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Geometry Optimization of $RbAgI_3$ via Density Functional Theory

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ABSTRACT

By using density functional theory (DFT), we analysed $RbAgI_3$, which belongs to the halide perovskite family. Halide perovskites have shown great potential for use in many optoelectronic devices, but more theoretical research is needed to fully understand their properties. Additionally, many high-performing perovskites contain toxic lead (Pb), so we chose to replace it with safer silver (Ag). we used quantum ESPRESSO with PBE exchange-correlation functional to optimize the structure.

Introduction

In the past 20 years, halide perovskites have become one of the most promising materials used in photovoltaics and light-emitting devices [1]. The term "perovskite" was first introduced in 1839 by Gustav Rose, who named the mineral $CaTiO_3$ after Count Lev Alekseyevich von Perovski, a Russian nobleman and mineralogist. Later, in 1926, Victor Goldschmidt used the term to describe a group of materials with a similar crystal structure. The perovskites crystal structure is a unique arrangement characterized by a three-dimensional network of corner-sharing octahedral [2].

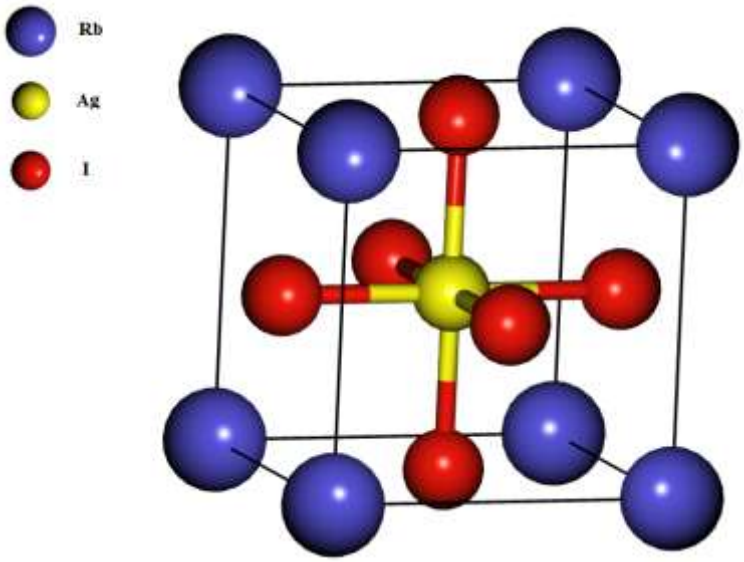

Figure 1: Cubic structure of $RbAgI_3$ perovskite.

The general formula for halide perovskites is ABX_3, where A represents a cation typically located at the corners of the cube and has relatively greater radius. B represents a cation located at the center of the cube and has relatively small radius, usually a metal atom. X represents a halide anion, which exists at the centers of the faces of the cube. ABX_3 perovskites are widely used in various energy devices [3], including solar cells, diodes (LEDs), photo detectors, and energy storage systems. ABX_3 perovskites have been extensively studied for their application in solar cells. They have demonstrated high performance and have been used in solar cell applications, showing potential for high efficiency and stability. In nature, perovskites are mostly found as oxides, with many being silicates like bridgmanite minerals. However, they can also appear as fluorides, chlorides, hydroxides, arsenides, and intermetallic compounds [4].

Research Methodology

The crystal structure of $RbAgI_3$ was optimized using first-principles density functional theory (DFT) calculations. The simulations were performed using the Quantum ESPRESSO software package. The BURAI GUI was used to prepare and manage the input files for the calculations. The Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional under the Generalized Gradient Approximation (GGA) was employed to describe electron interactions. An ultra-soft pseudopotential (USPP) with a plane-wave basis set having cut off energy 70Ry and cut off for charge 400Ry is used. The Brillouin zone was sampled with a 9×9×9 k-point mesh to ensure accurate results.

Results and Discussion

The cubic crystal structure of $RbAgI_3$ is related to the pm-3m space group. The Rb atoms lies at the corner of the cell (0, 0, 0), Ag lies at the center of the unit cell (0.5, 0.5, 0.5), the iodine atoms are lied at the center of the faces of the cubic unit cell I_1 (0.5, 0.5, 0), I_2 (0.5, 0, 0.5), and I_3 (0, 0.5, 0.5). In DFT calculations, the energy cut-off is the limit on the total energy of plane waves used to describe the electronic wavefunctions in a periodic system [5]. It controls how many plane waves are included in the calculations. A higher energy cut-off means using more plane waves, which increases accuracy but also makes the calculations take more time and computational resources. The energy cut-off is usually chosen by performing a convergence test to ensure accurate results without unnecessary computational cost. In Figure 2, we determine the value of cut-off energy through the convergence tests and we got minimum total energy for the value of cut off energy 70Ry. After setting the value the optimized cut off value, we optimized the k-point mesh for Brillouin zone sampling. Figure 3 shows the variation in total energy with different k-point grids. At 1×1×1, the energy is very high, but it decreases as the k-point density increases. The energy stabilizes at 9×9×9, where the curve flattens, confirming this as the optimal k-point mesh for well-converged result. Geometry optimization refers to the process of adjusting the positions of atoms in a material (and sometimes the shape or size of the unit cell) to minimize the total energy of the system. In computational materials science, this process is used to find the most stable arrangement of atoms that represents the material's equilibrium state. In Figure 4, for each lattice parameter we calculated the total energy. After plotting the graph of lattice parameter versus total energy in Origin software, we got a U-shaped curve. Initially, the total energy decreases as the lattice parameter increases, reaching a minimum point, and then starts to increase again. To find the exact lattice parameter corresponding to the lowest total energy, we used the Birch-Murnaghan equation of state for curve fitting [6].

$$E_{tot}(V) = E_o + \frac{9V_oB_o}{16}\left([\left(\frac{V_o}{V}\right)^{2/3} - 1]^3 B'_o + [\left(\frac{V_o}{V}\right)^{2/3} - 1]^2 [6 - 4\left(\frac{V_o}{V}\right)^{2/3}]\right) \quad (1)$$

Where $E(V)$ is the calculated total energy at any volume V. V_o is the equilibrium volume at which the energy is minimized i.e. Eo. B_o is the bulk modulus and B_o' is the pressure derivative. The value of lattice parameter is obtained is 5.85Å, V_o = 200.29 (Å)^3, B_o = 0.0094 and B_o' = 5.37 respectively.

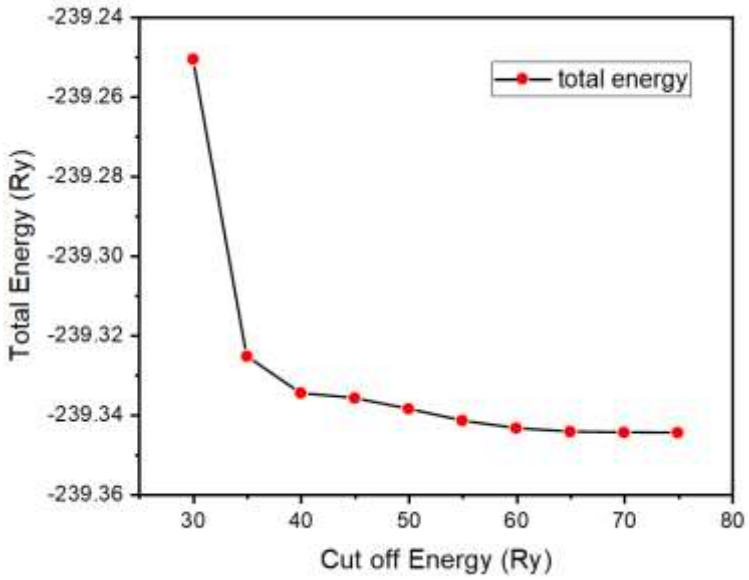

Figure 2: Convergence of cut-off energy of $RbAgI_3$ using USPP.

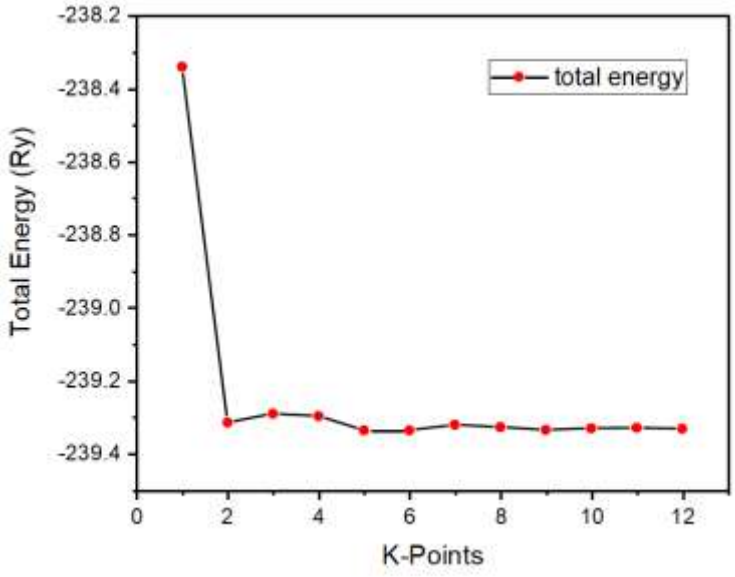

Figure 3: Convergence of k-points of $RbAgI_3$ using USPP.

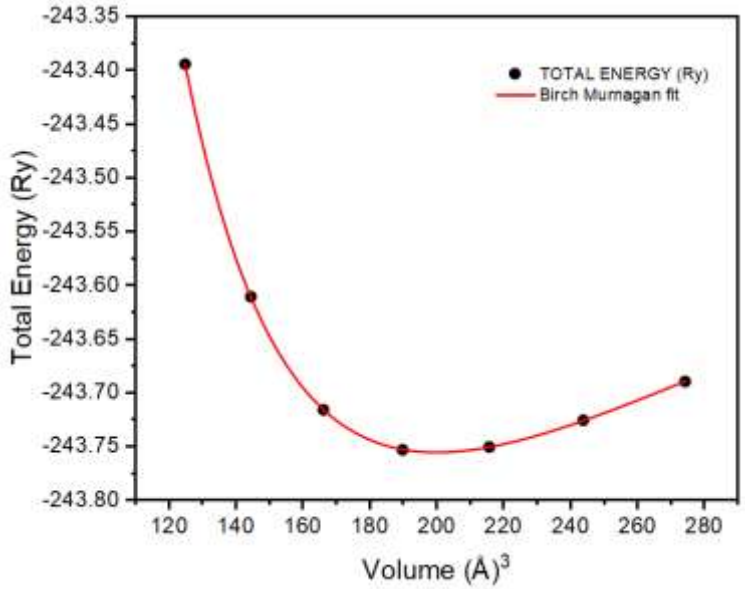

Figure 4: Total energy of cubic $RbAgI_3$ as a function of unit cell volume calculated using USPP and the XC functional PBE.

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Conclusion

In this study, we investigated the structural properties of $RbAgI_3$ using DFT calculations. The optimal energy cut-off was determined to be 70 Ry, and the 9×9×9 k-point mesh provided well-converged results. Geometry optimization revealed an equilibrium lattice parameter of 5.85 Å, confirmed by the Birch-Murnaghan equation of state. The findings provide insights into the stable crystal structure of $RbAgI_3$, which could be useful for further studies on its electronic and optical conductivity. This work establishes a reliable computational framework for future research on similar materials.

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