

Study of DOS and band structures of fluoride perovskites (RbCaF₃) : ab initio study

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Abstract— In this paper, we present the result of density of states (DOS) and band structures for fluoride perovskite like RbCaF₃. Calculation has been done by using the FP-LAPW method where generalized gradient approximation (GGA) is used. From our study we have found that the band gap of RbCaF₃ is 6.8 eV.

Key words: DFT; GGA; FP-LAPW; DOS; band structure.

I. INTRODUCTION

The ternary fluoroperovskite like RbCaF₃ 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 and semiconducting. In the last decade, experimental and theoretical investigations have been done to the study of perovskite-type fluorides. In this paper, we will present a theoretical study of the electronic properties of RbCaF₃ by using density functional theory (DFT) in which GGA is applied. The calculations of DOS and energy band have been done by using the full potential linearized augmented plane wave (FP-LAPW) method within the framework of density functional theory (DFT) as implemented in the WIEN2K code [3]. The generalized gradient approximation (GGA) as proposed by Perdew *et al.* [4] has been used to calculate exchange-correlation potential. We will present here the results of DOS and energy bands for the fluoride system.

II. COMPUTATIONAL DETAILS

The unit cell of fluoro perovskite RbCaF₃ (space group Pm-3m) contains three atoms that from the ideal cubic structure. The atoms are located at the Wyckoff positions Rb(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) [5]. For computation, we have used the calculated lattice constant $a = 4.435\text{\AA}$. The electronic structures are calculated by using the full potential linearized augmented plane wave (FP-LAPW) method of KS-DFT [6], as implemented in the WIEN2K code. 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 $R_{\text{MT}} \times K_{\text{max}}=7$ 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 $G_{\text{max}}=12 \text{ a.u}^{-1}$. 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.

III. RESULTS AND DISCUSSIONS

a. Density of states (DOS)

Fig. 1 shows the plot of total density of states (DOS) in the case of RbCaF₃ and individual atoms Rb, Ca and F respectively. We find from this plot that in the valence region, the total DOS of RbCaF₃ showed the occurrence of a maximum peak at 0.29 eV below the Fermi level. Similarly we find another narrow peak below the Fermi level at 0.88 eV in the valence region. 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 Rb 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 only at 10.0 eV and small peaks in DOS occur from 11.16 eV to 14.06 eV due to the contribution of Ca, F and Rb atoms.

It is difficult to understand the origin of peaks in DOS in the valence and the conduction regions only from the total DOS calculations and hence one need to study also the partial DOS plots. From the partial DOS plots of Rb atom as shown in Fig. 2, 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 peak is very small. However, in the conduction band, *d* state electron contributes mainly which is evident from the occurrence of parallel peaks in DOS at 12.2 eV and 12.5 eV respectively. Similarly other three small peaks are observed at 10.0 eV, 12.8 eV and 14.06eV in conduction band in Fig. 2 due to the contribution of *d* state electron and the contribution of *s* and *p* states electrons are less in comparison of *d* state electron.

From the partial DOS of plots of Ca atom as shown in Fig. 3, we find that in the valence band, only *p* and *d* state electrons are contributing to the DOS providing a very small peak. However, in the conduction band, *d* state electron

contributes to the occurrence of peak at 10.0 eV and small peaks 11.0 eV to 14.0 eV energies. There is no contributions to DOS by *s* and *p* state electrons in the conduction band which is evident from Fig. 3.

Fig. 4 shows the plot of total and partial DOS of F. In the valence band, there are two sharp peaks occurring at 0.29 eV and at 0.88 eV below the Fermi level which are due to the *p* state electrons and virtually with no contribution by *s* and *d* state electrons. However, in the conduction band, a very small peak occurs at 10.0 eV which is due to the *p* state electrons.

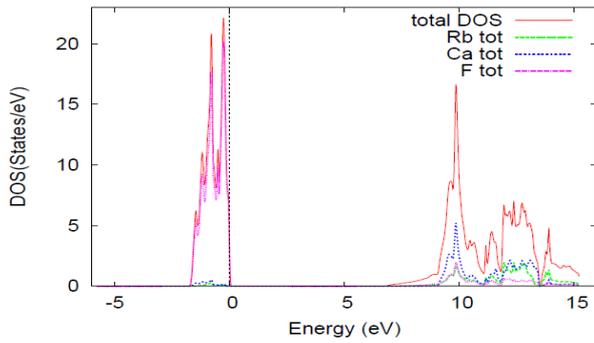


Figure 1. Plot of total DOS for RbCaF₃, Rb, Ca and F. Fermi energy is set at zero.

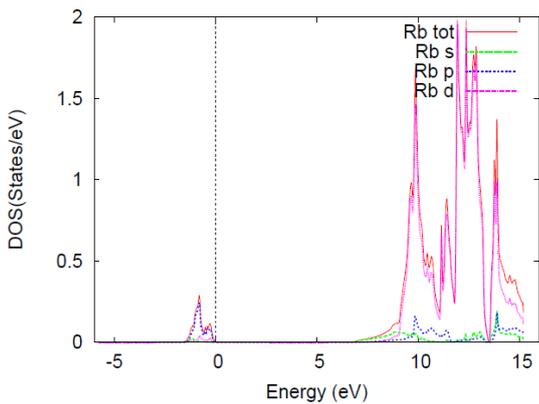


Figure 2. Plot of total and partial DOS of Rb. Fermi energy is set at zero.

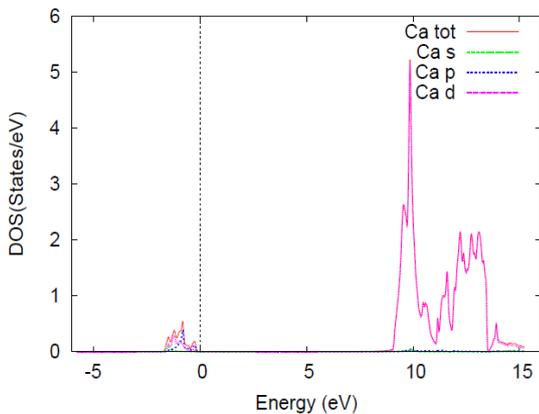


Figure 3. Plot of total and partial DOS of Ca. Fermi energy is set at zero.

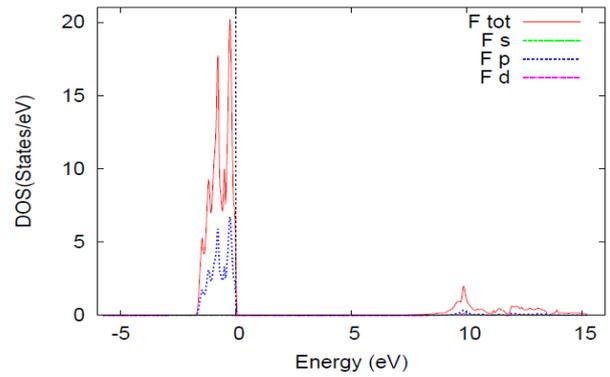


Figure 4. Plot of total and partial DOS of F. Fermi energy is set at zero.

b. Energy bands

The calculated electronic band structure for fluoro perovskite RbCaF₃ along the high-symmetry directions of the Brillouin zone is shown in Fig. 5. In the valence band, the lowest lying band has been found to occur at 7.1 eV below Fermi level due to the core state electrons of Rb, Ca and F atoms. We also observe from Fig. 5 that the maximum in band energy in valence region occurs at 0 eV at the symmetry point R. In the conduction band, minimum in energy occurs at 6.8 eV above the Fermi level at the point symmetry Γ . From this plot 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 6.8 eV which is 0.15 eV higher than that obtained by Babu *et al.* [7] theoretically. However our value seems to be lower than the band gap obtained from experiment [8] which is 10.9 eV.

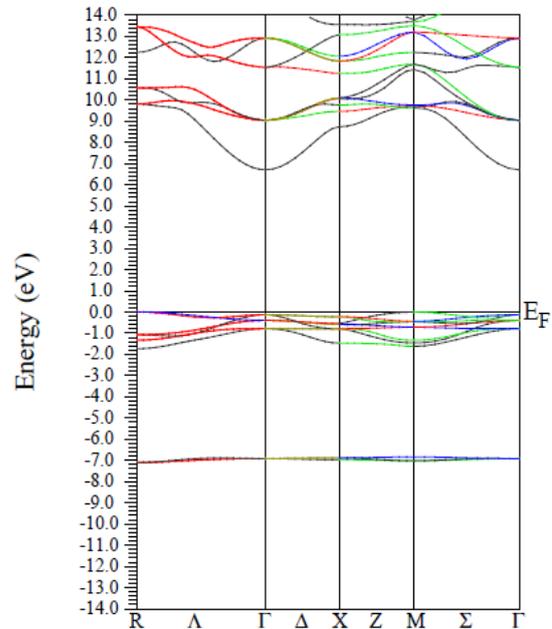


Figure 5. Electronic band structures of RbCaF₃ along the high-symmetry directions. Fermi energy is set at zero.

IV. Conclusions

From the total DOS plots of RbCaF_3 as given in Fig. 1, we find that maxima in peaks in the valence region are due to F atom. This is also evident from the partial DOS plots of F atom as given in Fig. 4. We find here also that the maxima in peak is due to p -state electrons of F atom. The peak heights in partial DOS due to electrons from Rb and Ca atoms in the valence region are negligible. Similarly in the conduction region, it is only d -state electrons of Ca (Fig.3) which is contributing to the maxima in the total DOS of RbCaF_3 . We have found from our study that the band gap of RbCaF_3 is 6.8 eV which is large and hence RbCaF_3 is an insulator.

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