Study of Structural and Electronic Properties of KCaF$_3$ Type Fluoro-Perovskite

K. Neupane[1], Himanshu Joshi[1], Lalhriatpuia Hnamte[1], R. K. Thapa[1*]

[1]Department of Physics, Mizoram University, Aizawl, Mizoram, India-796009

*Author for correspondence, Email: r.k.thapa@gmail.com

Abstract—*Results of structural and energy bands in case of KCaF$_3$ fluoro perovskite is presented in this paper. Calculation is done by using full-potential linearized augmented plane wave (FP-LAPW) method within density functional theory. Energy gap obtained for the case is 6.1 eV and it is wide band insulator.*

Keywords— *Band gap, density of state, energy bands, perovskite, insulator.*

I. INTRODUCTION

Since late 2012, organic and inorganic halides with the perovskite structure have strongly attracted the attention of the photovoltaic community. This is due to attaining efficiency close to 10% in solar cells [1]. It is therefore pertinent to evaluate the potential and analyze the prospects of this exciting technology that have galvanized the photovoltaic research community. Organic/inorganic metal halides are light absorbers although these class of materials have been widely studied for decades [2], but only recently have they been introduced in solar cells. Perovskite is a brown, yellow or grayish-black mineral with an oxide of calcium and titanium and sometimes containing rare earth elements. The ideal structure is a cubic perovskite, ABO$_3$ 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.

In this paper, we report the study of structural, and electronic properties of KCaF$_3$ type perovskite. The results of total and partial density of states and also the energy bands of these systems will be presented. Calculations have been done by using the full-potential linearized augmented plane wave (FP-LAPW) method within density functional theory [3], where full-potential linearized augmented plane wave (FP-LAPW) [4].

II. METHODOLOGY

FP-LAPW method is adopted for the basis set. In this method, the space is divided into non-overlapping muffin-tin spheres separated by an interstitial region. The basis functions are expanded into spherical harmonic functions inside the muffin-tin sphere and the Fourier series in the interstitial region. R$_{MT}$ X K$_{MAX}$ calculates the LAPW basis functions for the expansion of the charge density and the potential in the interstitial region and lattice harmonics for the expansion inside the muffin-tin spheres (where R$_{MT}$ is the average radius

of the muffin-tin spheres and K$_{MAX}$ is the maximum value of the wave vector **K** = k + **G**). The convergence of basis set was controlled by a cutoff parameter R$_{MT}$ x K$_{MAX}$ = 7. Non-spherical contributions to the charge density and potential within the MT spheres were considered up to l_{max} = 6, while charge density and the potential were expanded as a Fourier series with wave vectors up to G$_{max}$ = 12 (a.u.)$^{-1}$. The dependence of the total energy on the number of k points in the irreducible wedge of the first Brillouin zone has been explored within the linearized tetrahedron scheme [5]. The cutoff energy which defines the separation of valence and core states was chosen as -6.0 Ry. Core states will be treated in a fully relativistic manner and the valence states are treated semi-relativistically. Self-consistency is achieved by setting the convergence of both the total energy and the eigen values to be smaller than 10^{-4} Ry.

III. RESULTS AND DISCUSSION

(i) Structural Optimization

All physical and electronic properties of a solid are related to its structure, lattice constants and the total energy of the crystal. We present in this section, the calculations of structural optimization to calculate lattice constants for cubical fluoride perovskites KCaF$_3$. The lattice constants that minimizes the total energy is the equilibrium lattice constant of a crystal. The structural relaxation was performed by volume optimization method based on Murnaghan's equation of states [6]. The lattice constant thus obtained from relaxed structure with minimum ground state energy is the theoretical equilibrium lattice constant which is used for the calculational purposes. We have calculated the total energy of the crystal in its equilibrium position. In order to investigate the synthesizability of the related compounds, the enthalpy (*H*) can be calculated by using the following relation,

$$H = E_0 + PV_0 \tag{1}$$

where, *P* is the bulk pressure, V_O is bulk volume corresponds to minimum energy (E_o) of the system. The negative values of enthalpy indicate the stability of the compounds against decomposition into stable solid structures [7]. The calculated lattice constants, bulk modulus and its pressure derivative are given in table I.

TABLE I. Calculated lattice constant a (in Å), bulk modulus B (in GPa) and pressure derivative B' of ACaF$_3$. Calculated data is compared with other theoretical and experimental results.

Compounds	Previous results a(in Å)	Calculated results a(in Å)	Previous results B(GPa)	Calculated results B(GPa)	Previous results B'	Calculated results B'
KCaF$_3$	4.41[8]	4.498	49.53[8]	49.334	3.577[8]	5.199
	4.529[9]	-	46.0[9]	-	3.95[9]	-

[8] (Babu *et al.*, 2015), [9] (Erdinc, 2011)
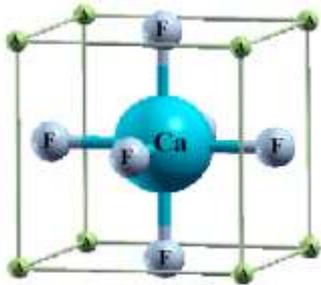
Fig. 1. Crystal structure for KCaF$_3$.
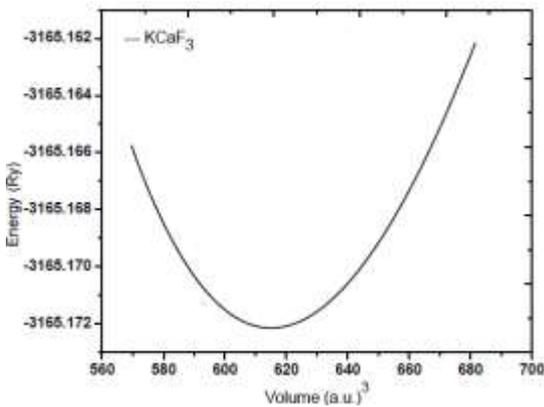
Fig. 2. Volume optimization curve for KCaF$_3$.

(ii) Results of DOS by using GGA Method for KCaF$_3$

In this section the calculated results of total density of states (TDOS) and partial density of states (PDOS) for KCaF$_3$ compound are given. The plot of TDOS of KCaF$_3$ and individual atoms K, Ca and F are given in Fig. 3. In the valence region below the Fermi level, we have found the maximum peak in TDOS for KCaF$_3$ at - 0.27 eV. The occurrence of this maximum in peak in TDOS of KCaF$_3$ at - 0.27 eV appears to be the contribution due to F atom. The reason being that the TDOS of F atom is also maximum at - 0.27 eV. Also in valence band region, we find from the plots that the contributions to the origin of peak in TDOS of KCaF$_3$ by other atoms K and Ca is very low and hence are negligible. Similarly, in the conduction band above the Fermi level in Fig. 3, the maximum peak in TDOS for KCaF$_3$ is observed at 9.68 eV. The occurrence of this maximum in peak in TDOS of KCaF$_3$ at 9.68 eV is due to the main contribution by Ca atom. The reason being that the TDOS of Ca atom is also maximum at 9.68 eV. We find from the plots in Fig. 3, TDOS of KCaF$_3$ by other atoms K and F are very low.

In Fig. 4, the plots of TDOS and partial density of states (PDOS) of K atom in KCaF$_3$ compound are shown. In the valence band, we have found that there is negligible contribution to TDOS and PDOS by electrons of K atom.

However in the conduction band region, we find from the plots that the maximum peak in TDOS occurs at 11.92 eV. This is due to the main contribution by the K *d-t2g* electrons of K atom. The reason being that the maxima of PDOS of K *d-t2g* is also found at 11.92 eV.
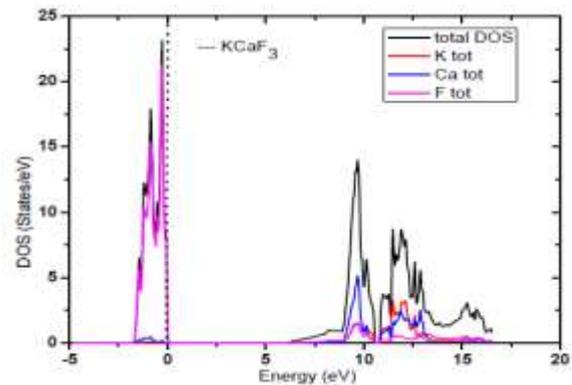
Fig. 3. Plots of total DOS for KCaF$_3$ and atoms K, Ca, F.
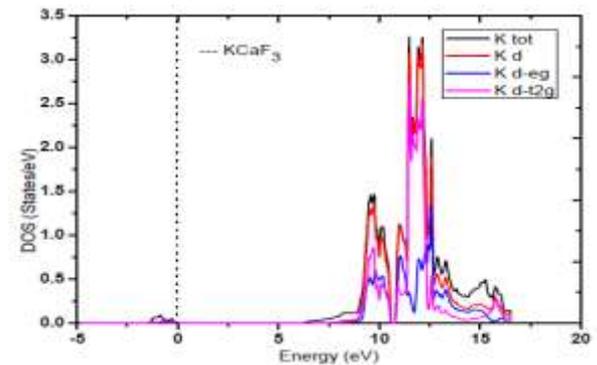
Fig. 4. Total and partial DOS plots of atom K.

Fig. 5 shows the plot of TDOS and PDOS of Ca atom of KCaF$_3$ compound. There is negligible contribution to TDOS and PDOS in the valence band below the Fermi level by Ca atom. However in the conduction band, a maximum peak in TDOS is observed at 9.68 eV in the conduction band. This can be attributed to Ca *d-t2g* state electrons as shown in Fig. 5.

The plot of TDOS and PDOS of F atom in KCaF$_3$ compound is shown in Fig. 6. The maximum peak in TDOS is found at - 0.27 eV in the valence region below the Fermi level. From the plot we find that the contribution to the occurence of this peak at -0.27 eV is due to the contribution by F*px+py* state electrons. There is negligible contribution to TDOS and PDOS in conduction band of F atom as shown in Fig. 6.
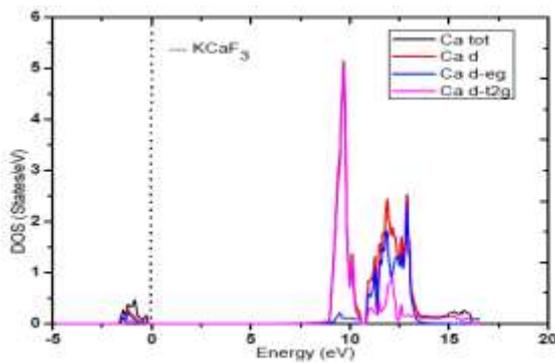
Fig. 5. Total and partial DOS plots of atom Ca.
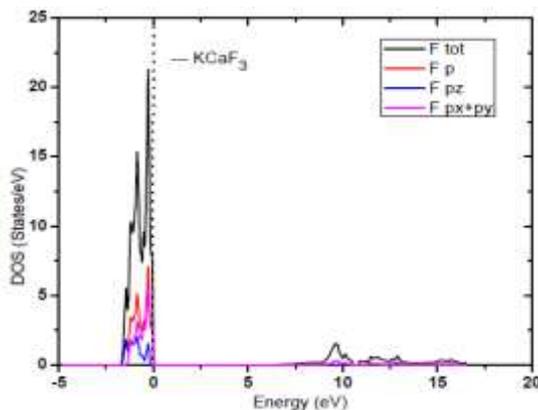
Fig. 6. Total and partial DOS plots of atom F.

(iii) Study of Energy Bands in KCaF₃

In this section, the results of calculation of band structures in the case of a combination of $KCaF_3$ is presented. Calculations have been done by using FP-LAPW method as discussed in Chapter 2. For this purpose, the approximations for exchange-correlation potential used is Generalised Gradient approximation (GGA). We have found that the maximum of the valence band are found to be at a symmetry point R whereas the minimum conduction bands are located at the Γ point of the Brillouin zone. This has resulted into indirect band gap in the compounds. The calculated indirect band gap along R - Γ direction is found as 6.1 eV for $KCaF_3$.
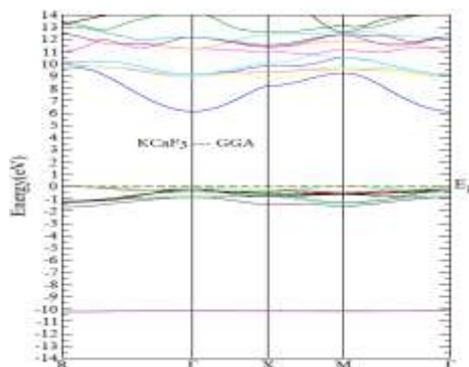
Fig. 7. Band structures for KCaF₃.

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