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First Principle Study of the Lattice Constant and Band Structure of ABX_3, a Perovskite Compound

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ABSTRACT

The first principle study of the lattice constant and band structure has been performed on the cubic structure (pm-3m) of CsAgI3 using plane-wave pseudopotential method within the generalized gradient approximation (GGA). The investigation of the above-mentioned properties is given by applying exchange-correlation functional PBE along with ultrasoft pseudopotential (USPP). There is no theoretical or experimental data available at the time of this study. So, the results reported in this study are subject to experimental confirmation.

Keywords: First principle, DFT, Perovskite, Electronic properties

Introduction

Perovskite is a class of compounds having a specific crystal structure and can be represented as ABX_3, where A and B are the monovalent or divalent cations and X can be the anion. Mostly A-site cations are from alkali or alkaline earth metals, while B-site cations are selected from transition metals and X tpically could be oxygen or one of the halogens i.e. Cl, Br or I [1]. Perovskites are known for their structural flexibility, which is due to the differences in size and type of ions forming the crystal lattice. This flexibility explains the wide range of physical and chemical properties manifested. The ideal perovskite structure is cubic, usually stable at high temperatures, with ions arranged perfectly in an undisturbed pattern. However, such ideal structure is not observed due to changes in temperature, pressure, or composition. The effects of this phenomenon are largely reflected in structural distortions that include tetragonal, orthorhombic, or rhombohedral symmetries derived from the tilting and rotation of the BX_6 octahedra in the lattice [2].

Perovskites have a wide range of chemicals and the ways in which they can be altered. This is because many ions can fit into the A, B, and X spots in their crystal structure. This means that the composition can be adjusted to fine-tune electronic, optical, and structural properties to meet certain needs. By substituting varying cations at the A or B sites we can tailor the bandgap, the dielectric constant. Further, varying X-site anions, typically halides or oxides, could prove equally crucial in altering bonding and lattice dynamics. These tailoring capabilities have translated into the remarkable performance of perovskites in photovoltaics, high-efficiency solar cells, optoelectronics for LEDs and lasers. This flexibility underlines their importance as a platform for next-generation functional materials [3].

The power conversion efficiency (PCE) of perovskite based solar cells from 2013 to 2024 has increased from 14% to 27% respectively showing the remarkable potential in perovskite based solar cells [4]. And the main component of these perovskite solar cells (PSC) is lead Pb, which is famous for its toxicity. The commercialization of these is hindered due to the toxicity of lead, low resistance to the light, moisture and thermal stress along with degradation of the device due to ion migration. Apart from the toxicity of lead all the other problems can be due to perovskites defective chemistry. There are three different types of defects in perovskites points defects, line defects and plane defects. Point defects can be divided further into two types which are intrinsic defects and extrinsic defects. Intrinsic defects are those which are inside the crystal structure while the extrinsic defects are those which is related to the displacement of an atom from its original site when it is replaced by the impurity atom [5].

Presently the demand for environmentally friendly energy is growing rapidly, which is forcing researchers to conduct research for new efficient materials and make them commercially viable. This is a great responsibility and day by day researchers are getting closer to commercially viable perovskite-based energy devices. This search for new environmentally friendly energy materials has led us to the widespread use of the density functional theory (DFT). In simple words, DFT can be explained as it gives us an approximate solution of the system under investigation by using the modified Schrodinger equation based on some approximation, the charge density and the exchange correlation (XC) functional. Though the exact form of XC functional is unknown but there are some approximations.

The reasons for choosing silver based $CsAgI_3$ a perovskite composition because it can be a lead free environmentally friendly alternative. We could have selected the hybrid perovskites, but the available computational resources suggest otherwise. Cs and I both are tested choice for A-site cation and X-site anion respectively. Cu, Ag and Au lies in the same group 11 or 1B of the periodic table out of which only Cu and Au were investigated as B-site cation, but Ag was not. Another reason for silver is that it shares the same electronic configuration as Cu and Au, which make it chemically identical.

Research methodology

The first principle calculations were performed using quantum espresso [6]. The electronic states of Cs $5s^2$ $5p^6$ $6s^1$, Ag $5s^2$ $4d^9$ and I $4d^{10}$ $5s^2$ $5p^5$ are treated as valence states. Monkhorst-pack scheme [7] was used to generate the k-points for the 10x10x10 and 12x12x12 grid of optimized k-points for geometric optimization and band structure calculation respectively. The optimized cutoff energy of 60 Ry and charge density cutoff of 600 Ry was used to perform the geometric optimization and band structure calculations. $1\text{x}10^{-3}$ Ry/Bohr and $1\text{x}10^{-6}$ Ry are used as force and energy convergence threshold respectively. For smearing, Methfessel-Paxton method was used.

Result and discussion

The cubic structure of the $CsAgI_3$ related to the pm-3m space group is shown in Figure 1. The values of optimized lattice constant (a_o), equilibrium volume (Vo), bulk modulus (B_o), pressure derivative (B`) using ultrasoft pseudopotential are 5.88 Å, 203.74 Å^3, 138.87 GPa, 5.27, respectively. The calculated band structure of $CsAgI_3$ using ultrasoft pseudopotential is given in figure 3. The minimum energy difference between valence band maximum (VBM) and conduction band minimum (CBM) is known as the band gap of the material. We can see in Figure that $CsAgI_3$ has an indirect band gap of 0.58 eV because the VBM lies at R wavevector and CBM lies at G wavevector. Due to lower band gap this material can be classifies as low band gap semiconductor. The indirect nature of the transition from R to G requires a phonon which reduces the probability of indirect transition. The effective mass of hole at the VBM is $0.03m_o$ where m_o is the rest mass of an electron, this means a less massive hole is present at R which means the charge transport properties of this material is good.

Conclusion

The band gap 0.58eV of the $CsAgI_3$ lies in the range of narrow band gap semiconductors. The effective mass of the hole at the top of VBM is also small, which means good charge carriers transport property. But all of this is undermined by the indirect band gap of the $CsAgI_3$. Further investigation is required to investigate the effect of this indirect band gap nature of the transition between VBM and CBM on the optical properties to see how the material will react to the incident light.

Figures

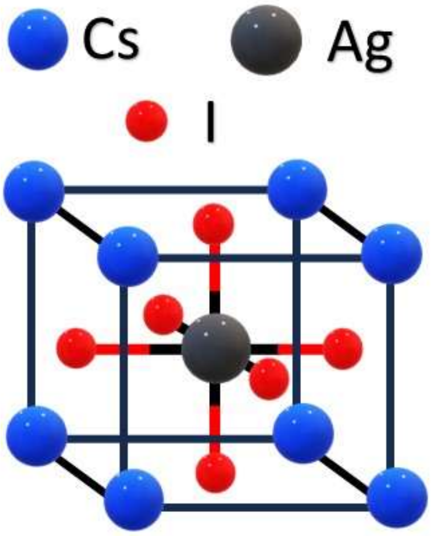

Figure 1: Cubic perovskite structure of $CsAgI_3$ related to the pm-3m space group. Where Cs is at (0,0,0), Ag is at (0.5, 0.5, 0.5), I_1 is at (0, 0.5, 0.5), I_2 is (0.5, 0, 0.5) and I_3 is at (0.5, 0.5, 0) positions.

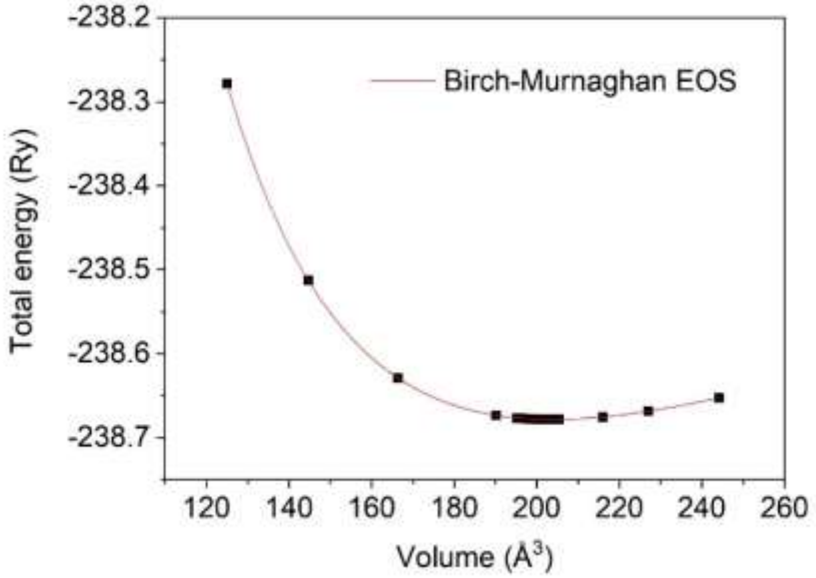

Figure 2: Fitting of Birch-Murnaghan EOS on energy vs volume graph while using ultrasoft pseudopotentials.

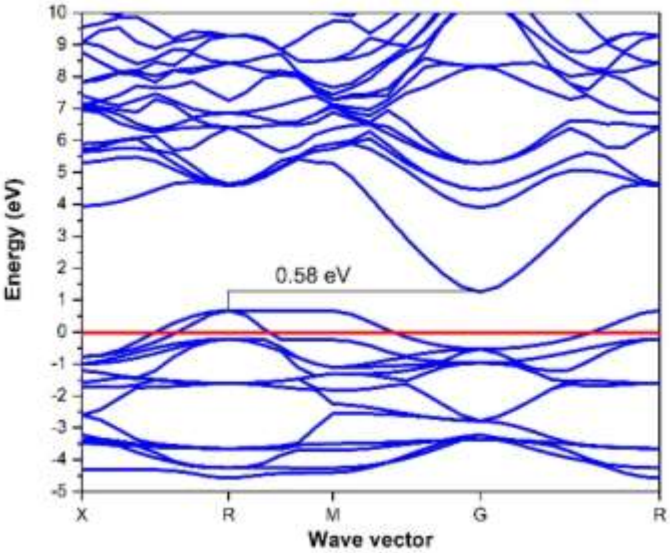

Figure 3: Band structure of $CsAgI_3$ calculated using PBE with ultrasoft pseudopotential, represented for the energy of -5 to +10 eV.

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