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STUDY OF STRUCTURAL, ELECTRONIC AND OPTICAL PROPERTIES OF FLUORIDE PEROVSKITE XCaF_3 (X= K AND Rb) USING GENERALIZED GRADIENT APPROXIMATION (GGA) EXCHANGE POTENTIAL

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ABSTRACT

The first principles calculation within the full potential linearized augmented plane wave (FP-LAPW) method is applied to study the structural, electronic and optical properties of cubical perovskite XCaF_3 on the base of density functional theory (DFT). The exchange correlation effects are included through the generalized gradient approximation (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 and RbCaF_3 are 6.1 eV and 6.3 eV respectively that indicates insulating nature of XCaF_3 compound. Calculation of optical spectra such as real and imaginary parts of dielectric function, refractive index and absorption coefficient are performed on the range of energy 0 - 40 eV.

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INTRODUCTION

The ternary compounds belonging, having the general formula ABF_3 , where A and B stand for the alkali metals and alkaline earth or transition metals respectively. The ternary fluoroperovskite like XCaF_3 (X= K and Rb) has great potential for a variety of device applications in optical, ferroelectric, antiferromagnetic systems due to their wide band gaps (Ouenzerfi *et al.* 2004). 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. CsCaF_3 and KMgF_3 are used as a vacuum- ultraviolet-transparent material for lenses in optical lithography steppers in electro- optical applications (Hoersch *et al.* 1986; Fukuda *et al.* 2001). and they have many applications for a tunable laser due to their unique properties (Knierim *et al.* 1986). Murat *et al.* (2016) have investigated structural, electronic and optical properties of CsCaF_3 when doped with Eu atoms and they found that the energy band gap decreases 6.9 eV to 0.13 eV when added

dopant Eu atom in CsCaF_3 compound. Babu *et al.* (2015) have studied the structural, electronic and optical properties of cubic fluoride CsCaF_3 compound using FP-LAPW $+l_0$ method within the generalized gradient approximation (GGA) in the framework of density functional theory. Mubark *et al.* (2012) have studied structural, electronic and optical properties of fluoroperovskite BXF_3 (X= Li, Na, K and Rb) compounds, using FP-LAPW method with exchange- correlation functional GGA in which energy band gap decreases as traverses from Li to Rb. In this paper, we will do the theoretical investigations of the structural, electronic and optical properties of fluoride type perovskite XCaF_3 which will be benefit in electro-optical applications.

Crystal Structure and Computational Details

The unit cell of fluoro-perovskite XCaF_3 with space group (Pm-3m) contains three atoms that form the cubical structure. The atoms of XCaF_3 (X= K and Rb) are located at the Wyckoff positions X(0, 0, 0), Ca(0.5,0.5,0.5), and F(0,0.5,0.5) (Gregory S. Rohrer, 2004) to form the crystal structures as shown in Fig.1. For volume optimization of KCaF_3 and RbCaF_3 , we have used the experimental lattice constant $a=4.41 \text{ \AA}$ (Tranet *al.*,

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2009) and $a = 4.455 \text{ \AA}$ (Bulou *et al.*, 1980) respectively. The optimized volume versus energy curves are shown in Fig.2. The obtained optimized lattice constants are used to study the density of state (DOS) and band energy of XCaf_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 (Blaha *et al.*, 2012). The generalized gradient approximation (GGA) as proposed by Perdew *et al.* (1996) 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 $R_{\text{MT}} \times K_{\text{max}} = 7$ 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. The optical properties of a material can be described on the base of the dielectric function $\varepsilon(\omega)$, which is expressed as

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

The imaginary part $\varepsilon_2(\omega)$ of the dielectric function $\varepsilon(\omega)$ was calculated from the electronic band structure of a solid.

$$\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{i,j,k} \langle i | M | j \rangle^2 f_i (1 - f_j) \times \delta(E_{j,k} - E_{i,k} - \omega) d^3 k$$

Where e is the charge of free electrons, m be the mass of free electrons, ω is the angular frequency of the incident photons, M is the dipole matrix, i and j be the initial and final states respectively, f_i be the Fermi distribution function for the i -th state and E_i be the energy of the electro in i -th state with crystal wave vector k . The real part $\varepsilon_1(\omega)$ of dielectric function can be extracted from the imaginary part using the Kramers-Kronig dispersion relation:

$$\varepsilon_1(\omega) = 1 + \frac{\pi}{2} p \int_0^{\infty} \frac{\omega' \varepsilon_2(\omega')}{(\omega'^2 - \omega^2)} d\omega'$$

Here p represents the principal value of integral. The refractive index $n(\omega)$ and the absorption coefficient $\alpha(\omega)$ of the sample are given by the relations

$$n(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} + \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$

$$\alpha(\omega) = \sqrt{2} \omega \left[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{\frac{1}{2}}$$

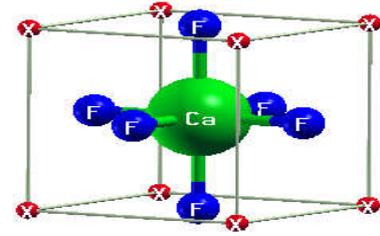


Figure 1 Crystal structure for XCaf_3 ($X = \text{K andRb}$)

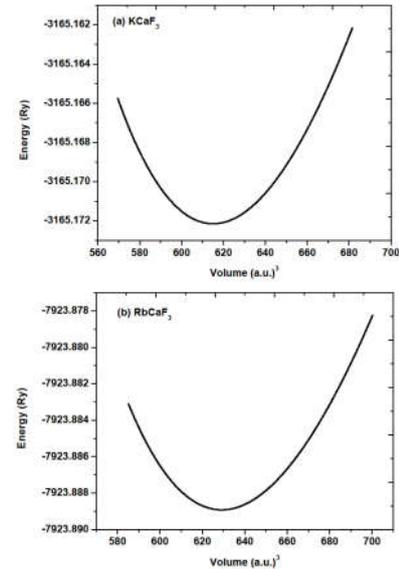


Figure 2 Volume optimization curve (a) KCaf_3 and (b) RbCaf_3

RESULT AND DISCUSSIONS

Crystal structure

To study the crystal structure, we start with the total energy minimization of cubic XCaf_3 as a function of volume. The variation in the total energy as a function of volume is shown in Fig.2. 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'). 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 constants obtained within our GGA calculations are in increasing order from K to Rb.

Table 1 Calculated lattice constant a (in \AA), bulk modulus B (in GPa) and its pressure derivative B' of XCaf_3 compared with other theoretical and experimental results.

Lattice Constant a (in \AA)	Bulk Modulus B (GPa)	Pressure Derivative B'
For KCaf_3		
Our study	4.498	
Other, GGA	4.41 ^a	
	4.45 ^b	49.334
	4.5293 ^c	49.583 ^a
Experimental	46.0 ^c	3.95 ^c
	4.410 ^d	
	4.4584 ^e	
For RbCaf_3		
Our study	4.5134	
Other, GGA	4.452 ^f	48.067
Experimental	4.455 ^h	49.77 ^f
		5.00 ^f

^aRef. (Babu *et al.*, 2015), ^b Ref. (Soleimanpour *et al.*, 2015), ^c Ref.(BahattinErdinc, 2011),
^d Ref.(Tran *et al.*, 2009), ^e Ref. (Demetriou *et al.*, 2005), ^f Ref(Murtaza *et al.*, 2013),
^h Ref. (Bulou *et al.*, 1980)

Density of states (DOS) and band structures of XCaf_3

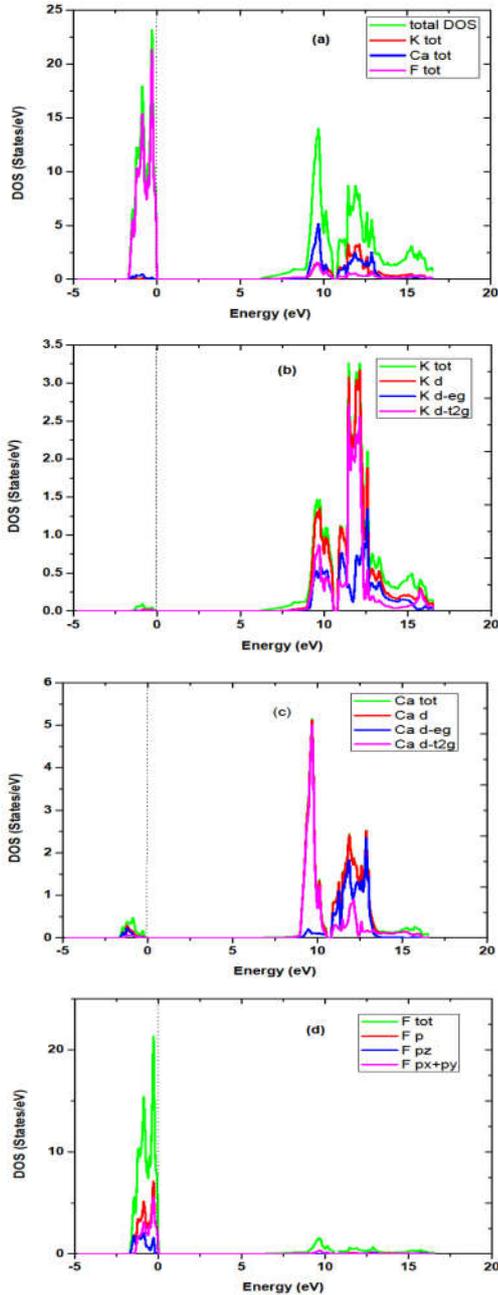


Figure 3 (a) TDOS of KCaF_3 , K, Ca and F, (b) PDOS of K, (c) PDOS of Ca and (d) PDOS of F

Fig. 3 (a) shows the plot of total density of states (TDOS) of KCaF_3 , K, Ca and F. In the valence region below the Fermi level, we have found the maximum peak at 0.27 eV due to the main contribution of F atom and negligible contribution of Rb and Ca atoms. In the conduction band above the Fermi level in Fig. 3 (a), the maximum peak is observed at 9.68 eV due to the main contribution of Ca atom, less contribution of K atom and negligible contribution of F atom. Fig. 3 (b) shows the partial density of states (PDOS) of K atom of KCaF_3 compound.

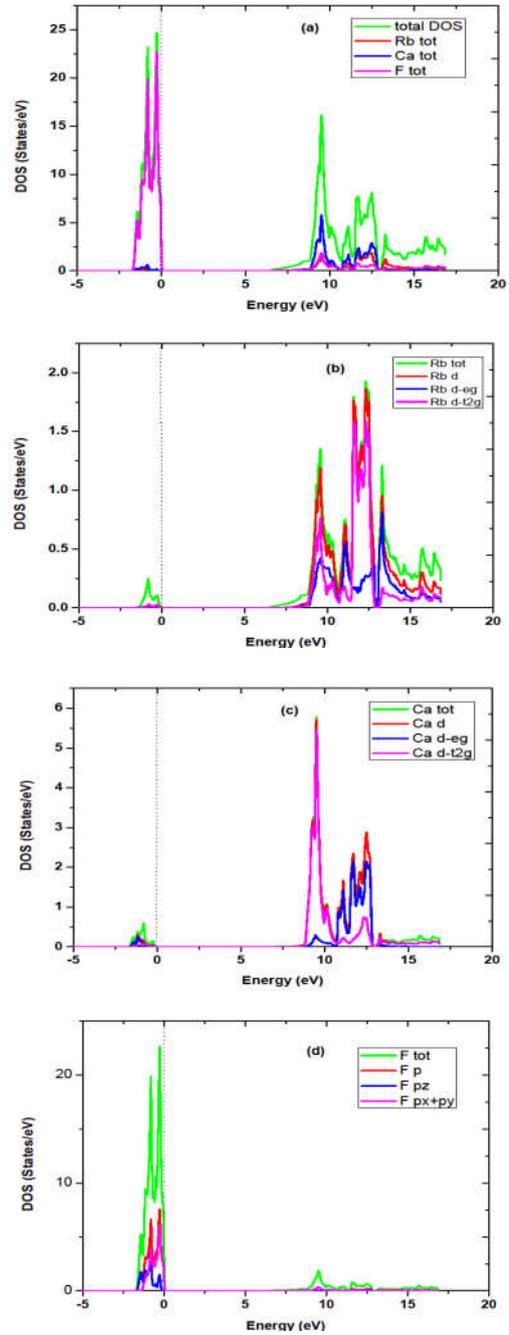


Figure 4 (a) TDOS of RbCaF_3 , Rb, Ca and F, (b) PDOS of Rb, (c) PDOS of Ca and (d) PDOS of F

The contribution of K-d state is negligible in the valence band and the maximum peak is found at 11.92 eV in the conduction band due to the contribution of K $d-t2g$ which is seen in Fig.3 (b). Fig.3 (c) shows the plot of partial DOS of Ca atom of KCaF_3 compound. The negligible contribution of Ca-d is found in the valence band below the Fermi level and a maximum peak is observed at 9.68 eV in the conduction band due to the main contribution of Ca $d-t2g$ states which is evident of Fig. 3 (c). The plot of partial DOS of F atom of KCaF_3 compound is shown in Fig. 3 (d). The maximum peak is found at 0.27 eV in the valence region below the Fermi level due the main contribution of F $px+py$ states of electrons. The negligible contribution is occurred in conduction band which is shown in Fig. 3 (d). Hence, the energy band gap of KCaF_3 is found due

to the contribution of F $px+py$ states in the valence band and K $d-t2g$ states in the conduction band.

The plot of total density of states (TDOS) of $RbCaF_3$, Rb, Ca and F is shown in Fig. 4 (a). In the valence region below the Fermi level, a maximum peak is found at 0.25 eV due to the main contribution of F atom and negligible contribution of Rb and Ca atoms. In the conduction band above the Fermi level in Fig.4 (a), a maximum peak is found at 9.51 eV due to the main contribution of Ca atom, less contribution of Rb atom and negligible contribution of F atom. The plot of total and partial DOS of Rb atom of $RbCaF_3$ compound is shown in Fig.4 (b). The contribution of Rb- d state is negligible in the valence band and a maximum peak is found at 12.5 eV in conduction band due to the main contribution of Rb- $d-t2g$ state which is seen in Fig. 4 (b). The total and partial DOS of Ca atom of $RbCaF_3$ compound is plotted in Fig. 4 (c), in the valence band below the Fermi level, no contribution of Ca- d state is found. In the conduction band above the Fermi level, a maximum peak is observed at 9.51 eV due to the main contribution of Ca- $d-t2g$ state that is seen in Fig.4 (c). Fig. 4 (d) shows the total and partial DOS of F atom of $RbCaF_3$ compound. In the valence band, a maximum peak is found at 0.25 eV due to the main contribution of F $px+py$ states of electrons and negligible contribution F- p state is observed in the conduction region which is seen in Fig. 4 (d). From the study of DOS, the energy band gap of $RbCaF_3$ is observed due to the contribution of F $px+py$ states in the valence band and Ca- $d-t2g$ states in conduction band.

Hence, from the study of total and partial DOS of $XCaF_3$ compound, we have found that the energy band gap occurs due to the contribution of F $px+py$ states in the valence band and Ca- $d-t2g$ states in the conduction band.

The electronic properties of $XCaF_3$ ($X = K$ and Rb) are calculated with first principles FP-LAPW method using GGA exchange potential. To calculate DOS and band structure of $XCaF_3$, the optimized lattice parameters are used. The calculated electronic band structures for fluoroperovskites $XCaF_3$ ($X = K$ and Rb) along the high-symmetry directions of the Brillouin zone are shown in Fig. 5 (a-b).

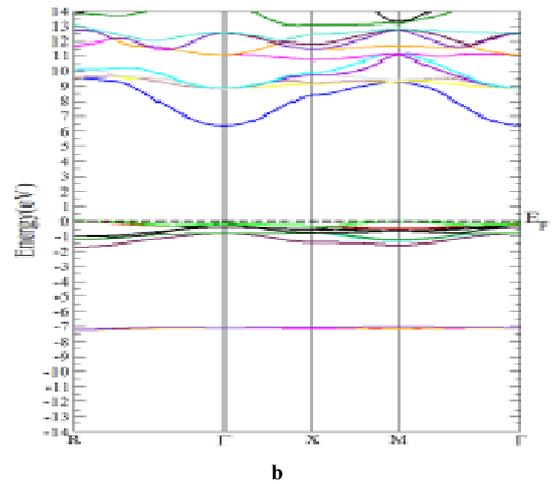
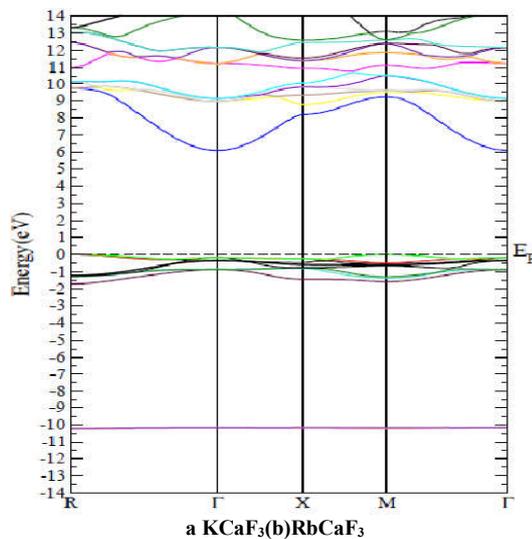


Figure 5 Band structure for (a) $KCaF_3$ and (b) $RbCaF_3$ along the high-symmetry directions of the first Brillouin zone.

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 in $XCaF_3$ compounds, resulting into indirect band gaps in all the compounds. The calculated band gaps ($R - \Gamma$) are found as 6.1 eV and 6.3 eV for $KCaF_3$ and $RbCaF_3$ respectively. From the study of DOS, the band gaps are found due to the contribution of F- p state electrons in the valence band below the Fermi level and most of Ca $d-t2g$ state electrons in conduction band above the Fermi level. From our study, we have found the energy band gaps increase from K to Rb for $XCaF_3$ compound.

Optical properties

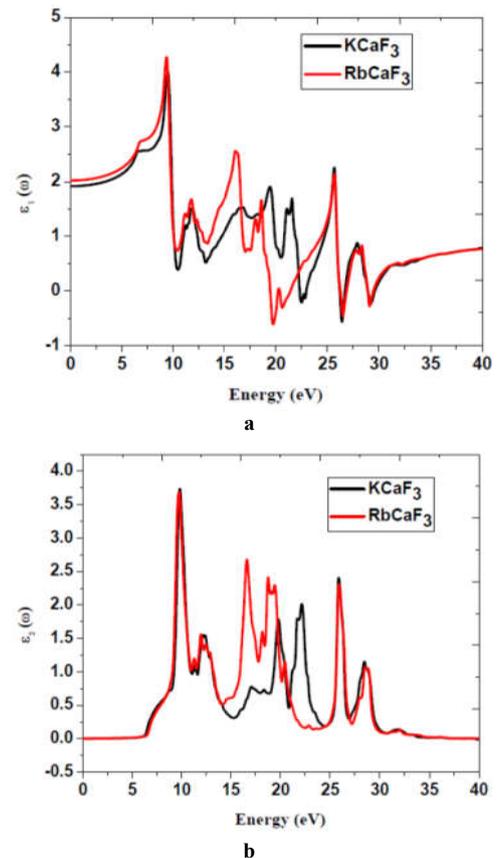


Fig 6 (a) Real $\epsilon_1(\omega)$ part, (b) Imaginary $\epsilon_2(\omega)$ part of dielectric function

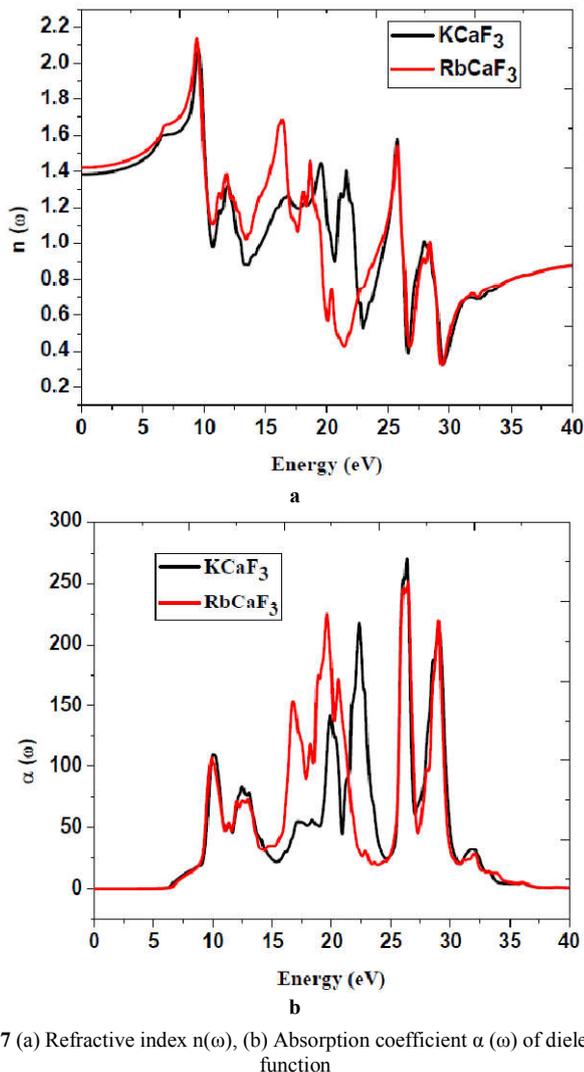


Fig 7 (a) Refractive index $n(\omega)$, (b) Absorption coefficient $\alpha(\omega)$ of dielectric function

The optical spectra as a function of photon energy for cubical fluoroperovskite XCaf_3 ($X=\text{K}$ and Rb) are shown in Fig. (6, 7). The optical properties are studied in the energy range of 0 – 40 eV. The Fig.6 (a) represents real part $\epsilon_1(\omega)$ of dielectric function $\epsilon(\omega)$ of photon energy for cubic XCaf_3 . The function $\epsilon_1(\omega)$ provides the information about electronic polarizability of the material. The static dielectric constant at energy zero is $\epsilon_1(0) = 1.92$ for KCaF_3 and $\epsilon_1(0) = 2.02$ for RbCaF_3 . From zero frequency limit, real part of XCaf_3 starts to increase and reaches the maximum value of 4.01 at 9.41 eV for KCaF_3 and 4.28 at 9.347 eV for RbCaF_3 . After reaching the 1.69 at 21.56 eV for KCaF_3 , real part starts to decrease below zero in the negative scale for the range of 22.326–22.925 eV, 26.28–26.68 eV and 28.939–29.565 eV. Similarly for RbCaF_3 , the negative values are found as for the range of 19.469–20.204 eV, 20.39–21.40 eV, 26.27–26.82 eV and 28.91–29.429 eV. These negative values of real dielectric function indicate that these materials be metal otherwise dielectric. Fig.6 (b) represents the imaginary part $\epsilon_2(\omega)$ of dielectric function $\epsilon(\omega)$ which provides information about absorption behavior of XCaf_3 . In the imaginary part $\epsilon_2(\omega)$, the threshold energy of dielectric function occurs at $E_0 = 6.1$ eV and 6.3 eV for KCaF_3 and RbCaF_3 respectively which correspond to the fundamental gaps at the equilibrium. We have observed six peaks for KCaF_3 at 9.80 eV, 12.36 eV, 19.76 eV, 22.10 eV, 25.86 eV and 28.45 eV having

imaginary part of dielectric function as 3.74, 1.55, 1.76, 2.01, 2.41 and 1.15 respectively. Similarly for RbCaF_3 , we have observed six peaks at 9.67 eV, 11.93 eV, 16.61 eV, 18.72 eV, 25.89 eV and 28.50 eV having imaginary part of dielectric function as 3.68, 1.56, 2.68, 2.41, 2.31 and 1.07 respectively. Fig.7 (a) represents the refractive index $n(\omega)$ of photon energy for cubic XCaf_3 . The static refractive index $n(0)$ are found to have the values 1.38 and 1.42 for KCaF_3 and RbCaF_3 respectively. The refractive index reaches the maximum value of 2.08 at 9.58 eV for KCaF_3 and 2.14 at 9.42 eV for RbCaF_3 . The refractive index greater than one means photons which travelling in the material are slowed down due to the interaction with electrons of the medium. Fig.7 (b) shows the absorption coefficient $\alpha(\omega)$ of photon energy. The absorption characters are observed in the range up to 40 eV. The maximum absorption coefficient is 2.55% at 26.32 eV for KCaF_3 and 2.5% at 26.42 eV for RbCaF_3 . XCaf_3 is wide band gap compound with high absorption power in ultraviolet energy range and it can be used in the optoelectronic devices like UV detectors.

CONCLUSIONS

The structural and electronic properties of XCaf_3 are studied using the FP-LAPW method based on density functional theory (DFT) with GGA exchange-correlation potential. From the volume optimization curve in Fig. 2 (a-b), we have found the optimized lattice constants, pressures and pressure derivatives of XCaf_3 ($X = \text{K}$ and Rb) which are mentioned in table 1 in which experimental and theoretical values are noted. Our optimized lattice constants are slightly more than the experimental values and they increase from K to Rb (table 1). From the total and partial DOS plots of KCaF_3 in Fig. 3 (a-c) and in Fig. 4 (a-c) for RbCaF_3 , we have found that $\text{F } px+py$ state electrons are contributing in valence band and $\text{Ca } d_{t2g}$ state electrons contribute in the conduction band which provides band gap energy. From the study of band structure of XCaf_3 in Fig. 6 (a-b), we have found the band gaps are as 6.1 eV and 6.3 eV for KCaF_3 and RbCaF_3 and respectively which is the indication of insulating behavior. The optical properties such as real and imaginary parts of dielectric function, refractive index and absorption coefficient of XCaf_3 compound are studied as the energy range of 0 - 40 eV. This compound has a wide band gap and high absorption power, which suggests that it is useful for optoelectronic devices.

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