Study of structural and electronic properties of fluoride perovskite KMgF3 using FP-LAPW method

Study of structural and electronic properties of fluoride perovskite $KMgF_3$ using FP-LAPW method

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Abstract. In this paper, we present the electronic properties of fluoride perovskite $KMgF_3$ by using the full potential linearized augmented plane wave (FP-LAPW) method. The densities of states and energy band structures have been calculated by using the generalized gradient approximation (GGA) as exchange-correlation potential. The results obtained are in agreement with the previous experimental and theoretical results. The obtained value of energy band gap of 7.2 eV indicates the insulating behaviour of the sample material.

1. Introduction

The ternary fluoro-perovskite like $KMgF_3$ has great potential for a variety of device applications in optical, ferroelectric, antiferromagnetic systems due to their wide band gaps [1-2]. It is always an advantage to know the physical and electronic properties of such order to understand their possible applications. Perovskites are well known for their applications in different fields of science and technology because of their wide range of electro- optic, mechanical, semiconducting and insulating properties. $KMgF_3$ is a technologically important fluoro-perovskite which finds applications as a vacuum- ultraviolet-transparent material for lenses in optical lithography steppers in electro- optical applications [3-5]. It is desirable for scintillators and radiation dosimeters when it is doped approximately [6]. Neupane *et al.* [7] have reported an energy band gap of 6.8 eV for $RbCaF_3$ from the FP-LAPW method based calculation, which also suggests an insulating behaviour of this material.

In this paper, we will do the theoretical investigations of perovskite-type fluoride $KMgF_3$. For this purpose for exchange correlation, generalized gradient approximation (GGA) is employed which is implemented in wien2k code [8].

2. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The unit cell of fluoro-perovskite $KMgF_3$ with space group (Pm-3m) contains three independent atoms that form the cubical structure. The atoms of $KMgF_3$ are located at the Wyckoff positions K(0.0,0.0,0.0), Mg(0.5,0.5,0.5), F1(0.0,0.5,0.5), F2(0.5,0.0,0.5) and F3(0.5,0.5,0.0) [10] to form the crystal structure as shown in figure1.

The generalized gradient approximation (GGA) as proposed by Perdew *et al*. [9] has been used to correct the exchange-correlation effect. For volume optimization of $KMgF_3$, we have used the experimental lattice constant a=3.979 Å [10] and the optimized volume versus energy curve is shown in Fig.1. This optimized lattice constant is used to study the density of state (DOS) and band energy of $KMgF_3$ by using the full potential linearized augmented plane wave (FP-LAPW) method of KS-DFT [11].We used here GGA 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 $R_{MT} \times K_{max} = 7$ 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 $a.u^{-1}$. 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.

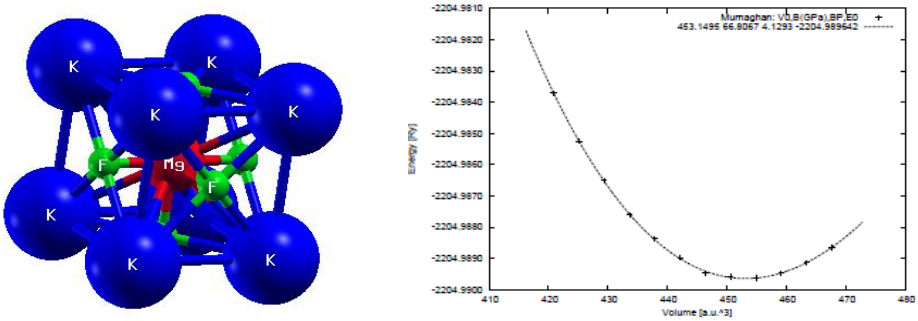

Figure 1. (Left) Crystal structure of $KMgF_3$, (right) volume optimization curve.

3. RESULT AND DISCUSSIONS

3.1. *Crystal structure*

The variation in the total energy as a function of volume is shown in figure1.The calculated value of the equilibrium lattice constant (a) is found as 4.0646 Å. The energy versus volume data was fitted to a Murnaghan equation of state [12] to obtain the bulk modulus (B) and its first pressure derivative (B'). Our calculated values of lattice constant, B, and B' are compared with previous experimental and theoretical results which are shown in table 1. We note that the result of the lattice constant obtained is slightly higher than the experimental values [10, 15].

Table 1.

	Lattice Constant a (in Å)	Bulk Modulus B (in GPa)	Pressure Derivative B'
This study	4.0646	66.8067	4.1293
Other, GGA	4.081 [13]	72.01 [13]	4.65[13]
	4.040 [14]	72.15 [14]	4.68 [14]
Experimental	3.989 [15]	70.40 [15]	
	3.979 [10]		

3.2 *Density of states (DOS)*

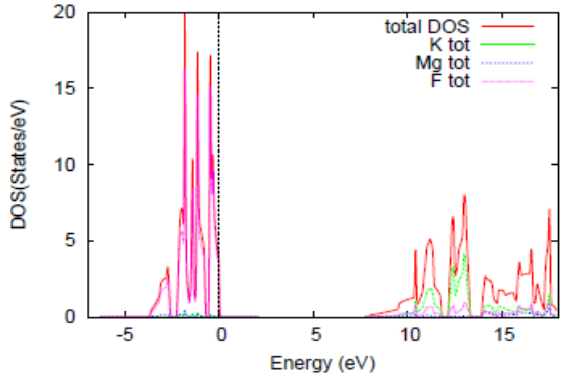

Figure 2. Plot of total DOS for $KMgF_3$, K, Mg and F (Fermi energy is at zero)

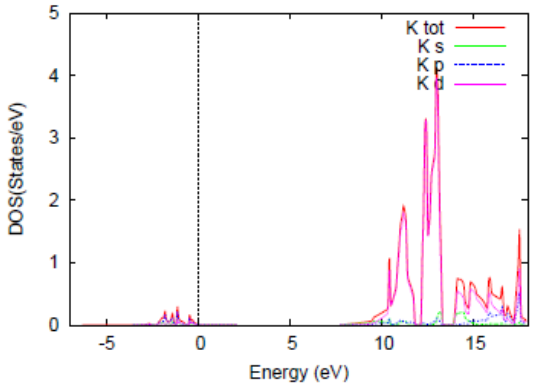

Figure 3. Plot of total and partial DOS for K Fermi energy is at zero)

Figure 2 shows the plot of total density of states (DOS) of $KMgF_3$ and individual atoms K, Mg and F respectively. The maximum peak and other two narrow peaks are occurred at 1.82 eV, 1.14 eV and 0.45 eV respectively in valence region below the Fermi level. In the case of total DOS, contribution of the individual atoms in the valence region, we find only the contribution due to F atom which is accountable in the valence region. The total contribution by K and Mg atoms are more or less negligible in the valence region which is evident from the small hump in DOS. In the conduction region above the Fermi level in figure 2, we find the value of DOS is maximum at 13.07 eV due to the main contribution of K atom and small peaks in DOS occur from 10.45 eV to17.50 eV due to the contribution of K, Mg and F atoms.

From the total and partial DOS plots of K atom as shown in figure 3, we find no sharp peaks in valence band but only *p* and *d* state electrons are contributing to the DOS in negligible height. However, in the conduction band, the highest peak in DOS is contributed by *d* state electron of K atom at 13.0 eV and other smaller peaks are observed from 10.33 eV to 17.55 eV due to the main contribution of *d* state electrons of K atom.

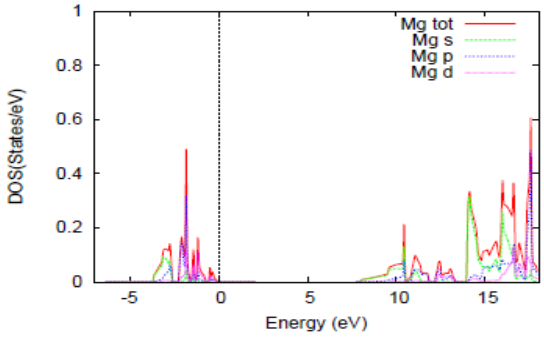

Figure 4. Plot of total and partial DOS for Mg (Fermi energy is at zero)

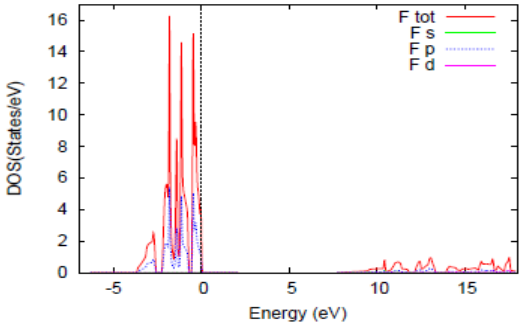

Figure 5. Plot of total and partial DOS for Mg (Fermi energy is at zero)

From the total and partial DOS of plots of Mg atom as shown in figure 4, we find a narrow peak at 1.85 eV in the valence band due to the *p* and *d* state electrons and small peaks are observed from 0.43 eV to 2.93 eV due to the contribution of *s*, *p* and *d* state electrons below the Fermi level. However, in the conduction band, *p* state electron of Mg atom contributes to the occurrence of peak at 17.55 eV and small peaks are observed from 10.33eV to 17.55eV due to the contribution of *s*, *p* and *d* state electrons of Mg atom.

Figure 5 shows the total and partial DOS of plots of F. In the valence band, there is a sharp peak occurring at 1.82 eV and other two small peaks are observed at 1.14 eV and 0.45 eV respectively below the Fermi level due to the *p* state electrons and virtually with no contribution by *s* and *d* state electrons. However, in the conduction band, there are very small peaks occur due to the *s*, *p* and *d* state electrons of F atom.

3.2. Band structures

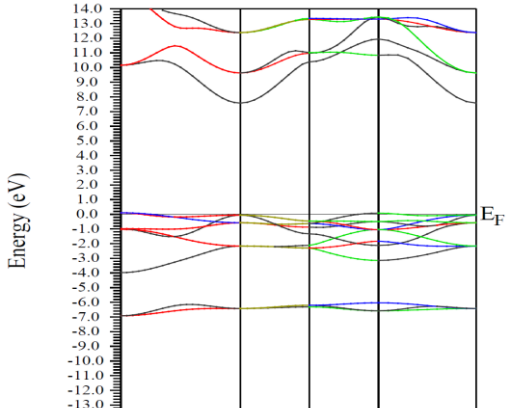

Figure 6. Electronic band structure of $KMgF_3$ along the high-symmetry directions of the first Brillouin zone.

The calculated electronic band structure for fluoro-perovskite $KMgF_3$ along the high-symmetry directions of the Brillouin zone is shown in figure 6. In the valence band (figure 6), the lowest lying band has been found to occur at 9.5 eV below Fermi level due to the core state electrons of K, Mg and F atoms. We also observe from figure 6 that the maximum band energy occurs at the Fermi level at the symmetry point R. In the conduction band, minimum in energy occurs at 7.2 eV above the Fermi level at the point symmetry and from this plot in figure 6, we find that it is an indirect type of transition which takes place along R - symmetry directions. The calculated value of indirect band gap is 7.2 eV, which is much smaller than the experimental value 12.4 eV [16] for $KMgF_3$.

4. CONCLUSIONS

From the volume optimization in figure1, we have found the optimized lattice constant, pressure, pressure derivative and total energy are as 4.0646 Å, 66.8067 GPa, 4.1293 and -2204. 9896 Ry respectively. From the total DOS plots of $KMgF_3$ as given in figure 2, we find that maxima in peaks in the valence region are due to only F atom. This is also evident from the partial DOS plots of K, Mg and F atoms as given in figure 3, figure 4 and figure 5 respectively. We find the maxima in peak is due to *p*-state electrons of Mg and F atoms in the valence region of partial DOS of Mg and F atoms. The peak heights in partial DOS due to electrons from K atom in the valence region is negligible. Similarly in the conduction region, it is only *d*-state electrons of K (figure 3) which is a main contribution to the maxima in the total DOS of $KMgF_3$.We have found from our study (figure 6) that the band gap of $KMgF_3$ is 7.2 eV which is large and hence $KMgF_3$ is an insulator.

References

[1] Ouenzerfi R E, Ono S, Quema A, Goto M, sakai M 2004 *J. Appl. Phys.***96** 7655
[2] Zhang F, Mao Y, part T J, Wong S S 2008 *Adv. Funct. Mater.* **18** 103
[3] Nishimatsu T N, Terakubo N, Mizuseki H, Kawazoe Y, Pawlak D A,Shimamura K, Ichinose N, Fukuda T 2003 *Jpn. J. Appl. Phys.* **42** 5082
[4] Ho¨rsch G, Paus H J 1986 *Opt. Commun.***60** 69
[5] Fukuda T, Shimamura K, Yoshikawa A, Villora E G 2001 *Opt. Elect. Rev.* **9** 109
[6] Furetta C, Santopietro F, Sanipoli C, Kitis G 2001 *Appl Radiat Isot* **55** 533
[7] Neupane K Thapa R K 2016 *IJEART* 2454-9290 **2** 31-33
[8] Blaha P, Schwarz K, Madsen G K H, Kvasnicka D, Luitz J, Schwarz K 2012 *An Augmented Plane Wave plus Local Orbitals Program for Calculating Crystal Properties* Wien2K User's Guide Techn. Universitat Wien,Wien
[9] Perdew J P, Burke F S I, Borodi G 1996 *J. Cryst. Growth.* **169** 89
[10] Darabont A, Neamtu C, Ouenzerfi R E, Ono S, Quema A, Goto M, sakai M 2004 *J. Appl. Phys.* **96** 7655.

[11] Kohn W, Sham L J 1965 *Physical Review* **A140** 1133
[12] Murnaghan F D 1944 *Proc Natl Acad Sci* **30** 244
[13] Vaitheeswaran G, Kanchana V, Kumar R S, Cornelius A L, Nicol M F, Svane A, Delin A, Johansson B 2007 *Phys. Rev.* **B 76** 014107
[14] Pilania G, Sharma V 2013 *J. Mater. Sci.* **48** 7635-7641
[15] Rosenberg H M, Wigmore J K 1967 *Phys. Lett.* **A 24** 317
[16] Heaton R A, Lin C C 1982 *Phys. Rev.* **B 25** 3538