Ab initio modeling of band gaps of cesium lead halide perovskites depending on the dopant amount

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Abstract. Ab initio simulations of optical band gaps of cesium lead halide perovskites $CsPb(I_{1-x}Cl_x)_3$ 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 on the content $x$ are investigated over the whole range $0 \leq x \leq 1$.

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 dependence 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 structures: the supercell approach \cite{7, 8} and the coherent potential approach implemented within a Green function method \cite{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 \cite{11, 12}.

3. Dependence of band gaps on dopant content
We consider the cubic phase of the compounds $CsPb(I_{1-x}Cl_x)_3$ 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 $2 \times 2 \times 2$ 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, $n_{Cl}$ is the number of positions occupied by chlorine (bromine) atoms, the total number of configurations is determined by the number of combinations equal to

$$N_C = \frac{(n_I + n_{Cl})!}{n_I!n_{Cl}!}$$

(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 $2 \times 2 \times 2$ supercluster with various proportions between iodine and chlorine or bromine.

| Content $x$, Cl or Br | Total number of configurations, $N_C$ | The number symmetrically independent configurations, $N_{SIC}$ | $E_{gap}$, eV $CsPb(I_{1-x}Cl_x)_3$ | $E_{gap}$, eV $CsPb(I_{1-x}Br_x)_3$ |
|----------------------|--------------------------------------|-------------------------------------------------|-----------------|-----------------|
| 0                    | 1                                   | 1                                              | 1.75            | 1.75            |
| 1/6                  | 343                                 | 80                                             | 1.93 ± 0.13     | 1.90 ± 0.12     |
| 1/3                  | 21252                               | 2664                                           | 2.07 ± 0.17     | 1.98 ± 0.13     |
| 1/2                  | 87980                               | 8797                                           | 2.19 ± 0.14     | 2.03 ± 0.14     |
| 2/3                  | 21252                               | 2664                                           | 2.34 ± 0.17     | 2.06 ± 0.13     |
| 5/6                  | 343                                 | 80                                             | 2.54 ± 0.20     | 2.16 ± 0.04     |
| 1                    | 1                                   | 1                                              | 2.90            | 2.36            |

The width of the band gap for each class of symmetrically independent atomic configurations of the ordered structure $E_{gap}^l$ 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

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

where $w_l = \frac{n_L}{\sum_{l=1}^{L} n_l}$, $L = N_{SIC}$, and $n_L$ is the number of configurations of a certain symmetry class. For cases where $N_{SIC} \leq 200$ the averaging was carried out for all symmetrically independent configurations. The statistical dispersion is calculated by the formula: $D(E_{gap}) = (E_{gap}^2 - (E_{gap})^2)^{1/2}$, where $E_{gap}^2 = \sum_{l=1}^{L} w_l (E_{gap}^l)^2$. With $N_{SIC} > 200$, the average was performed over 200 randomly chosen configurations, i.e. in the formula 2 it was assumed that $N_{SIC} = 200$. 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.

Then, 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 $3 \times 10^{-2}$ 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 pseudo-potentials 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 $\text{PbHAYWL}C-211(1d)G$ with four-electronic valence basis, cesium - $\text{CsSCHAYWSC-31G}$ with two-electron basis, iodine - $\text{IHWAYWLC-31G}$ with two-electronic basis, bromine - $\text{BrHAYWL}C-31$ with two-electron basis, chlorine - $\text{ClLCHAYWL}C-31$ with two-electronic basis. The effective atomic potentials of the type HAYWL (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. 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 best description of the energy band gaps of pure lead-halogen compounds: $\text{CsPbI}_3$, $\text{CsPbBr}_3$ and $\text{CsPbCl}_3$. The results of calculating 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 $\text{CsPb(I}_1-x\text{Br}_x)_3$ 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

![Figure 1. The electronic band structures for pure compounds: orange – $\text{CsPbI}_3$, red – $\text{CsPbBr}_3$, blue – $\text{CsPbCl}_3$.](image-url)
dependence on $x$ for the $CsPb(I_{1-x}Cl_x)_3$ compound is in good agreement with the expected linear law, but experimental data for this compound are absent yet and our calculations can be considered as predictions.

Figure 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 function of doping content, $x$. Boxes on the left and right panels are the experimental data from [2, 3]. Error bars correspond statistical errors $\Delta E_{\text{gap}}$.

Figure 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 statistically independent configurations, $N_{\text{SIC}}$.

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 function of number of statistically independent configurations, $N_{\text{SIC}}$. The statistical error is defined as follows: $\Delta E_{\text{gap}} \simeq 3D^{1/2}(E_{\text{gap}})/\sqrt{N_{\text{SIC}}}$. Our choice, $N_{\text{SIC}} = 200$, guarantees an error about 0.03 eV for average values of band gaps.

4. Conclusions
In this work, we have studied band gap energy, $E_{\text{gap}}$, dependence on relative contents of iodine, bromine and chlorine for cubic phases of cesium lead-halogen perovskites. Ab initio calculations for disordered structures performed in supercell approach. 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 $0 \leq x \leq 1$. 
5. References

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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.
1.520  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

Basic 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