid potentials, since calculations with exchange potentials in the density functional theory, without taking into account the Hartree–Fock contribution, strongly underestimate the value of the band gap. Calculations using hybrid potentials significantly increase the computation time, which is a fundamental difficulty in the method of supercells where it is necessary to average over a large number of configurations.

In the package CRYSTAL14, a mixed numerical-analytical method for calculation of the overlap integrals is realized for this purpose; the wave functions of the electrons are sought in the basis of Gaussian atomic orbitals. For the number of electrons in an atom $Z < 35$, there are all-electron basic sets. However, for arbitrary $Z$, the effective-core potential method can be used, when only valence electrons are explicitly taken into account, and the potential of the nucleus and internal electrons is replaced by an effective potential of the “atomic core”. Calculations with the all-electron basis are much more expensive in terms of processor time than calculations with an effective atomic-core potential, and since we need to perform multiple computations of the energy of a supercell of 40 atoms, the effective core pseudopotentials were used not only for many-electron atoms like lead ($Z = 82$), cesium ($Z = 55$) and iodine ($Z = 53$), but also for bromine ($Z = 35$) and chlorine ($Z = 17$).

Electron configuration of lead is described by the effective pseudopotential PbHAYWLC-211(1d)G with four-electronic valence basis, cesium—CsSCHAYWSC-31G with two-electronic basis, iodine—I1HAYWLC-31G with two-electronic basis, bromine—BrHAYWLC-31 with two-electronic basis, chlorine—ClLCHAYWLC-31G with two-electronic basis. The effective atomic potentials of the type HAYWLC (large core) or HAYWSC (small core) are proposed in 16 and have been repeatedly tested in calculations of a different type, both for molecules and crystals. The parameters of the electronic bases of lead and cesium were used with the standard values given in the library on the website of the CRYSTAL14 program. The values of the diffusion exponential index for iodine, bromine and chlorine were changed to achieve a best description of the energy band gaps of pure lead-halogen compounds: CsPbI3, CsPbBr3, and CsPbCl3. Used parameters of basis sets for cesium, lead, iodine, bromine and chlorine are collected in Appendix. In Fig. 1, the electronic band structures for pure compounds are shown: orange—CsPbI3, red—CsPbBr3, blue—CsPbCl3. The band gaps calculated in the point of high symmetry R agree with data with an error of about 0.05 eV.

4. DEPENDENCE OF BAND GAPS ON DOPANT CONTENT

The width of the band gap for each class of symmetrically independent atomic configurations of the ordered structure $E_{\text{gap}}^l$ can be calculated within the DFT. The width of the band gap of a disordered structure, corresponding to a certain proportion of halogens in the composition, is determined by the formula

$$E_{\text{gap}} = \sum_{l=1}^{L} w_l E_{\text{gap}}^l,$$

where $w_l = n_L / \sum_{l=1}^{L} n_l$, $L = N_{\text{SIC}}$, and $n_L$ is the number of configurations of a certain symmetry class. For cases where $N_{\text{SIC}} \leq 200$ the averaging was carried out for all symmetrically independent configurations. The
standard deviation is calculated by the formula:

\[ D(E_{\text{gap}}) = (E_{\text{gap}}^2 - \langle E_{\text{gap}} \rangle^2)^{1/2}, \]

where 

\[ E_{\text{gap}}^2 = \sum_{i=1}^{L} w_i (E_{\text{gap}}^i)^2. \]

With \( N_{\text{SIC}} > 200 \), the average was performed over 200 randomly chosen configurations, i.e. in the formula 2 it was assumed that \( N_{\text{SIC}} = 200 \). At each given ratio between halogens, a set of symmetrically independent ordered structures is generated in the first step and the multiplicity of \( n_L \) configurations in each set is determined.

The results of computation of the band gaps as a function of doping content \( x \) are collected in Table 1 (columns 4 and 5) and in Fig. 2. The calculated dependence of the band gap on the impurity content deviates substantially from the linear dependence for the CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) compound, as well as the available experimental data [3]. Last ones are described fairly well by a linear law with the different slope for regions \( 0 < x < 0.5 \) and \( 0.5 < x < 1 \). The calculated dependence on \( x \) for the CsPb(I\(_{1-x}\)Cl\(_x\))\(_3\) compound is in a good agreement with the expected linear law, but experimental data for this compound are absent yet and our calculations can be considered as predictions.

To demonstrate the convergence of MC procedures, we show in Fig. 3 the statistical error for band gap energy for structure CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) with \( x = 0.5 \) as a function of number of symmetrically independent configurations, \( N_{\text{SIC}} \). The statistical error is defined as follows: \( \Delta E_{\text{gap}} = 3D(E_{\text{gap}})\sqrt{N_{\text{SIC}}}. \) Our choice, \( N_{\text{SIC}} = 200 \), guarantees an error about 0.03 eV for average values of band gaps.

5. DEPENDENCE OF BULK MODULI ON DOPANT CONTENT

The computation scheme of bulk moduli \( x \)-dependence for discussed here solid solutions is the same as for the \( x \)-dependence of band gaps. We calculate bulk moduli for a certain number of symmetrically independent ordered configurations using the third-order

![Fig. 2. Band gap energy for CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) (left panel) and CsPb(I\(_{1-x}\)Cl\(_x\))\(_3\) (right panel) as a function of doping content, \( x \). Boxes on the left and right panels are the experimental data from 2, 3. Error bars correspond statistical errors \( \Delta E_{\text{gap}} \).](image1)

![Fig. 3. Statistical error \( \Delta E_{\text{gap}} \) for band gap energy for structure CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) with \( x = 0.5 \) as function of number of symmetrically independent configurations, \( N_{\text{SIC}} \).](image2)
Birch-Murnaghan isothermal equation of state (based on the Eulerian strain) [17]. The latter reads:

\[
E(V) = E_0 + \frac{9V_0B}{16} \left[ \left( \frac{V_0}{V} \right)^{3/2} - 1 \right] + \frac{B'}{2} \left[ \left( \frac{V_0}{V} \right)^{3/2} - 1 \right]^2 - \frac{3}{2} \left( \frac{V_0}{V} \right)^{3/2} \right], \tag{3}
\]

where \( B \) is the equilibrium bulk modulus, \( B' \) is the first derivative of \( B \) with respect to the pressure, \( V_0 \) and \( E_0 \) are the equilibrium volume and energy, at zero pressure. To find \( B \), we should obtain the \( E(V) \) curve. Taking into account the huge number of configurations, we need to restrict a number of points in the \( E(V) \) curve to the lowest feasible value. Thereby, we use five-points fitting procedure with variation coefficient from 0.98 to 1.02 for volumes around the equilibrium volume \( V_0 \) which corresponding variation coefficient equal to 1.

The results of our calculations for bulk moduli are presented in Table 2 and Fig. 4. Bulk moduli of pure PbCsI\(_3\) and PbCsCl\(_3\) are equal to 16.15 and 24.37 GPa, correspondingly. We should expect linear growth of bulk moduli with chlorine content \( x \), from 0 to 1, taking into account that chemical bonding for chlorine atoms is stronger than for iodine atoms. But in reality, we obtain a fall of bulk moduli with chlorine doping of PbCsI\(_3\) till the minimum value of \( B = 12.97 \) GPa at the \( x = 1/3 \). Only at the \( x = 5/6 \) bulk modulus for solid solution CsPb(I\(_{1-x}\)Cl\(_x\))\(_3\) becomes equal to the bulk modulus of pure crystal PbCsI\(_3\). The same picture is realized also for solid solution CsPb(I\(_{1-x}\)Br\(_x\))\(_3\); at the \( x = 1/6 \) one has \( B = 14.09 \) GPa despite \( B = 16.15 \) for

![Fig. 4. Bulk moduli for CsPb(I\(_{1-x}\)Br\(_x\))\(_3\) (left panel) and CsPb(I\(_{1-x}\)Cl\(_x\))\(_3\) (right panel) as function of dopant content, \( x \). Error bars correspond statistical errors \( \Delta B \).](image)
pure PbCsI₃. The obtained result seems non-trivial and should be experimentally examined.

6. CONCLUSIONS

In this work, we performed the first-principles calculations for band gap energies, $E_{\text{gap}}$, and bulk moduli, $B$, as functions of the relative dopant amount ($x$) of bromine and chlorine for cubic phases of cesium lead iodide perovskite CsPbI₃. Ab initio calculations for solid solutions were performed in the supercell approach. In case of band gap dependence, we have obtained an approximate agreement with experimental data for cubic phase of CsPb(I$_{1-x}$Br$_x$)$_3$ and we have predicted $x$-dependence for cubic phase of CsPb(I$_{1-x}$Cl$_x$)$_3$ at the whole range $0 \leq x \leq 1$. Our predictions for bulk modulus $x$-dependencies show the strong non-linear behaviour, which demonstrates the importance of disordering effects over the chemical content for the cesium lead-halide solid solutions.

APPENDIX

Basis set for chlorine:
217 2
HAYWLC
0 1 3 7. 1.
4.221 -0.0338 -0.0657
1.769 -0.3131 0.090
0.498 .8138 0.5776
0 1 1 0. 1.
0.131 1.0 1.0

Basis set for bromine:
235 2
HAYWLC
0 1 3 8. 1.
1.547 -0.3827 -0.3476
1.164 0.0798 0.3994
0.320 0.9091 0.5937
0 1 1 0. 1.
0.092 1.0 1.0

Basis set for iodine:
253 2
HAYWLC
0 1 3 7. 1.
1.520 0.5606 -0.0300
1.252 -1.0108 -0.0719
0.295 0.9297 0.6278
0 1 1 0. 1.
0.083 1.0 1.0

Basis set for cesium:
255 2
HAYWSC
0 1 3 8. 1.
0.986 -1.1924 -0.8737
0.833 0.8133 0.9449
0.330 0.9076 0.5185
0 1 1 1. 1.
0.147 1.0 1.0

Basis set for lead:
282 4
HAYWLC
0 1 2 4. 1.
1.335104 -0.1448789 -0.1070612
0.7516086 1.0 1.0
0 1 1 0. 1.
0.5536686 1.0 1.0
0 1 1 0. 1.
0.1420315 1.0 1.0
0 3 1 0. 1.
0.1933887 1.0

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