

Study of Structural and Electrical Properties (using GGA) of Fluoride Perovskite BaKF₃ Using FP-LAPW Method

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Abstract:

To study the structural and electronic properties of cubical perovskite BaKF₃, the first principles calculation within the full potential linearized augmented plane wave (FP-LAPW) method is applied. The exchange correlation effects are included through the GGA exchange potential. The calculated structural properties such as equilibrium lattice constant, the bulk modulus and its pressure derivative are in agreement with the published results of other authors. From our study we have found that the band gap of BaKF₃ is 4.8 eV which is the indication of insulating behavior.

Keywords

Band structure, DFT, DOS, FP-LAPW, GGA.

1. Introduction

Perovskite is a brown, yellow or grayish-black mineral with an oxide of Calcium and Titanium and sometimes containing rare Earth elements. It was first discovered in Ural mountain of Russia by Gustav Rose in 1839 and is named after Russian mineralogist L.A. Perovski. The general chemical formula for perovskite compounds is represented as ABX₃, where A and B are two cations and X is an anion that bonds to both. Perovskite material exhibit many interesting properties from both theoretical and application point of view. Colossal magnetoresistance, ferroelectricity, superconductivity, charge ordering, spin dependent transport, high thermo-power and transport properties are commonly observed features. These compounds are used as sensors and catalyst electrodes in certain type of fuel cells and are candidates for memory devices and spintronics application (Piskunov *et al.*, 2004). Ferroelectric and related materials, having the chemical formula ABO₃, have been the subject of

extensive investigation, both because of their technical importance and their fundamental interest to physical and materials sciences. The ideal structure is a cubic perovskite, where A and B cations are arranged on a simple cubic lattice, and O ions lie on the face centers nearest to the B cations. Barium titanate (BaTiO₃) is one of the most important ferroelectric oxides used in electronic applications. It has been widely used in electro-mechanical actuators and in sensor applications, as a major component of ceramic capacitor dielectrics, and in photogalvanic devices (Bagayoko *et al.*, 1998, Gardana., 1965 & Mara *et al.*, 1954). It is also an important photo-refractive material used for applications in distortion correction and in combination with laser power.

The ternary fluoroperovskite like BaKF₃ has great potential for a variety of device applications in optical, ferroelectric, antiferromagnetic systems due to its wide band gaps (Quenzerfi *et al.*, 2004). This compound belongs to ternary fluoro-perovskite family

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having a general formula ABF_3 , where A and B are the alkali metals and alkaline metals or the transition metals. It is always an advantage to know the physical and electronic properties of such order to understand their possible applications. The tremendous growths of technology in the last few decades have widened the utility of these compounds to ultraviolet-transparent material for lenses in optical lithography steppers in electro-optical applications (Horsch *et al.*, 1986; Fukunda *et al.*, 2001). Perovskites are well known for their applications in different fields of science and technology due to their wide range of band gaps. This shows photo-luminescence properties when it is doped with lanthanide ions (Mazurak *et al.*, 1999). Neupane *et al.* (2017) have studied the electronic properties of $BaLiF_3$ from the full potential-linearized augmented plane wave (FP-LAPW) method based on density functional theory (DFT), which also suggests an insulating behavior of this material. Salehi *et al.* (2004) have studied the electronic structures and density of states (DOS) in paraelectric crystal $BaTiO_3$ by using the FP-LAPW method in the framework of density functional theory (DFT). In this method, exchange potentials is calculated using the generalized gradient approximation (GGA). They found the electronic energy bands and density of states for $BaTiO_3$ to be in good agreement with both the theoretical and experimental results. Since late 2012, organic and inorganic halides with the perovskite structure have strongly attracted the attention of the photovoltaic community when efficiencies close to 10% were first achieved in solid state cells (Lee *et al.*, 2012). The excellent properties and the innovative device possibilities in perovskite-structured organometal and metallic halides have resulted in a frenzied increase of publications reporting high efficiencies (Ball *et al.*, 2013). Recently, 15% efficient solar cells were reported with $CH_3NH_3PbI_3$ target efficiencies of 20% identified as a feasible goal (Park, 2013). It is therefore pertinent to evaluate the potential and analyze the prospects of

this exciting technology that have galvanized the photovoltaic research community

In this paper, the theoretical investigations of the structural and electronic properties of fluoride type perovskite $BaKF_3$ are calculated. In this work for exchange correlation, the generalized gradient approximation (GGA) is employed in WIEN2K code (Blaha *et al.*, 2012) for its implementation.

2. Crystal Structure and Computational Details

The unit cell of fluoro-perovskite $BaKF_3$ with space group (Pm-3m) contains three atoms that form the cubical structure. The atoms of $BaKF_3$ are located at the Wyckoff positions Ba (0, 0, 0), K (0.5, 0.5, 0.5), F (0, 0.5, 0.5) (Rohrer, 2004) to form the crystal structure. For volume optimization of $BaKF_3$, we have used the calculated lattice constant $a = 4.43 \text{ \AA}$ (Mubark *et al.*, 2012) and we have found the volume optimization curve as shown in Fig.1. The obtained optimized lattice constant is used to study the density of state (DOS) and band energy of $BaKF_3$ by using the full potential linearized augmented plane wave (FP-LAPW) method of KS-DFT (Kohn *et al.*, 1965) as implemented in the WIEN2K code. The generalized gradient approximation (GGA) as proposed by Perdew *et al.* (1996) has been used to describe the electron exchange and correlation potential. Non spherical contributions to the charge density and potential within the muffin tin (MT) spheres are considered and the cut-off parameter is $RMT \times K_{max} = 7$ where K_{max} is the maximum value of the reciprocal lattice vector in the plane wave expansion and RMT is the smallest atomic sphere radii of all atomic spheres. In the interstitial region, the charge density and potential are expanded as a Fourier series with wave vectors up to $G_{max} = 12 \text{ (a.u.)}^{-1}$. The number of k-points used in the irreducible part of the Brillouin zone is 1000. The criterion for the convergence of the self-consistent DFT calculation is 0.0001 Ry in total energy. However the core states are treated relativistically, the semi-core states are treated semi-relativistically by ignoring the spin-orbit (SO) coupling.

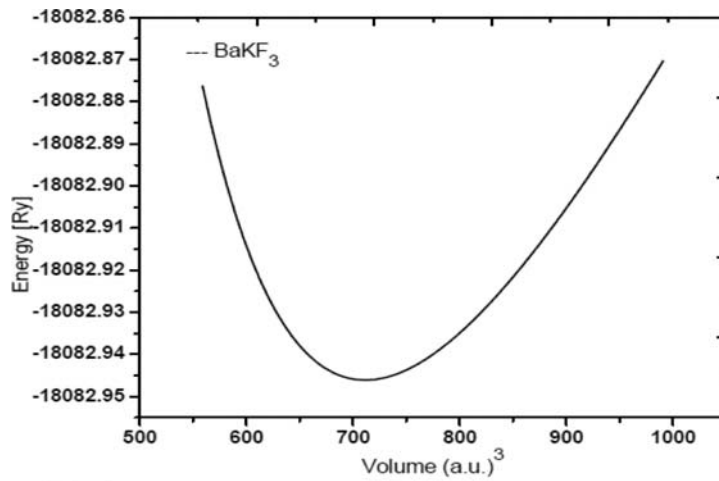


Fig. 1. volume optimization curve

3. Results and discussions

3.1 Crystal Structure

To study the crystal structure, we start with the total energy minimization of cubic BaKF_3 as a function of volume. The variation in the total energy as a function of volume is shown in Fig.1. The energy

versus volume data was fitted to a Murnaghan equation of state (1944) to obtain the equilibrium lattice constant (a), the bulk modulus (B) and its first pressure derivative (B'). The calculated values of a, B and B' are found as 4.724 Å, 37.556 GPa and 5.02 respectively.

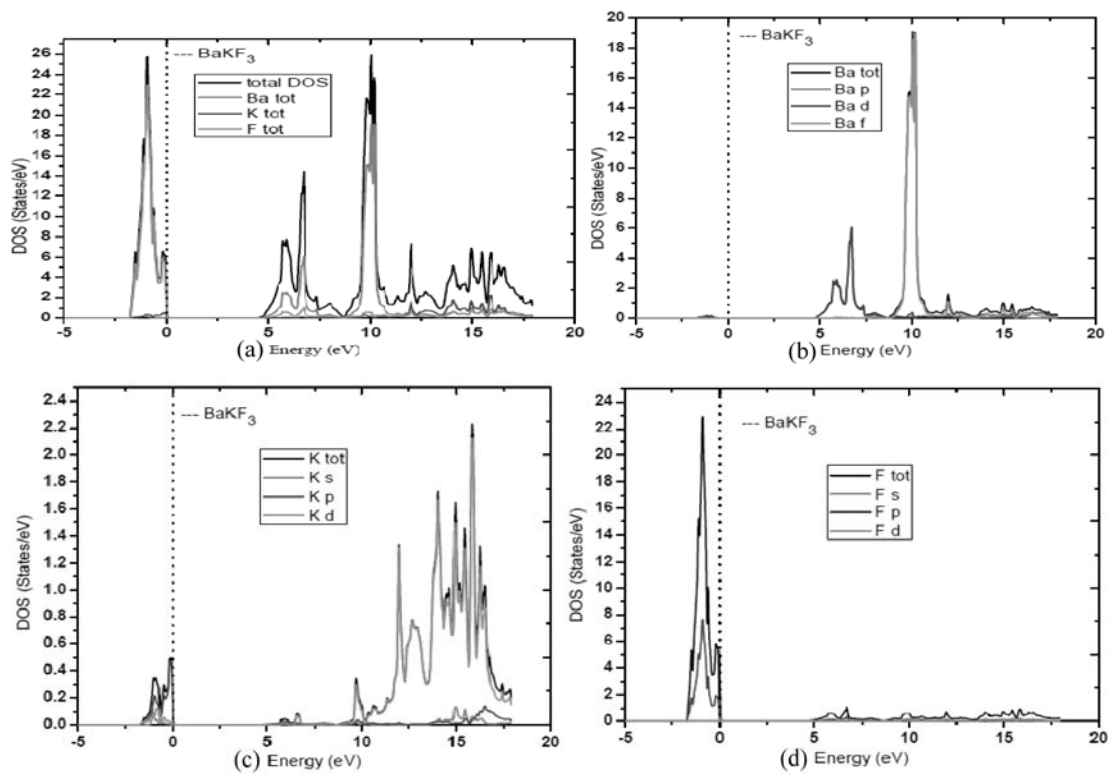


Fig. 2. (a) Total DOS of BaKF_3 . Partial DOS of (b) Ba (c) K (d) F

3.2 Density of States (DOS)

The calculated results of total density of states (TDOS) and partial density of states (PDOS) for BaKf₃ compound are given in Fig. 2. Fig.2.(a) shows the plot of total density of states (TDOS) for BaKf₃ and individual atoms Ba, K, and F. In the valence region below the Fermi level, we have found the maximum peak in TDOS for BaKf₃ at -0.63 eV. The occurrence of this maximum in peak in TDOS of BaKf₃ at -0.63 eV appears to be the contribution due to F atom. The reason being that the TDOS of F atom is also maximum at -0.63 eV. Also in valence band region, we find from the plots that the contributions to the origin of peak in TDOS of BaKf₃ by other atoms Ba and K is very low and hence are negligible. Similarly, in the conduction band above the Fermi level in Fig.2.(a), the maximum peak in TDOS for BaKf₃ is observed at 9.92 eV. The occurrence of this maximum in peak in TDOS of BaKf₃ at 9.92 eV is due to the main contribution by atom Ba. The reason is that the TDOS of Ba atom is also maximum at 9.92 eV. We find negligible contribution in TDOS of BaKf₃ by atoms K and F which is seen in Fig.2.(a).

In Fig. 2.(b), the plots of TDOS and partial density of states (PDOS) of Ba atom in BaKf₃ compound are shown. In the valence band, we have found that there is negligible contribution to TDOS and PDOS by electrons of atom Ba. However in the conduction band region, we find from the plots that the maximum peak in TDOS occurs at 9.92 eV. This is due to the main contribution by the Ba-f state electrons. The reason is that the maximum of PDOS of Ba-f is also found at 9.92 eV which is seen in Fig.2.(b).

The plot of TDOS and PDOS of K atom of BaKf₃ compound is shown in Fig.2.(c). We have found in the valence band below the Fermi level, the contribution of K-p state is found in TDOS in atom K. However in the conduction band, a maximum peak in TDOS is found at 13.81 eV. This can be attributed to K-d state electrons of atom K as shown in Fig.2.(c). The plot of TDOS and PDOS of F atom in BaKf₃ compound is shown in Fig.2.(d). The maximum peak in TDOS is found at -0.63 eV in the valence region below the Fermi level. From the plot we find that the contribution to the occurrence of this peak at -0.63 eV

is due to the contribution by F-p state electrons. There is negligible contribution to TDOS and PDOS in conduction band in F atom as shown in Fig.2.(d).

3.3 Band structures

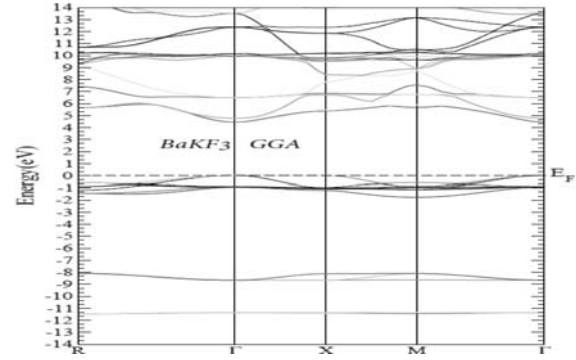


Fig. 3. Electronic band structure of BaKf₃ along the high-symmetry directions of the first Brillouin zone.

The electronic properties of BaKf₃ are calculated with first principles FP-LAPW method using GGA on basis of density functional theory. To calculate DOS and band structure of BaKf₃, the optimized lattice parameters are used. The calculated electronic band structures for fluoroperovskites BaKf₃ along the high-symmetry directions of the Brillouin zone are shown in Fig.3. We have found that the maximum of the valence band are found to be at a symmetry point Γ and the minimum conduction bands are located at the point of the Brillouin zone in BaKf₃ compound, resulting into direct band gaps. The calculated direct band gaps (Γ - Γ) is found as 4.8 eV on the GGA approach.

4. Conclusion

From the volume optimization in Fig.1, the optimized lattice constant, pressure and pressure derivative are found as 4.724 Å, 37.556 GPa and 5.02 respectively. From the total DOS plots of BaKf₃ as given in Fig. 2 (a), the maxima in peaks in the valence region are due to only F atom. This is also evident from the partial DOS plots of Ba, K and F atoms as given in Fig.2(b),(c)and (d) respectively. From Fig. 2. (d), we find that the maxima in peaks are due to p state electrons of F atom in the valence region. We have found a maximum peak at 9.92 eV due to the main contribution of Ba atom in the conduction region that is shown in Fig. 2(a). From the plot of partial

DOS of Ba, K and F in Fig.2(b),(c)and (d) respectively, we have found that the maxima peaks are observed due to the main contribution of f state electrons of Ba atom p state of electrons of F atom. In Fig.3, from the

calculation, the band gap of BaKF₃ is found as 4.8 eV which is large and hence BaKF₃ is an insulator which suggests that it is useful for optoelectronic devices.

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