Enthalpy of formation of $CsSn(Cl_x(Br,I)_{1-x})_3$ and $CsPb(Cl_x(Br,I)_{1-x})_3$

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Abstract. Organic-inorganic hybrid halide perovskites, e.g., $MAPbI_3$, have revolutionized the field of solution-processable photovoltaic applications. However, due to organic cation, they are found to be unstable under external environment such as moisture and high temperature. Moreover, the toxicity of lead (Pb) in their structure is harmful for human health and hurdle for commercialization. These inspire us to pursue for families of perovskites structure with the formula $CsSn(Cl_x(Br,I)_{1-x})_3$ with $x = 1/3,\ 2/3,\ 1$. which are nontoxic and could have better structural stability under ambient conditions. We have investigated the enthalpy of formation of $CsSn(Cl_x(Br,I)_{1-x})_3$ and in based on the density functional theory (DFT) with the generalized gradient approximation (GGA). The main objective is to seek for structural stability with respect to the composition x's. We found that the structural stability increases linearly with composition x's of halide atom from I to Br to Cl. We also calculate enthalpy of formation of $CsPb(C_{lx}(Br,I)_{1-x})_3$ perovskites for comparative purpose, and found that the structural stability of $CsSn(C_{lx}(Br,I)_{1-x})_3$ is slightly lower than its Pb-counterpart. Thus $CsSn(C_{lx}(Br,I)_{1-x})_3$ is still the promise candidate for photovoltaics. These studies could serve as a guidance to compromise the stability, by varying composition of halide atoms, with the optimal band gap or other solar-cell-desired properties.

1. Introduction

According to the third-generation of photovoltaic cell, the methylammonium lead iodide perovskite ($MAPbI_3$) has recently gained a great deal of interest. This is as, to date, the solar cell made of this material has been able to reach efficiencies 22.7% in 2017 [1] and is much cost efficient to manufacture compared with that from the conventional silicon based. However, there are limitations impeding the commercialization of $MAPbX_3$, e.g., including lead toxicity, being an under-optimal bandgap and poor long-term stability. The toxicity issue of lead halide perovskites may be remove by replacing lead with tin metal cation (Sn^{2+}) because it has the similar s^2 valence electronic configuration to Pb^{2+} and has close ionic radius (Pb^{2+}: 119 pm, Sn^{2+}: 110 pm), which makes it possible to form a perovskite with a basic formula $ASnX_3$ in analogy to lead compounds. Small monovalent A-site cations, e.g. MA^+, FA^+, Cs^+ lead to the formation of three-dimensional structures, whereas larger ones cause a reduced. Furthermore, the existence of organic molecule in this material is a major obstacle to their stability [2-3]. The effective way to remove this problem directly is to replace the organic cation with inorganic counterpart. Except for francium (Fr) which is a radioactive element, cesium might be the most appropriate substitution to organic site, because its atomic size is almost the largest in the

periodic table to hole the three dimensional stable perovskite structures. These inspire us to pursue for families of perovskites structure with the formula $CsSn(Cl_x(Br,I)_{1-x})_3$ with x = 1/3, 2/3, 1. In this work, we have investigated the enthalpy of formation of $CsSn(Cl_x(Br,I)_{1-x})_3$ based on the density functional theory (DFT). The main objective is to seek for structural stability with respect to the composition x's. To ensure that these results come from the main effect of mixing halide atoms in perovskite structures, we also performed calculations of the enthalpy of formation on the related perovskites $CsPb(Cl_x(Br,I)_{1-x})_3$ for comparative purpose. These studies suggest the ways how to tune the stability by varying composition of halide atoms.

2. Computational details

We calculated the enthalpy of formation of $CsSn(Cl_x(Br,I)_{1-x})_3$ and $CsPb(Cl_x(Br,I)_{1-x})_3$ within the framework of density functional theory (DFT) [4] by using the PWSCF code as implemented in the Quantum-Espresso packages. The effective interaction between valance electrons and ionic core of atom is described by the norm-conserving pseudopotentials. First, the lattice parameters, atomic positions and enthalpy of formation were obtained by using the generalized gradient approximation (GGA) formulated by Perdew-Burke-Ernzerhofer (PBE) [5]. The single-particle Kohn–Sham wavefunctions are expanded in the plane-waves basis set with a cutoff energy of 70 Ry and 80 Ry for lead and tin perovskite families, respectively and the corresponding Brillouin-zone integration is performed with 8 × 8 × 8 and 6 × 6 × 6 Monkhorst-Pack mesh [6]. The enthalpy of formation of these families of materials was calculated with respect to their stable phases at the standard pressure (1 bar) and at room temperature of constituent elements. Under these conditions, the enthalpy of formation is equal to the change of total energy of system. For example, the enthalpy of formation of the $CsSn(Cl_xBr_{1-x})_3$ is

$$\Delta H_{CsSn(Cl_xBr_{1-x})_3} = E_{CsSn(Cl_xBr_{1-x})_3} - \left(E_{Cs} + E_{Sn} + \frac{3}{2} x E_{Cl_2} + \frac{3(1-x)}{2} E_{Br_2} \right)$$

Here, $E_{CsSn(Cl_xBr_{1-x})_3}$ is the total energy per formula of $CsSn(Cl_xBr_{1-x})_3$. E_{Cs} and E_{Sn} are total energy per atom of Cs crystal in the body-centered-cubic structure and Sn crystal in the centered-tetragonal structure, whereas E_{Cl_2} and E_{Br_2} are ground-state total energies of a Chloride and Bromide molecule. The dependence of total energy on the number of k-points for the Brillouin Zone integration has been explored by varying k-points. The 6 × 6 × 6 Monkhorst-Pack mesh was chosen for Cs and Sn, while the 8× 8 × 8 grid of k-points was employed for the calcultaion of Pb. In the case of diatomic halide molecule, we constructed a cubc supercell, containing two halide atoms separated at a bond length distance, with 14 angstroms of superlattice parameters. This is large enough to assume that the interaction of each molecule due to the periodicity of the system can be negligible. Since the larger supercell in a real space corresponds to the smaller one in a reciprocal space, this means that accurate results are possible using 1 k-point sampling for the Brillouin Zone integration.

3. Results and discussion

The calculated equilibrium lattice parameters of various perovskites are reported in Table 1, which are good agreement with values from available experimental data. It is remarkable that one of lattice parameters of $CsSnICl_2$, for example, has the value close to that of $CsSnI_3$ whereas the other ones are close to that of $CsSnCl_3$. This suggests implicitly the relative strength of interaction between Sn atom and halogen atom, i.e., the interaction between Sn and Cl atom is stronger than that one between Sn and I atom. This effect can be understood by the concept of electronegativity, the measure of atom's ability to attract and bind with electrons. Since the electronegativity decreases linearly as increasing of atomic radius, the Cl atom which is smaller than Br and I, has the highest ability to attract electrons from Sn than the Br and I. In the same way, Br which is smaller than I can be formed bonding with Sn stronger than bonding between Sn and I. The explanation can also be applied to Pb-counterpart.

Table 1. Equilibrium lattice parameters (in unit of angstrom) of $CsSn(Cl_x(Br,I)_{1-x})_3$ and $CsPb(Cl_x(Br,I)_{1-x})_3$. The available experimental results are also reported.

Crystal	Lattice const.	Exp.	Crystal	Lattice const.	Exp.
$CsSnCl_3$	$a = b = c = 5.635$	5.560[a]	$CsPbCl_3$	$a = b = c = 5.743$	5.605[d]
$CsSnClBr_2$	$a = b = 5.913$, $c = 5.606$	5.74[c]	$CsPbClBr_2$	$a = b = 6.025$, $c = 5.725$	-
$CsSnClI_2$	$a = b = 6.316$, c = 5.578	-	$CsPbClI_2$	$a = b = 6.412$, $c = 5.690$	-
$CsSnBr_3$	$a = b = c = 5.892$	5.804[j]	$CsPbBr_3$	$a = b = c = 6.007$	5.874[d]
$CsSnBrCl_2$	$a = b = 5.629$, $c = 5.924$	-	$CsPbBrCl_2$	$a = b = 5.739$, $c = 6.033$	-
$CsSnBrI_2$	$a = b = 6.287$, $c = 5.860$	6.04[c]	$CsPbBrI_2$	$a = b = 6.393$, $c = 5.968$	-
$CsSnI_3$	$a = b = c = 6.252$	6.219[a]	$CsPbI_3$	$a = b = c = 6.354$	6.289[b]
$CsSnICl_2$	$a = b = 5.645$, $c = 6.322$	-	$CsPbICl_2$	$a = b = 5.746$, $c = 6.430$	-
$CsSnIBr_2$	$a = b = 6.889$, $c = 6.299$	5.93[c]	$CsPbIBr_2$	$a = b = 5.998$, $c = 6.415$	-

[a]Yuan et al. [7], [b]Trots et al.[8], [c]Peedikakkandy et al. [9], [d]Moreira et al. [10]

We calculated the enthalpy of formation at the standard conditions, i.e., at 1 bar of pressure and at room temperature, where the most stable phases of Cs is body-center cubic (Im_ 3m), Sn's is body-centered tetragonal (I41/amd), Pb's is face-centered cubic (Fm_3m), and halides are in gaseous. The enthalpy of formation for $CsSnCl_xI_{3-x}$ is thus determined according to the following equation.

$$\mathrm{Cs(bcc)} + \mathrm{Sn(tet)} + \frac{3x}{2}\mathrm{Cl_2(g)} + \frac{3(1-x)}{2}\mathrm{I_2(g)} \rightarrow \mathrm{CsSn}\left(\mathrm{Cl}_x\mathrm{I}_{1-x}\right)_3$$

All the calculated enthalpy of formation takes the negative values which indicate that the reaction is exothermic. There is amount of energy released to form the perovskite structure from its pure element structures, thus, atoms in the structures is more stable than in its pure structure. In $CsPb(Cl_x((Br,I)_{1-x})_3$, the enthalpy of formation is slightly less than its Sn-counterpart around 0.04-1.7 kJ/mol. The trend of enthalpy of formation of Sn- and Pb-family plotted versus the averaged ionic radius of halides in the formula is shown in Figure 1. We see that the enthalpy of formation is proportional to the averaged ionic radius, hence to the composition x's, in both tin and lead family. Its values decrease from the structure formed by large halide to the structure formed by small halide.

The enthalpy of formation can be used for assessing the relative structural stability of perovskite structures. The perovskites with the lower enthalpy of formation are more stable than those with higher enthalpy of formation. Since, the electronegativity of halogen atom decreases linearly with increasing of atomic radius, while the enthalpy of formation of halide perovskites decreases linearly with increasing of averaged halide radius in their chemical formula, Thus we can infer that the structural stability of halide perovskites correlate to the electronegativity of halide in the structure. The small halide atom has high electronegativity; it has more ability to bonding with Sn(Pb) atom than the larger atom do. So, the perovskite structure could be more stable if the smaller size of halide atom is incorporated to the structures. There are many studies indicate that $CsPbBrI_2$ is more stable than $CsPbI_3$ [11-12]. However, mixing halides in perovskites also affect the energy band gap. The smaller halide incorporated in the structure, the wider bandgap is obtained. Ma Q et al [13] demonstrated that $CsPbI_2Br$ has a more suitable (lower) band gap than $CsPbIBr_2$ as a light harvesting material but increasing of iodine content reduces structural stability due to the preference toward the non-perovskite orthorhombic phase when the film is exposed to air. Hence, to fabricate the halide perovskite solar cell, one have to compromise the stability, by varying composition of halide atoms, with the optimal band gap or other relevant solar-cell-desired properties.

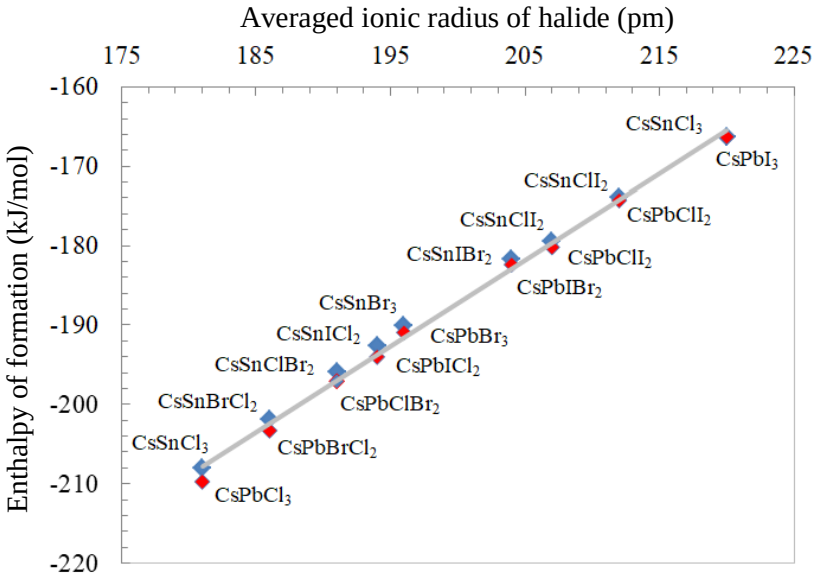

Figure 1. The enthalpy of formation of Cs-based mixed halide perovskites plotted versus the averaged ionic radius of halide in its formula. The blue dot belongs to Sn-family whereas the red dot belongs to Pb-family. The solid grey line is the trend of the relation.

4. Conclusion

We have investigated the relative structural stability of Cs-based mixed halide perovskites: $CsSn(Cl_x(Br,I)_{1-x})_3$ and $CsPb(Cl_x(Br,I)_{1-x})_3$ with x = 1/3, 2/3 and 1 by using the calculated enthalpy of formation as the assessed parameter. The key finding of this work is that the enthalpy of formation, relate to structural stability, increases linearly with composition x's of halide atom from I to Cl. These effects can be understood by considering at the trend of electronegativity of halide atoms which decreases linearly with increasing atomic radius from Cl to I**.** It indicates that the role of halide atom incorporated in perovskite structure has contribution to their structural stability. The lighter halide atoms in perovskite, the better stable will be.

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