Study of Structural and Electronic Properties of Fluoride Perovskite KCaF$_3$ using FP-LAPW Method

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Abstract: To study the structural and electronic properties of cubical perovskite KCaF$_3$, 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 KCaF$_3$ is 6.4 eV which is the indication of insulating behavior.

Keyword: Optical lithography, Density of states, Doping, Spin-orbit coupling

1. INTRODUCTION

The ternary fluoroperovskite like KCaF$_3$ 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 behavior. KCaF$_3$ is used as a vacuum- ultraviolet-transparent material for lenses in optical lithography steppers in electro- optical applications [3-5]. This shows photo-luminescence properties when it is doped with lanthanide ions [6]. It is desirable for scintillators and radiation dosimeters when it is doped approximately [7]. Neupane *et al.* [8] 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 behavior of this material.

In this paper, we will do the theoretical investigations of the structural and electronic properties of fluoride type perovskite KCaF$_3$. In this work for exchange correlation, the generalized gradient approximation (GGA) is employed in WIEN2k code [9] for its implementation.

2. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The unit cell of fluoro-perovskite KCaF$_3$ with space group (Pm-3m) contains three atoms that form the cubical structure. The atoms of KCaF$_3$ are located at the Wyckoff positions K(0.0,0.0,0.0), Ca(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) [11] to form the crystal structure as shown in Fig.1. For volume optimization of KCaF$_3$, we have used the experimental lattice constant a=4.41 Å [12] and the optimized volume versus energy curve is shown in Fig.1. The obtained optimized lattice constant is used to study the density of state (DOS) and band energy of KCaF$_3$ by using the full potential linearized augmented plane wave (FP-LAPW) method of KS-DFT [13], as implemented in the WIEN2K code. The generalized gradient approximation (GGA) is 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 $R_{MT} \times K_{max} = 7$ where K_{max} is the maximum value of the reciprocal lattice vector in the plane wave expansion and R_{MT} 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.
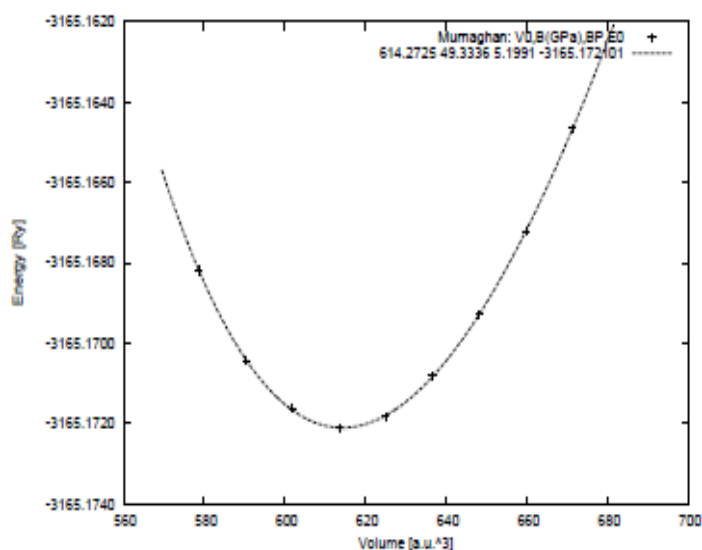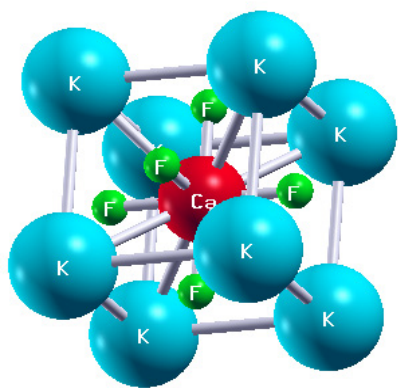
Figure 1.Crystal structure of KCaF₃ (top) and volume optimization curve (bottom)

Table1. Calculated lattice constant a (in Å), bulk modulus B (in GPa) and its pressure derivative B' of KCaF₃ compared with other theoretical and experimental results.

	Lattice Constant a(in Å)	Bulk Modulus B(GPa)	Pressure Derivative B'
This study	4.498	49.334	5.199
Other, GGA	4.41 [15]	49.583[15]	3.577[15]
	4.45 [16]	46.0 [16]	3.95[16]
	4.5293[17]		
Experimental	4.410 [12]		
	4.4584[18]		

Density of states (DoS)
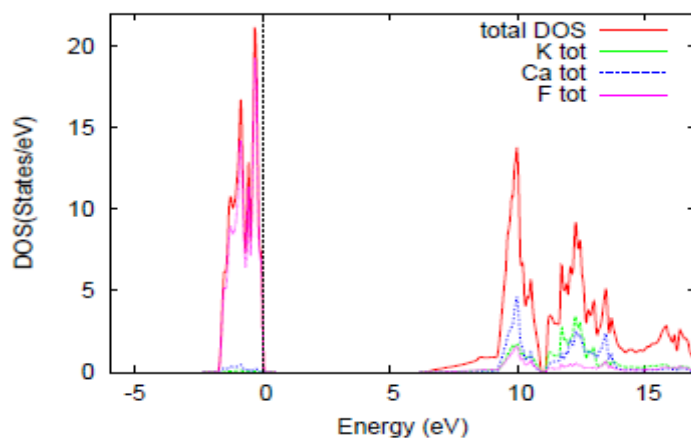
Figure 2. Total DoS of KCaF₃, K, Ca and F
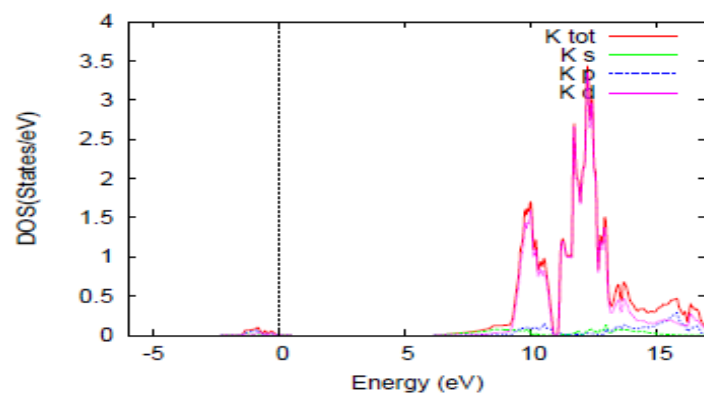
Figure 3. Total and partial DoS of K

3. RESULT AND DISCUSSIONS

3.1 Crystal structure

To study the crystal structure, we start with the total energy minimization of cubic KCaF₃ 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 [14] to obtain the equilibrium lattice constant (a), the bulk modulus (B) and its first pressure derivative (B'). Our calculated values of a, B, and B' are compared with previous experimental and theoretical results which are mentioned in table 1. We note that the result of the lattice constant obtained within our GGA calculations is slightly higher than the corresponding experimental values [12, 18] and calculated value [15, 16] but it is slightly less than calculated value [17].
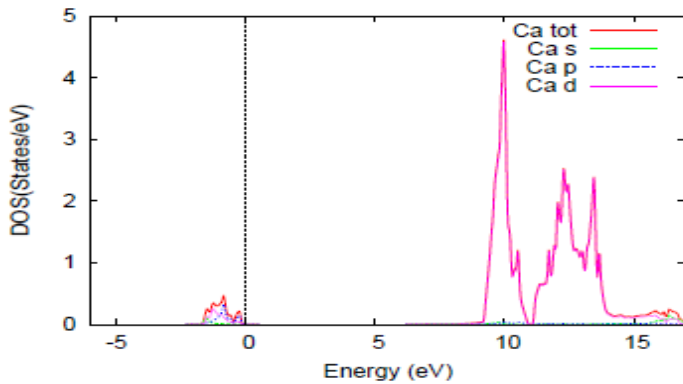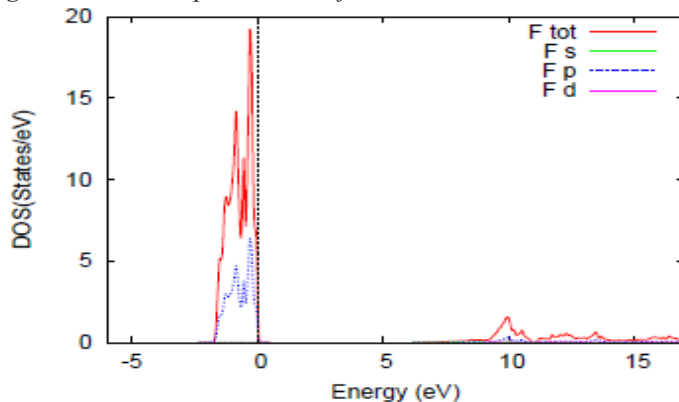
Figure 4. Total and partial DoS of Ca

*Figure 5. Total and partial DoS of F*

Fig. 2 shows the plot of total density of states (DOS) in the case of $KCaF_3$ and individual atoms K, Ca and F respectively. We find from this plot that in the valence region, the total DOS of $KCaF_3$ showed the occurrence of a maximum peak at 0.31 eV below the Fermi level. Similarly we find other two narrow peaks below the Fermi level at 0.78 eV and at 0.47 eV in the valence region. We find only the contribution of F atom in the valence region for the study of total DOS contribution of the individual atoms. The total contribution by K and Ca 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, we find that occurrence of maximum peak in DOS occurs at 10.0 eV due to the main contribution of Ca atom. Two other small peaks occur at 12.34 eV and at 13.44 eV respectively in the conduction region due to the contribution of K and Ca atoms. From the partial DOS plots of K atom as shown in Fig. 3, we find that in the valence band, only *p* and *d* state electrons are contributing to the DOS but very negligibly as the height of the peaks are very small. However, in the conduction

band, *d* state electron contributes mainly which is evident from the occurrence of the highest peak in DOS at 12.34 eV. Similarly other two smaller peaks are observed at 11.72 eV and at 10.0 eV in the conduction band in Fig.3 due to the main contribution of *d* state electrons but the contribution of *s* and *p* states electrons are less in comparison of *d* state electrons.

From the partial DOS of plots of Ca atom as shown in Fig.4, we find that in the valence band, *p* and *d* state electrons are contributing to the DOS providing a small peak at 0.78eV. However, in the conduction band, a sharp narrow peak is observed at 10.0 eV and other two smaller peaks are observed at 12.34 eV and at 13.44 eV. All these peaks in the conduction band in Fig.4 are obtained due to the contribution of *d* state electron.

Fig.5 shows the plot of total and partial DOS of F. In the valence band, there is a sharp peak occurring at 0.31 eV and other two small peaks are observed at 0.78 eV and 0.47 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.

3.2 Band structures
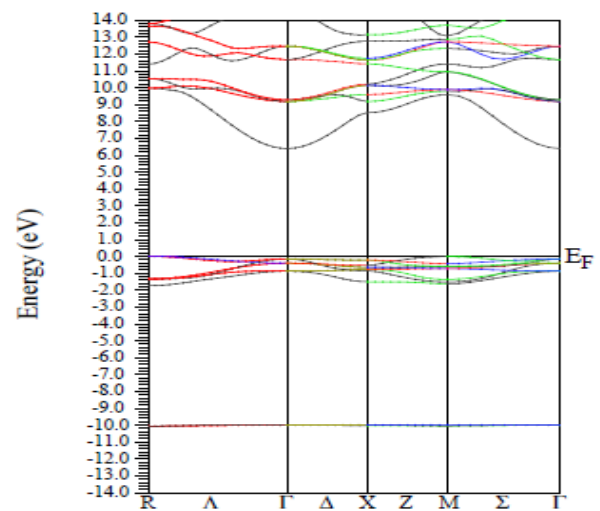
Figure 6. Electronic band structure of $KCaF_3$ along the high-symmetry directions of the first Brillouin zone.

The calculated electronic band structure for fluoroperovskites $KCaF_3$ along the high-symmetry directions of the Brillouin zone is shown in Fig. 6. In the valence band (Fig.6), the lowest lying band has been found to occur at 10.2 eV below Fermi level due to the core state electrons of K, Ca and F

atoms. We also observe from Fig.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 6.4 eV above the Fermi level at the point symmetry Γ and from this plot in Fig.6, we find that it is an indirect type of transition which takes place along R - Γ symmetry directions. The calculated value of indirect band gap is 6.4 eV, which is higher than the calculated value [15] through 0.3 eV and slightly smaller than other calculated value [16].

4. CONCLUSIONS

From the volume optimization in Fig.1, we have found the optimized lattice constant, pressure and pressure derivative are as 4.498 Å, 49.334 GPa and 5.199 respectively. From the total DOS plots of KCaF₃ as given in Fig. 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, Ca and F atoms as given in Fig.3, Fig.4 and Fig.5 respectively. From Fig.5, We find that the maxima in peaks are due to *p* and *d* state electrons of F atom in the valence region. We find maximum peak at10.0 eV due to the main contribution of Ca atom other peaks are observed due to the contribution of K and Ca atoms in Fig.2 in the conduction region. We find that the maxima peaks are observed due to the contribution of *p* and *d* state electrons of K atom in Fig.3. Similarly, *d* state electrons of Ca atom contributes to give maxima in peaks in the conduction region in partial DOS plot for Ca atom in Fig.4. In Fig.6, We have found from our study that the band gap of KCaF3 is 6.4 eV which is large and hence KCaF₃ is an insulator.

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