Ultra-wide bandgap semiconductor behavior of NaCaF₃ fluoro-perovskite with external static isotropic pressure and its impact on optical properties: First-principles computation

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Ultra-wide bandgap semiconductor behavior of NaCaF₃ fluoro-perovskite with external static isotropic pressure and its impact on optical properties: First-principles computation

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Abstract

A comprehensive theoretical study to investigate the outcomes of externally applied static isotropic pressure (0 GPa - 50 GPa) on electronic, optical and structural properties of NaCaF₃, using density functional theory (DFT) based CASTEP (Cambridge Serial Total Energy Package) code with ultra-soft pseudo-potential USP plane wave and Perdew Burke Ernzerhof (PBE) exchange-correlation functional of Generalized Gradient Approximation (GGA), is reported. The electronic bandgap shows the increasing trend 4.773 eV - 6.203 eV (direct bandgap) with increasing external pressure. The increase in bandgap is significant up to 20 GPa as compared to higher external pressures. The mystery of increasing band gap is nicely decoded by total density of states (TDOS) and elemental partial density of states (EPDOS). Optical properties have been calculated to analyze the impact of increment in band gap on them. We observed that highest peak of energy loss function $L(\omega)$ shows the blue shift which confirms the increment of band gap. At zero photon energy, for 0 GPa, the static refractive index $n(\omega)$ has value of 1.4456. After applying external pressure, there is a slight increase in $n(\omega)$ which favors the semiconducting behavior of ternary compound. The energy points at which the absorption peak is maxima, the refractive index has lowest value.

Keywords: Fluoro-perovskite; First-principles computation; Ultra-wide bandgap; Structural optimization; Electronic band transition; Refractive index, Blue-shift in loss function.

1. Introduction

After the very first discovery of perovskites in 1839, many materials have been discovered carrying the same crystalline structure, from the list one of the most common material is CaTiO_3 . The structural composition of cations and anion in some particular order leads to the basic structure of any perovskites defined by the general formula of ABX_3 . Here A and B are cations, and mostly they belong to alkali metals or alkaline earth metals, whereas X is the anion commonly oxygen has been used in place of X [1]. However, the halogen perovskites have also drawn attention X is replaced by an element of group VII-A (most commonly Fluorine F). This X is further attached with mono-valent A and divalent B cations in a quite attractive yet technical way. This stoichiometry then exposes numerous electronic, magnetic, and optical changes in response to a variety of temperature and pressure [2].

Fluoride perovskites exhibits a quite wide bandgap which helps then to become suitable for being applied in lenses, ferroelectric, antiferromagnetic systems and optical technologies such as transparent and optical coatings. These applications make KCaF_3 , RbCaF_3 , BaLiF_3 and SrLiF_3 and some other members of this peculiar class of enormous interest [3] but still more and more investigations are required to be done both experimentally and theoretically. Their magnetic, electronic, and optical properties are catching all the attention as they show promising features when it comes to these properties. Research has explored perovskites showing superconductivity, piezoelectric effect, ferroelectricity, magneto resistance and some highly beneficial thermal properties and yet quite more to find out to make these properties useful in a broad way [4-7]. Their wide bandgap is also their key feature allowing them to be used in lenses, memory devices, sensors, fuel cells whereas the absorption property leads to LEDs and colors TVs.

Changing different variables explore different properties and variation in any material. As long as perovskites are concerned, research has shown by varying some parameters lead to a whole set of varied properties. For instance, by applying pressure or thermal conditions we may know how the material responds. The purpose of varying these parameters is to know the elastic limit, sheer (shear) strength, bulk modulus, conductivity, magnetic

behavior, energy band gap and a lot of other properties. For KCaX_3 ($X = \text{F}, \text{Cl}$), theoretical study was carried to unveil elastic, optical, and electronic behavior in linear density functional theory. The indirect bandgap for KCaX_3 (Γ -R) was revealed. Moreover, the linear relation of Electronic bandgap and hydrostatic pressure was also a result of the study [8]. For KCaF_3 optimization method provided derivation for Bulk modulus, pressure and equilibrium lattice parameters. Elastic moduli were seemed to be pressure dependent along with the directional dependence of Young's Moduli, whereas the pressure was provided in the range of 0-40 GPa. A linear dependence of Energy band gap on pressure was also shown, however, different techniques gave different results for the value of band gap, but the main value is 6.1 eV in $\text{R}-\Gamma$, which varied on providing pressure [9].

Another perovskite, BaZrO_3 is also famous for its diverse properties and have been investigated with and without doping and under high pressure [10]. An experimental study showed that the cubic structure of BaZrO_3 was transformed to tetragonal phase on applying high pressure. The provided pressure was 17.2 GPa on which the phase transition occurred [11]. Later a theoretical research was carried to investigate the accuracy experimental results. The material was studied in density functional theory, and it was found that material carries the indirect band-gap for both tetragonal and cubic structures. And after the phase transition from Cubic to tetragonal there was merely 1 eV increment in the bandgap. So, the results were in the favor of the previous experimental literature. The mechanical stability of both tetragonal and cubic phases was also inferred [12]. Another research explored the electronic, elastic, optical and structural properties of LiBeF_3 , showing the indirect bandgap of this perovskites. The reported value of bandgap was 7.83 eV. Whereas the absorption value of this material lies in ultraviolet region [13].

Under discussion material is NaCaF_3 (NCF) which is also a fluoro- perovskite following the same structure, here sodium is alkali metal carrying positive charge and is mono-valent cation. On the other hand, Ca is divalent cation, and is alkaline earth metal possessing positive charge. For the purpose of stability B positioned ions are greater than the ions at A position. Whereas the highly electronegative element fluorine belongs to the family of halogens, i. e. Group VII-A, and the value for its electronegativity is 4 [14]. Fluorides based

on alkali metals and alkaline earth metals have attained limelight because of their ferromagnetic, piezoelectric and photoluminescence properties [15].

Currently the optical, electronic, and structural properties of NaCaF₃ have been explored by applying different external isotropic static pressure. Moreover, by the end of the paper some questions will be answered, how changing the pressure is affecting the bandgap of this perovskite and whether or not by applying pressure the materials conducting behavior changes from semiconductor to insulator or it shows ultra-wide bandgap semiconductor nature?

2. Computational methodology

For ternary compound NaCaF₃, having cubic structure of *Pm3m* space group has been considered. The settlement for Ca and Na atoms is (0, 0, 0) and (1/2, 1/2, 1/2) respectively, however the three F atoms are at (1/2, 1/2, 0), (1/2, 0, 1/2), (0, 1/2, 1/2). The configuration of valence electrons for NaCaF₃ compound is given as: F has 2s², 2p⁵, while Na has 2s², 2p⁶, 3s¹ and Ca has 3s², 3p⁶, 4s².

In this paper, the technique of ultra-soft pseudo-potential USP plane wave [16, 17] and Perdew Burke Ernzerhof (PBE) [18, 19] exchange correlation functional of Generalized-Gradient-Approximation (GGA) has been applied, based on density functional theory (DFT), for the calculations of structural, electronic and optical properties, employed in CASTEP (Cambridge Serial Total Energy Package) code [20]. All these calculations have been done by solving Kohn-Sham equations [21-23]. By implementing this method; both quick and efficient computations can be achieved simultaneously, without taking into consideration the approximation of shape of orbitals in advance. The outcome of interaction of nuclei with inner shell electrons is the formation of ionic core. Then there is an interaction between valence electrons and ionic core resulting in convergence of electron-ion potential. By using special *k*-points, integrations have been performed in the Brillion zone, with *k*-points mesh designed in order of 8 × 8 × 8 on Monkhorst pack grid for structural optimization [24]. Here the value of total energy is taken as 5×10⁻⁵eV/atom. While during optimization of structure, the cell parameters and positions of atoms are varied to minimize the total energy under the prescribed boundaries of the symmetry.

Further, all of the forces applied on the atoms are converged during geometrical optimization, to a value of 0.002 eV/Å [25]. All the properties of material are calculated after geometry optimization.

3. Result and discussion

3.1. Structural properties

After the geometrical optimization, the unit cell of NaCaF₃ is shown in Fig.1. It appears from the figure that NCF has a cubic phase with space group *Pm3m*. The lattice constant of NCF in cubic phase at zero pressure is $a = b = c = 4.154 \text{ \AA}$. As the pressure is applied in intervals (5, 10, 15, 20, 25, 30, 35, 40, 45, 50) GPa the lattice constant appears to be (4.049, 3.964, 3.903, 3.848, 3.805, 3.765, 3.731, 3.696, 3.668, 3.643) Å, respectively.

Fig. 1. $2 \times 2 \times 2$ supercell of NCF.

The decrement in lattice constant can be seen with an increment in pressure. This reduction in lattice constant by increasing pressure proposes that there exist stronger atomic interactions. Hence, the unit cell volume also reduces which is because of the decrease in lattice parameters. It has also been noticed that no literature either experimental or theoretical, for pressure induced NCF compound for evaluation. Thus, all the results calculated in this paper will be confirmed by future measurements.

Table 1: Literature comparison of impact of pressure after geometry optimization of NaCaF₃ providing volume for unit cell and parameters of lattice.

NaCaF ₃	Lattice Constants			Volume	References
Pressure (GPa)	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	(Å ³)	
P = 0	4.460	4.460	4.460	88.717	[26]
	4.438	4.438	4.438	87.410	[27]
	4.378	4.378	4.378	83.913	[27]
	4.316	4.316	4.316	80.398	[28]
	4.350	4.350	4.350	82.313	[29]
	4.154	4.154	4.154	71.680	Present work
P = 5	4.049	4.049	4.049	66.381	Present work
P = 10	3.964	3.964	3.964	62.288	Present work
P = 15	3.903	3.903	3.903	59.456	Present work
P = 20	3.848	3.848	3.848	56.778	Present work
P = 25	3.805	3.805	3.805	55.089	Present work
P = 30	3.765	3.765	3.765	53.370	Present work
P = 35	3.731	3.731	3.731	51.937	Present work
P = 40	3.696	3.696	3.696	50.489	Present work
P = 45	3.668	3.668	3.668	49.350	Present work
P = 50	3.643	3.643	3.643	48.348	Present work

3.2. Electronic band structure and density of states

The information about the levels of energy which are occupied by the electrons (Energy band) and those which are not available for the electrons to occupy i. e. zero availability (band gap) is given by the structure of electronic bands. The energy bands are of two types. One goes up beyond the Fermi level (E_F) named as conduction band (CB) and the other one lays down the E_F named as Valence band (VB). Because all the computations have been worked out at 0K, therefore, without considering the finite temperature

Fig. 2 At 0GPa, (a) energy band structure and (b) DOS of NCF. At 5 GPa, (c) energy band structure and (d) DOS of NCF.

impacts, the highest point of valence band is accredited as Fermi level. The determination of band gap value by ascertaining the difference between maxima of VB and minima of CB. If the point of symmetry of maxima of VB and that of minima of CB are upon the same point, then character of band gap would be recognized as direct band gap. However, in an inverse situation when they are not found on same point of symmetry, the gap between them can be categorized as indirect band gap.

The electronic band structure of NCF in highly symmetric Brillouin zone direction is being discussed in succeeding paragraphs and shown in Fig. 2, with the Brillouin zone symmetry points displayed along the x-axis and the energy range -5 eV to 15 eV at y-axis was selected, under the influence of pressure ranging from 0 - 5GPa.

Fig. 3 (a-i) The energy band spectrum at different pressure (10 GPa - 50 GPa), respectively.

If NCF is without any pressure i. e. $P = 0$ GPa, both the crest (maxima of VB) and trough (minima of CB) then find their place in Brillion zone on G-symmetry and ternary compound evinces direct band gap as shown in Fig. 2a. Arithmetically, the value of direct band gap in this case works out to 4.773 eV behaving as a semiconductor with wide bandgap. Figure 2b exhibits the graphical scheme of its density of states (DOS) illustrating that none of the states exists in this energy region.

The band gap structure and DOS for NCF at pressure ($P = 5$ GPa) is shown in Fig. 2(c, d), respectively. In NCF at a pressure of 5 GPa, there is an increase in band gap value which appears to be 5.158 eV, with both valence band maximum (VBM) and conduction band minimum (CBM) lying on same symmetry point of Brillion zone i. e. G-symmetry point as that at zero pressure, manifesting again direct (G-G) band gap. This rise in band gap is because of the shifting of conduction band away from the Fermi level which is because of decrease in lattice constant with isotropic.

The electronic band gap structure of NCF at pressure ($P = 10, 15, 20$ GPa) is shown in Fig. 3(a, b, c). For NCF at pressure 10 GPa, 15 GPa and 20 GPa, there is still an increase in band gap value which is found to be 5.503 eV, 5.772 eV and 5.977 eV, respectively. Even at these pressures ($P = 10, 15, 20$ GPa), band gaps appear at G-point of symmetry of Brillion zone. However, the band gap nature again appears to be direct band gap.

Fig. 4. Value of bandgaps of NaCaF₃ with pressure which is showing increasing trend.

The band gap structure and DOS for NCF at pressure ($P = 25, 30, 35$ GPa) is shown in Fig. 3(d, e, f). For NCF at pressure 25 GPa, 30 GPa and 35 GPa, there is a slight increase in band gap value which is found to be 6.037 eV, 6.084 eV and 6.121 eV, respectively. Moreover, the crest of VBM and trough of CBM do lie on G-point of symmetry under these three conditions and band gap is appeared as direct band gap.

The band gap structure and DOS for NCF at pressure ($P = 40, 45, 50$ GPa) is shown in Fig. 3(g, h, i). For NCF at pressure 40 GPa, 45 GPa and 50 GPa, there is also a systematic increase in value of band gap which is computed as 6.159 eV, 6.184 eV and 6.203 eV, respectively. The material behaves as an ultra-wide bandgap semiconductor. Furthermore, the band gap appears to be a direct band gap.

Fig. 5. Partial density of states (PDOS) of NaCaF₃ at pressure (a) 0 GPa and (b) 5 GPa.

It can be concluded from the band structure analysis that band gap is increased (4.773eV-6.203eV) with static external isotropic pressure from 0GPa to 50GPa and VBM and CBM, in all cases, remains at the same symmetry point G which exhibits the same nature of band gap which is direct. So, we can say that pressure and band gap have direct relation (Fig. 4). The lattice parameters are also changed (**Table 1**) when the external pressure is applied. This change in lattice constants causes the variation of band gap at symmetry points. The external applied pressure affects the overlap integral, which causes the variation in width of band gap, as a result the electronic band structure is altered. This increase in the band gap can be explained well with three density of states DOS i. e. partial density of states (PDOS), total density of states (TDOS) and elemental partial density of sates (EDOS). Figure 5 (a, b) depicts the partial density of states (PDOS) at pressure 0GPa and 5GPa and Fig. 6 (c-k) portrayed the PDOS under pressure 10 - 50 GPa of NaCaF₃. The Fermi energy E_F is shown by the vertical line in each spectrum. It can be clearly seen that in all cases *d*-states are sharper than *s*- and *p*-states. It can be scrutinized that bellow E_F *p*-states contribute majorly than *s*- and *d*-states while *d*-states play important contribution above E_F than *s*- and *p*-states. The *s*- and *p*-states are hybridized above E_F . As the external applied pressure is enhanced the hybridization between *s*- and *p*-states is reduced so the band gap is increased progressively.

Fig. 6. Partial density of states of NaCaF₃ under different pressure ranging 10 GPa – 50 GPa.

It can be cleared from the all spectrums that states in the valance band shifts towards lower energy such as the states in conduction band shifts towards higher energies on the application of external pressure which is the basic reason for the increment of bandgap.

It has been observed that that Ca-*s*-states, F-*p*-states, Na-*s*-states, and Na-*p*-states exists to contribute in the upper valance band. Whereas *p*-states of F and Na perform the major role to form valence band maxima. F-*p*-states are more prominent near E_F and Na-*p*-states are prominent quite bellow E_F . Furthermore, in the conduction band Ca-*p*-states, Na-*s*-states and Na-*p*-states are present to contribute. Here Ca-*p*-states have huge involvement in the minima of the conduction band around 5-10 eV and Na-*s*-states and Na-*p*-states are present above of conduction band around 10-20 eV.

We can conclude from the above results that elemental PDOS is shifted to the higher and lower energies due to various pressures leads to the increment of band gap and this influenced the optical properties which are discussed below.

3.3. Optical properties under static isotropic pressure

The electronic structure of solids can be explained by the optical properties of a perovskite material such as function of energy loss, coefficient of absorption, reflectivity, and index of refraction as well as relative permittivity. They propose the suitability and feasibility of materials in nano-electronics and optoelectronics industries thus playing a noteworthy role [30].

All of these optical properties come into existence as a consequence of wave (Electromagnetic waves) matter (material) interaction and they are inter-related to each other, hence, complex dielectric function is used for this purpose, which is:

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega) \quad (1)$$

here $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$ symbolize the real as well as imaginary part of dielectric function, respectively. The real part of dielectric function $\varepsilon_1(\omega)$ provides information about intensity of polarization of a material. The value of static-dielectric function $\varepsilon_1(0)$ for NCF appears at 2.090 eV at zero pressure and slightly increases towards higher value as pressure increases as shown in Fig.8a. The main peak of the real part appears after this static value and shifts towards higher energies 2.084 eV, 2.108 eV, 2.128 eV, 2.148 eV, 2.119 eV, 2.135 eV, 2.149 eV, 2.166 eV, 2.180 eV and 2.194 eV as the pressure increases from (5, 10, 15, 20, 25, 30, 35, 40, 45, 50) GPa, respectively. The complex part of dielectric function $\varepsilon_2(\omega)$ plays a significant character in optical properties for every material, which is related to the energy dissipation. The imaginary part of dielectric function has been exhibited in Fig. 8b and its value appears to be zero at 0eV for NCF both in case of without and with application of high pressure. The main peak of $\varepsilon_2(\omega)$ for NCF at zero pressure seems about 26.840 eV and as the rise in pressure intensity of this peak decreases with

minor shift towards higher energy value. This main peak corresponds directly with the main peak of absorption (Fig. 8c).

Fig. 8. Optical properties of NaCaF₃ with inclusion and exclusion of a variety of pressure. **(a, b)** Dielectric function consist of real and imaginary part **(c)** absorption spectra, **(d)** refractive index, **(e)** energy-loss function and **(f)** reflectivity.

With pressure increase from 0 to 50 GPa, the main peaks have moved to a higher energy region from 28.2819 eV, 28.3879 eV, 28.5163 eV, 28.5870 eV, 28.5056 eV, 28.3900 eV, 28.4018 eV, 28.4511 eV, 28.5158 eV, 28.5901 eV and 28.6534 eV, respectively.

As the pressure increases up to 20 GPa, all peaks shift to the higher energy gradually and the reflectivity increases correspondingly. Thus, blue shift takes place in whole energy region due to pressure.

To compute additional optical properties such as refractive index $n(\omega)$, energy-loss $L(\omega)$, absorption-coefficient $I(\omega)$ and reflectivity $R(\omega)$, equations given below are applied [52];

and the associated results have been acquired for NaCaF₃ ternary compound without and with pressure ranging from (0 - 50) GPa and have been presented in Fig 8.

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

$$L(\omega) = -Im(\varepsilon(\omega)^{-1}) = \frac{\varepsilon_2(\omega)}{\varepsilon_1(\omega)^2 + \varepsilon_2(\omega)^2} \quad (3)$$

$$I(\omega) = \sqrt{2}\omega[\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega)]^{1/2} \quad (4)$$

$$R(\omega) = \frac{n+ik-1}{n+ik+1} \quad (5)$$

Table 2: Static value at 0eV of $\varepsilon_1(\omega)$ and $n(\omega)$ and major peaks of $\varepsilon_2(\omega)$, $I(\omega)$, $L(\omega)$ and $R(\omega)$ are presented.

Pressure GPa	Static value of $\varepsilon_1(\omega)$	Main peak, $\varepsilon_2(\omega)$ (eV)	Absorption peak, $I(\omega)$ (eV)	Static refractive index $n(\omega)$	Plasmon peak, $L(\omega)$ (eV)	Reflectivity peak, $R(\omega)$ (eV)
0	2.0898	26.8288	27.2922	1.4456	28.7962	28.2819
5	2.0999	26.8128	27.3243	1.4467	28.9210	28.3879
10	2.1083	26.7969	27.3205	1.4519	29.0827	28.5163
15	2.1276	26.8037	27.3167	1.4586	29.2328	28.5870
20	2.1437	26.8140	27.3337	1.4605	29.3946	28.5056
25	2.1491	26.8288	27.3507	1.4627	29.4482	28.3900
30	2.1551	26.8516	27.3866	1.4681	29.5804	28.4018
35	2.1672	26.8766	27.4131	1.4706	29.6817	28.4511
40	2.1684	26.8937	27.4490	1.4718	29.8083	28.5158
45	2.1804	26.9245	27.4905	1.4766	29.8984	28.5901
50	2.1944	26.9416	27.5189	1.4813	29.9546	28.6534

The surface behavior of any material can be investigated by measuring its reflectivity. The reflectivity versus energy for NCF at (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50) GPa is

Fig. 9. Trend of different optical properties. (a) $\epsilon_1(\omega)$, (b) $\epsilon_2(\omega)$, (c) $I(\omega)$, (d) $n(\omega)$, (e) $L(\omega)$ and (f) $R(\omega)$ versus external isotropic pressure. The values of $\epsilon_1(\omega)$ and $n(\omega)$ are taken at 0eV.

shown in Fig. 8f. It reveals that at zero frequency, reflectivity for NCF is equal to 0.0332, 0.0330, 0.0340, 0.0348, 0.0357, 0.0344, 0.0351, 0.0357, 0.0364, 0.0370 and 0.0376 at (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50) GPa, respectively. Then it starts increasing from these zero limits with increase in pressure where the highest peak of reflectivity is achieved at 28.2819 eV, 28.3879 eV, 28.5163 eV, 28.5870 eV, 28.5056 eV, 28.3900 eV,

28.4018 eV, 28.4511 eV, 28.5158 eV, 28.5901 eV and 28.6534 eV for (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50) GPa, respectively.

The energy loss function $L(\omega)$ is an imperative factor which gives information about how much energy has been lost for the electron which is moving inside the material is shown in Fig.8e for NCF. The energy loss function $L(\omega)$ has peaks that precisely describe features associated with plasma resonance and therefore, the connected frequency is acknowledged as plasma frequency. At zero pressure the value of highest peak is 28.7962eV and exceeds this value as pressure increases from 5 GPa - 50 GPa. The characteristics associated to plasma resonance can be described through peaks in energy loss function $L(\omega)$ and thus the associated frequency is named as plasma frequency.

For NCF system, both without and with pressure, the value of static-refractive index $n(\omega)$ for zero photon energy, has been calculated and seems merely the same which is 1.4456 (Fig. 8d). Before and after applying pressure, there is a slight shifting of $n(\omega)$ which favors the semiconducting behavior of ternary compound (Fig. 9d). When photon-energy is zero, the lowest absorption energy value corresponds to $n(\omega)$. At the energy point where absorption peak is maximum the value of refractive index is lowest. A material will be efficiently applicable in photovoltaic system whose optical conductivity; absorption and refractive index are high. It is also used in optical devices including waveguides, data storage media, photonic crystals and so on [31].

4. Conclusion

Current paper aimed a comprehensive theoretical investigation of the outcomes of externally applied pressure from 0GPa - 50GPa with 5 step increment i.e. (0, 5, 10, 15, 20, 25, 30, 35, 40, 45 and 50) GPa on optical, electronic and structural properties of NaCaF₃ by using density functional theory (DFT) based CASTEP code, through ultra-soft pseudo-potential USP plane wave and Perdew Burke Ernzerhof (PBE) exchange correlation functional of Generalized-Gradient-Approximation (GGA), has been explored. The structural parameters and unit cell volume are computed after geometry optimization, which are comparable to already reported results. The valence band is majorly controlled by *p*-states of F and Na. The electronic bandgap exhibits an increasing trend 4.773 eV -

6.203 eV with increasing external pressure. The sharp increase in bandgap is noticed up to 20GPa as compared to higher external pressures. Moreover, the nature of the band gap for all values of external pressures remained same i. e. direct bandgap. The mystery of increasing band gap is nicely decoded by total-density of states (TDOS) and elemental partial-density of states (EPDOS). We have also calculated different optical properties like the energy-loss function, refractive index, the reflectivity as well as absorption function for different pressures to analyze the result in optical properties by increasing bandgap. It is seen that energy loss function highest peak acknowledged as Plasmon peak and shifts towards higher energies (28.7962eV-29.9546eV) i. e. blue shift for different pressures which confirms the increment of bandgap. At zero photon energy for all applied pressures the static refractive index $n(\omega)$ has nearly the same value i. e. 1.4456 eV. Before and after applying pressure, there is a slight shifting of $n(\omega)$ which favors the semiconductor behavior of ternary compound. A material will be efficiently applicable in photovoltaic system whose optical conductivity; absorption and refractive index are high. It is also used in optical devices including waveguides, data storage media, and photonic crystals and so on.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Figures

Figure 1

$2 \times 2 \times 2$ supercell of NCF.

Figure 2

At 0 GPa, (a) energy band structure and (b) DOS of NCF. At 5 GPa, (c) energy band structure and (d) DOS of NCF.

Figure 3

(a-i) The energy band spectrum at different pressure (10 GPa - 50 GPa), respectively.

Figure 4

Value of bandgaps of NaCaF3 with pressure which is showing increasing trend.

Figure 5

Partial density of states (PDOS) of NaCaF₃ at pressure (a) 0 GPa and (b) 5 GPa.

Figure 6

Partial density of states of NaCaF₃ under different pressure ranging 10 GPa – 50 GPa.

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Figure 7

Figure not provided in this version

Figure 8

Optical properties of NaCaF3 with inclusion and exclusion of a variety of pressure. (a, b) Dielectric function consist of real and imaginary part (c) absorption spectra, (d) refractive index, (e) energy-loss function and (f) reflectivity.

Figure 9

Trend of different optical properties. (a) $\epsilon_1(\omega)$, (b) $\epsilon_2(\omega)$, (c) $I(\omega)$, (d) $n(\omega)$, (e) $L(\omega)$ and (f) $R(\omega)$ versus external isotropic pressure. The values of $\epsilon_1(\omega)$ and $n(\omega)$ are taken at 0eV.