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First Principle Study for Comparison of Lattice Constant and Band Gap of Silver Based Two Cubic ABX₃ Compounds with Varying Halides

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A B S T R A C T

Density functional theory (DFT) based first principle study is used to investigate and compare the effect of varying halide (Cl, Br) on the lattice constant and band gap of the two cubic perovskites RbAgX3 (X= Cl, Br). The investigated crystal structure of both compounds is cubic belongs to the 221-space group. The Perdew-Burke-Ernzerhof (PBE) functional is used for the structure optimization and band structure calculations. Ultrasoft pseudopotentials were used for the calculations. Systematic change is recorded in the lattice constants and band gap of both compounds with the change in the ionic radii of the halides.

Keywords: First principle, DFT, Perovskite, Electronic properties, PBE

Introduction

Perovskites are a group of materials with a special crystal structure, usually written as ABX₃. In this structure, the A atom sits at the corners of a cube, the B atom is in the centre, and the X atoms are in the middle of the cube's faces. The name "perovskite" comes from a mineral called calcium titanate (CaTiO₃), discovered in 1839 by Gustav Rose. These materials have gained attention because they show various useful properties, such as conducting electricity, absorbing light. Many different perovskite materials have been created and studied. Some well-known types are oxide perovskites and halide perovskites. Some of the Oxide Perovskites perovskite oxides like LiNbO₃, PbTiO₃ and BiFeO₃ have been reported to show photovoltaic properties, and many applications have been developed around them, but they do not show required semiconducting properties for any photovoltaic applications [1]. Other than oxides there is another class of perovskite known as halide perovskites. From their name it's clear that oxygen has been replaced by the halogen's atoms i.e. Cl, Br and I. These halide perovskites can be prepared as ionic crystal having semiconductor properties. For example, CH3NH3PbI3 have been known to have high absorption coefficient (10^{-5} cm^{-1}) due to the presence of Pb [1]. Perovskites have been developed for many applications and have shown promising results to be used as alternative to the traditional materials such as perovskite based solar cells and LEDs.

Perovskite solar cells have been recorded to have high power conversion efficiency (PCE), which has increased from 3.8% in 2009 to 25.5% in 2020. Which shows the interest of researchers in perovskites based solar cells. For which they need to develop clean and cost-effective material for solar cells [2]. Perovskite-based LEDs have been developed to emit a spectrum of colors that offer bright and colorful light and are promising for use in display screens. Most LEDs are made from gallium nitride (GaN) but still their efficiency is reduced by its poor hole-electron recombination. Perovskite based LEDs have received immense attention due to their high efficiency, low cost and easy fabrication [3].

To study the optoelectronic properties of perovskites many experimental techniques have been used and proved to be fruitful. In this era, we need new materials to keep improving, but to predict new suitable material for specific applications experimentally is expensive and time consuming. This process of predicting or investigation of optoelectronic properties of new materials or if we need to tailor them according to our needs, can be fast track using computational methods. Computationally new materials have been predicted before and then they were prepared in laboratory. Computational or theoretical methods allow us to investigate the optoelectronic properties of the material on the atomic level, and even the effects of doping can be investigated on the lattice constant, band gap, absorption and other optical properties. There are number of computational methods available which have been used like density functional theory (DFT) or GW basics etc. Both are regarded as first-principle methods.

Density Functional Theory (DFT) is a widely used method to calculate electronic structure, band gaps, and optical properties. In DFT, the electronic and optical properties are calculated using the density of electron as a variable. Hohenberg-Kohn theorems and Kohn-Sham equations showed that the amount of information that we can extract out of the system using electron density as variable is same as if we use the external potential as variable. There are two most widely used approximations in DFT known as local density approximation (LDA) and generalized gradient approximation (GGA). There are number of different functionals available developed for specific systems and they perform very well. Some of them are PBE, PBEsol, B3LYP etc. [4].

Although perovskites have been recognized for their excellent optical and electronic properties, they still have some challenges which are stopping the commercialization and wide use of perovskite-based applications. Some of these challenges are stability, toxicity, scalability and imperfections are

prominent. High temperature, moisture and oxygen effect stability and prevents their long-term use in any applications. Toxic effects of Pb on human health and environment made it necessary to find new materials. In laboratory perovskites have shown great results but producing them on a large scale changes their properties. Sometimes there are defects present in the crystal structure and at interfaces which reduce efficiency, and this problem can only be solved by applying better fabrication techniques.

Traditional perovskites often contain lead, which is harmful to humans and the environment. For which Ag is chosen as an alternative to Pb in our cubic phase ABX_3 perovskite which leads us to two compositions $RbAgCl_3$ and $RbAgBr_3$. Pb has high absorption and if we replace it with Ag, it will have its effect on the absorption and other optical properties as well. Unlike lead, silver is much safer and does not pose serious health risks. Also, by varying the halide ions will have its own effect on electronic and optical properties. This study focuses on Pb replacement i.e. Ag, while using first principle to compare the lattice constant and band gaps. And whether these materials show promising properties for a potential application in solar cells, LEDs, transistors etc. It will also reveal whether replacing Pb with Ag was beneficial or not.

Research methodology

Quantum espresso is used to calculate lattice constant and band gaps of both the compounds [5]. The electronic states of Rb $4s^2$ $5s^1$ $4p^6$, Ag $5s^2$ $4d^9$, Cl $3s^2$ $3p^5$, and Br $3d^{10}$ $4s^2$ $4p^5$ are treated as valence states. The optimized value of k-points grid is 10x10x10 and the Monkhorst-pack scheme [6] is used to map the reduced first Brillouin zone. The optimized cutoff energy and cutoff charge density values are used which are 60 Ry and 600 Ry respectively. The threshold for energy and force convergence is set at $1x10^{-6}$ Ry and $1x10^{-3}$ Ry/Bohr.

Result and discussion

For the optimization of lattice parameter (a_o) of both $RbAgCl_3$ and $RbAgBr_3$ was performed using Birch-Murnaghan equation of state as shown in **Figure 1**. BM equation also gives the minimum volume (V_o) at minimum energy (E_o), along with bulk modulus (B_o) and pressure derivative $(B`)$. For $RbAgCl_3$ these values are 5.16 Å $(a_o)$, 137.08 $Å^3$ $(V_o)$, -236.33571 eV $(E_o)$, 217.30 GPa $(B_o)$, and 5.41 $(B`)$. Similarly, for $RbAgBr_3$ these values are 5.44 Å (a_o), 160.93 $Å^3$ (V_o), -1040.59955 eV (E_o), 178.69 GPa (B_o), and 5.36 $(B`)$. We can see that when we replaced Cl with Br, the ionic radius of halide ion increased, the lattice constant has also increased from 5.16 Å to 5.44 Å. But the bulk modulus has decreased from 217.30 GPa to 178.69 GPa.

The calculated band structure of $RbAgCl_3$ and $RbAgBr_3$ is shown in **Figure 2**, we can see that the band gap of $RbAgCl_3$ is 1.84 eV which s greater than the band gap of $RbAgBr_3$ i.e. 1.07 eV. This lowering of band gap is clearly related to the replacement of Cl with Br. The band gap of $RbAgCl_3$ is in the visible range of electromagnetic spectrum i.e. 1.6 eV to 3.1 eV. The band gap of $RbAgBr_3$ is in the infrared region of the electromagnetic spectrum i.e. 0.01 eV to 1.6 eV. Due to their band gap values both materials can be classified as semiconductor materials. Both materials have shown the indirect band gap nature between VBM and CBM, because VBM lies at wave vector R and CBM lies at wave vector G.

Conclusion

Replacement of smaller halide i.e. Cl with the larger halide i.e. Br, have increased the lattice constant but decreased the band gap. The lowering of the band gap can be due to Ag and halides i.e. Cl and Br, but it can be only confirmed after the density of states calculation and its analysis. The importance of these compounds electronic properties, w.r.t any application can only be determined using their optical properties investigations.

Graphs
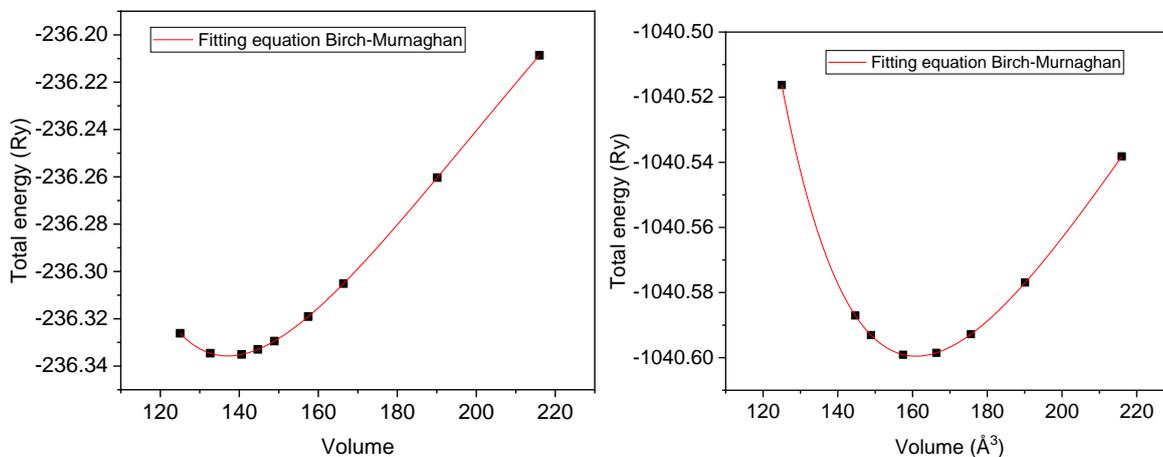
Figure 1: Fitting of Birch-Murnaghan EOS on energy vs volume graph for RbAgCl₃ (left) and RbAgBr₃ (right).
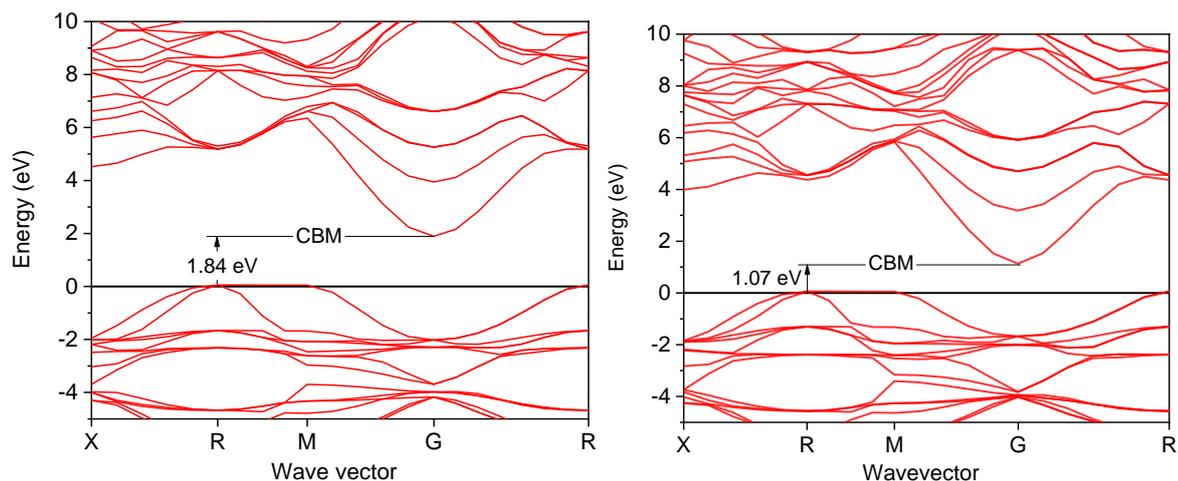
Figure 2: Band structure of RbAgCl$_3$ (left) and RbAgBr$_3$ (right) for the energy of -5 to +10 eV.

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