

Study of Structural, Electronic And Optical Properties of Fluoride Perovskite CsCaF₃ Using FP-LAPW Method

K Neupane¹, R. K. Thapa^{1,*}

¹Department of Physics, Condensed Matter Theory Research Group Mizoram University,
Aizawl, Mizoram

*Corresponding Author: K Neupane

ABSTRACT

A cubic perovskite CsCaF₃ has been investigated from the first principles calculation within the full potential linearized augmented plane wave (FP-LAPW). Most common exchange correlation effect called the generalized gradient approximation (GGA) was used to treat the electron. The calculated structural properties such as equilibrium lattice constant, the bulk modulus and its pressure derivative are in good agreement with the previous report. We have found that the compound is an insulator with large band gap of 6.9 eV. The optical spectra are also calculated from the Kramers - Kronig equation in relation to rigid band structure.

Keywords: DFT; GGA; FP-LAPW; DOS; band structure; dielectric function; refractive index; absorption coefficient;

I. INTRODUCTION

The ternary compounds belonging, having the general formula ABF₃, where A and B stand for the alkali metals and alkaline earth or transition metals respectively. The ternary fluoroperovskite like CsCaF₃ 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. CsCaF₃ and KMgF₃ are used as a vacuum- ultraviolet-transparent material for lenses in optical lithography steppers in electro-optical applications [3, 4] and they have many applications for a tunable laser due to their unique properties [5]. Brik and Ma made hybrid density functional calculation of structural, elastic and electronic properties of cubic fluoride CsMF₃ compounds (M = Ca, Cd, Hg and Pb) [6]. Murat et al. [7] have investigated structural, electronic and optical properties of CsCaF₃ 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 CsCaF₃ compound. Babu et al. [8] have studied the structural, electronic and optical properties of cubic fluoride CsCaF₃ compound using FP-LAPW +I₀ method within the generalized gradient approximation (GGA) in the framework of density functional theory. Mubark et al. [9] have studied structural, electronic and optical properties of fluoroperovskite BXF₃ (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 present the structural, electronic and optical properties of fluoroperovskite CsCaF₃ on the basis of density functional theory (DFT). This present work will help in electro-optical applications.

II. CRYSTAL STRUCTURE AND COMPUTATIONAL DETAILS

The unit cell of fluoro-perovskite CsCaF₃ with space group (Pm-3m) contains three atoms that form the cubical structure. The atoms of CsCaF₃ are located at the positions Cs (0, 0, 0), Ca (0.5, 0.5, 0.5) and F (0, 0.5, 0.5) and the origin is chosen to be at (0, 0, 0) [10]. For volume optimization of CsCaF₃, we have used the experimental lattice constant $a = 4.52 \text{ \AA}$ [11]. The obtained optimized lattice constant is used to study the density of state (DOS) and band energy of CsCaF₃ by using the full potential linearized augmented plane wave (FP-LAPW) method of KS-DFT [12], as implemented in the WIEN2K code [13]. The generalized gradient approximation (GGA) as proposed by Perdew et al. [14] 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 $G_{max} = 12 \text{ a.u.}^{-1}$. 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 $\epsilon(\omega)$, which is expressed as [15]

$$\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$$

The imaginary part $\epsilon_2(\omega)$ of the dielectric function $\epsilon(\omega)$ was calculated from the electronic band structure of a solid [16, 17].

$$\epsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2} \right) \sum_{i,j,k} \langle i | M | j \rangle^2 f_i (1 - f_j) \times \delta(E_{j,k} - E_{i,k} - \omega) d^3k$$

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 $\epsilon_1(\omega)$ of dielectric function can be extracted from the imaginary part using the Kramers- Kronig dispersion relation:

$$\epsilon_1(\omega) = 1 + \frac{\pi}{2} p \int_0^\infty \frac{\omega' \epsilon_2(\omega')}{(\omega'^2 - \omega^2)} d\omega'$$

Where 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

$$n(\omega) = \frac{1}{\sqrt{2}} \left[\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} + \epsilon_1(\omega) \right]^{\frac{1}{2}}$$

$$\alpha(\omega) = \sqrt{2} \omega \left[\sqrt{\epsilon_1^2(\omega) + \epsilon_2^2(\omega)} - \epsilon_1(\omega) \right]^{\frac{1}{2}}$$

III. RESULT AND DISCUSSIONS

3.1 Crystal Structure

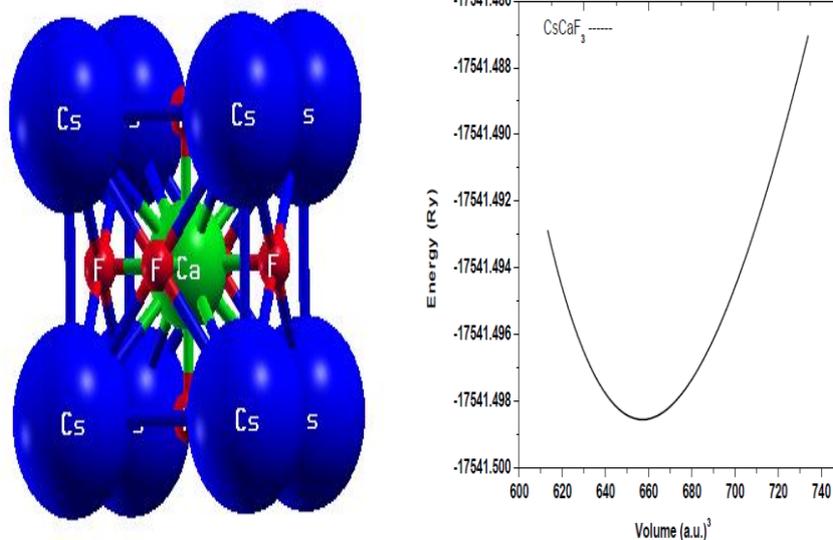


Fig.1. Crystal structure (left) and volume optimization curve (right) of CsCaF₃

The energy versus volume data was fitted to a Murnaghan equation of state [18] to obtain the equilibrium lattice constant (a), the bulk modulus (B) and its first pressure derivative (B') which are mentioned in table 1.

Table1.

| | Lattice Constant a (in Å) | Bulk Modulus B (GPa) | Pressure Derivative B' |
|--------------|---------------------------|----------------------|------------------------|
| This study | 4.6007 | 48.1655 | 5.8413 |
| Other, GGA | 4.5885 [8] | 45.7705 [8] | 4.6278 [8] |
| Experimental | 4.52 [11] | - | - |

3.2 Density of States (DOS) and Band Structures

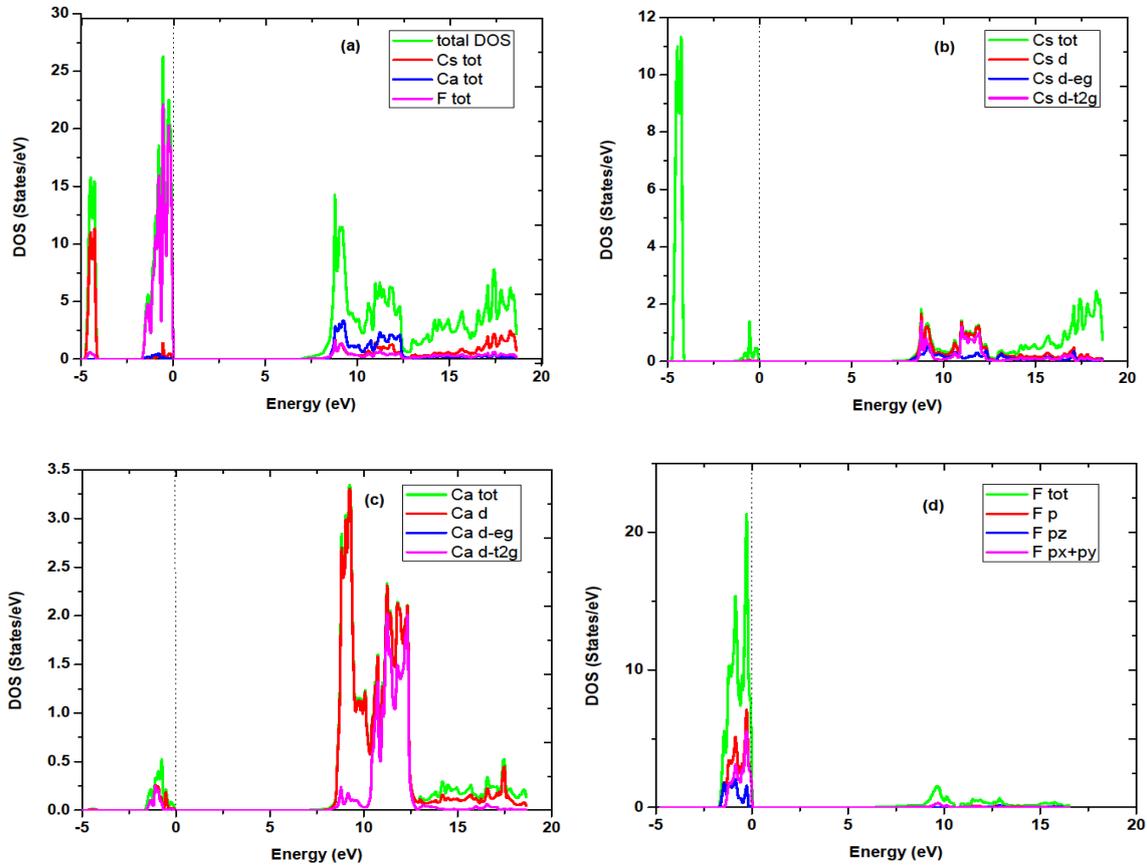


Fig. 2. (a) TDOS of CsCaF₃, Cs, Ca and F, (b) PDOS of Cs, (c) PDOS of Ca and (d) PDOS of F

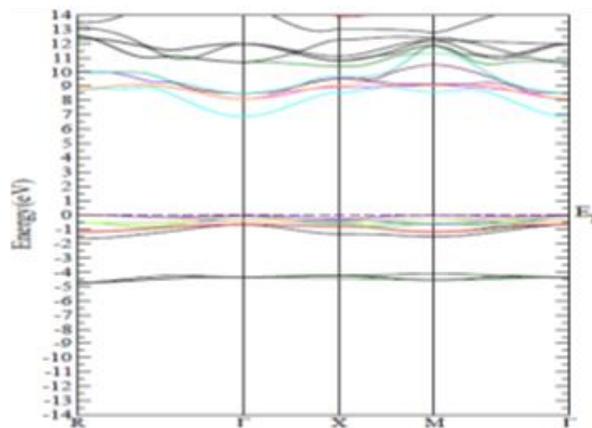


Fig.3. Band Structures

Fig. 2 (a) shows the total density of states (TDOS) of CsCaF₃, Cs, Ca and F. In the valence region below the Fermi level, a maximum peak is found at - 0.51 eV due to the main contribution of F atom and negligible contribution of Cs and Ca atoms. In the conduction band above the Fermi level in Fig. 2 (a), a maximum peak is found at 8.79eV due to the main contribution of Ca atom, less contribution of Cs atom and negligible

contribution of F atom. Fig. 2 (b) represents the total and partial plot of DOS of Cs atom of CsCaF₃ compound. In the valence band below the Fermi level, the contribution of Cs-d state is negligible and a very small peak is found at 8.79 eV in the conduction band due to the contribution of Cs d-t_{2g} states of electrons which is seen in Fig. 2 (b). The total and partial DOS of Ca atom of CsCaF₃ compound is plotted in Fig. 2 (c), in the valence band below the Fermi level, no contribution of Ca-d state is found. In the conduction band, a maximum peak is found at 9.25 eV due to the contribution of Ca d-t_{2g} states of electrons. Similarly, Fig. 2 (d) shows the partial DOS of F atom of CsCaF₃ sample. The maximum peak is found at 0.21 eV in valence band below the Fermi level due to main contribution of F p_x+p_y states of electrons and basically negligible contribution is found in conduction region that is seen in Fig. 2 (d).

The width of energy gap (E_g) is the difference in energies of the highest band at symmetry point R in valence region and the lowest band in conduction region at symmetry point Γ which is an indirect band gap (Fig.3). The wide indirect band gap is observed from the study of band structure which is 6.9 eV (Fig.3) due to the contribution of F-p states electrons in the valence band and Ca-p states electrons in the conduction band.

3.3 Optical Properties

The optical spectra as a function of photon energy for cubical fluoroperovskite CsCaF₃ are shown in Fig. (4-6). The optical properties are studied in the energy range of 0 – 40 eV. The Fig.4 represents real part $\epsilon_1(\omega)$ and imaginary part $\epsilon_2(\omega)$ of dielectric function $\epsilon(\omega)$ of photon energy for cubic CsCaF₃. The function $\epsilon_1(\omega)$ provides the information about electronic polarizability of the material. The static dielectric constant at energy zero is $\epsilon_1(0) = 2.25$. From zero frequency limit, it starts to increase and reaches the maximum value of 5.27 at 8.83 eV. After reaching the 2.7 eV, it starts to decrease below zero in the negative scale for the range 13.64-14.04eV, 15.82-17.37eV, 17.61-18.27eV, 18.43-18.78eV and 28.74-29.15eV. This negative value of real dielectric function indicates that this material be metal otherwise dielectric. The imaginary part $\epsilon_2(\omega)$ provides information about absorption behavior of CsCaF₃. In the imaginary part $\epsilon_2(\omega)$, the threshold energy of dielectric function occurs at $E_0 = 6.9$ eV, which corresponds to the fundamental gap at equilibrium. There are six peaks observed at 9.07 eV, 11.49eV,13.34 eV, 15.03 eV, 25.86 eV and 28.39 eV having imaginary part of dielectric function as 3.96, 2.25, 4.53,2.74, 1.75 and1.01 respectively. Fig.5 represents the refractive index $n(\omega)$ of photon energy for cubic CsCaF₃. The static refractive index $n(0)$ is found to have the value 1.5. The refractive index reaches the maximum value of 2.36 at 8.88 eV. 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.6 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 2.02% at 16.31 eV. CsCaF₃ 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.

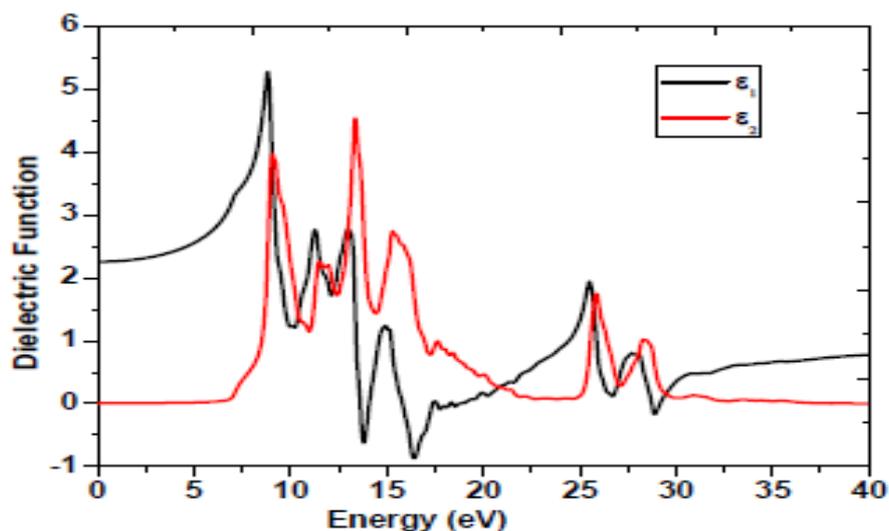


Fig.4. Dielectric function of real $\epsilon_1(\omega)$ and imaginary $\epsilon_2(\omega)$ parts for CsCaF₃

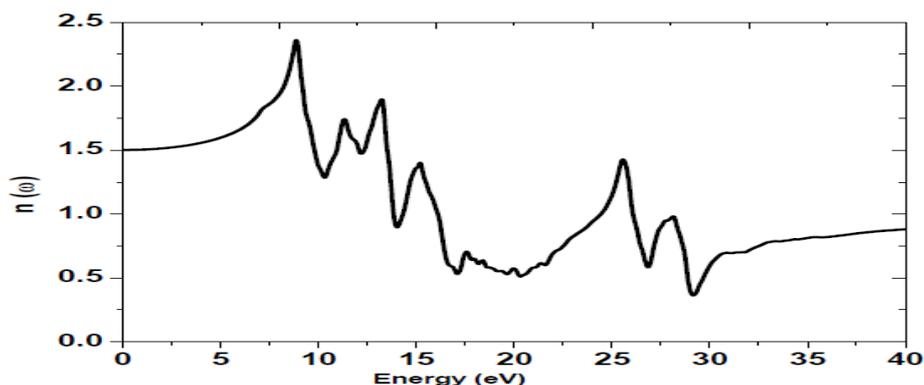


Fig.5. The refractive index $n(\omega)$ for CsCaF₃

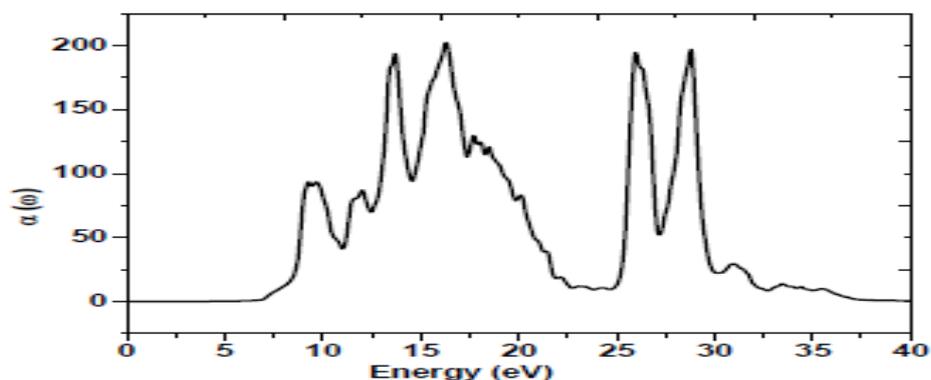


Fig.6. The absorption coefficient $\alpha(\omega)$ for CsCaF₃

IV. CONCLUSIONS

From the volume optimization in Fig.1, we have found the optimized lattice constant as 4.6007 Å which is slightly higher than experimental value [7]. From the study of total and partial plot of DOS, F-p and Cs-p state electrons are contributing to provide the peaks in the valence band. However in conduction band, Cs d -t_{2g} and Ca d -t_{2g} state electrons are contributing to provide peaks. From the study of band structures in Fig.3, the indirect and wide band gap is found as 6.9 eV which indicates that CsCaF₃ compound has insulating characters. The optical properties such as real and imaginary parts of dielectric function, refractive index and absorption coefficient are studied as the energy range of 0 - 40 eV. The calculated static dielectric constant $\epsilon_1(0)$ is found about 2.25 and the static refractive index $n(0)$ is found to be 1.5. This compound has a wide band gap and high absorption power, which suggests that it is useful for optoelectronic devices.

ACKNOWLEDGEMENT

KN thanks Mizoram University for a fellowship and RKT thanks SERB (India) for a research grant vide No. EMR/2015/001407, Dt. 10-08-16.

REFERENCES

- [1]. Riadh El Ouenzerfi, Shingo Ono, Alex Quema, Masahiro Goto, Masahiro sakai et al. (2004). *J. Appl.Phys.* **96**, 7655
- [2]. Fen Zhang, Yuanbing Mao, Tae-Jin part, and Stanislaus S. Wong, (2008). *Adv.* **18**, 103
- [3]. Ho`rsch G, Paus HJ (1986) *Opt. Commun.* **60**:69
- [4]. Fukuda T, Shimamura K, Yoshikawa A, Villora EG (2001) *Opto Electron Rev* **9**:109
- [5]. Knierim W, Honold A, Brauch U and Durr U 1986 *J. Opt.Soc. Am. B* **3** 119
- [6]. Doi 10.1103/Physrevb.80.174110
- [7]. Murat, A. and Bahattin, E. (2016). DFT Study of CsCAF₃:Eu, *GUJ Sci.* **29**(2):273-278
- [8]. Babu, K.E., Murali, N., Babu, V., Babu, B. K. and Veeraiah, V. (2015). Structural, electronic and elastic properties of KCaF₃ and RbCaF₃ for vacuumultraviolet- transparent lens materials. *AIP Conference Proceedings* **1661**, 100002
- [9]. Mubark, A.A. and Mousa, A.A. (2012). The electronic and optical properties of the fluoroperovskite BaXF₃ (X= Li, Na, K and Rb), *Computational Materials Science.* **59**, 6-13
- [10]. Gregory S. Rohrer (2004). *Structure and bonding in crystalline materials*, Cambridge university press, United Kingdom
- [11]. Jiang L Q et al 2006 *J. Phys. Chem. Solids* **67** 1531
- [12]. Kohn, W. and Sham, L. J. (1965). *Physical Review*, **A140**, 1133

- [16]. Blaha, P., Schwarz K., Madsen G. K. H., Kvasnicka D., Luitz J., Schwarz K. (2012), An Augmented Plane Wave plus
- [17]. Local Orbitals Program for Calculating Crystal Properties, Wien2K User's Guide, Techn. Universitat Wien, Wien
- [18]. Perdew, J. P., BurkeFarcas SI, Borodi G (1996) J Cryst Growth **169**:89
- [19]. Tell J.S., Phys, Rev. 104 (1956) 1760
- [20]. Fox M., Optical Properties of Solids, Oxford University Press, New York, 2001
- [21]. Dressel M., Gruner G., Electrodynamics of Solids: Optical Properties of Electrons in Matter, Cambridge University
- [22]. Press, UK, 2002
- [23]. Murmaghan FD (1944) Proc Natl Acad Sci **30**:244

K Neupane . “Study of Structural, Electronic And Optical Properties of Fluoride Perovskite Cscaf3 Using FP-LAPW Method.” International Journal of Computational Engineering Research (IJCER), vol. 07, no. 12, 2017, pp. 07-12.