Structural, electronic, optical and thermodynamic investigations of NaXF₃ (X = Ca and Sr): First-principles calculations


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ABSTRACT

The structural, electronic and optical properties for fluoroperovskite NaXF₃ (X = Ca and Sr) compounds have calculated by WIEN2k code based on full potential linearized augmented plane wave (FP-LAPW) approach within density functional theory (DFT). To perform the total energy calculations, exchange-correlation energy/potential functional has been utilized into generalized gradient approximation (GGA) and local density approximation (LDA). Our evaluated results like equilibrium lattice constants, bulk moduli, and their pressure derivatives are in agreement with the available data. The electronic band structure calculation has revealed an indirect band-gap nature of NaCaF₃, while NaSrF₃ has direct band gap. Total and partial densities of states confirm the degree of localized electrons in different bands. The optical transitions in NaCaF₃ and NaSrF₃ compounds were identified by assigning corresponding peaks obtained from the dispersion relation for the imaginary part of the dielectric function. The thermodynamic properties were calculated using quasi-harmonic Debye model to account lattice vibrations. In addition, the influence of temperature and pressure effects was analyzed on bulk modulus, lattice constant, heat capacities and Debye temperature.

1. Introduction

Perovskites are intensively investigated because of showing interesting and captivating properties due to its distinguished applications, its abundance and common mineral in the Earth [1]. Their observed features are ferroelectricity, charge ordering, superconductivity, colossal magneto resistance, high thermopower, spin-dependant transport alongside displaying exotic structural, electronic, magnetic, optical and transport properties. In addition, their promise in different technological applications like fuel cells, sensors, memory devices, spintronics, and photovoltaics, they are also considered potential materials for microelectronics and telecommunications [2–4]. The discovered high-temperature superconducting oxides and high-performance perovskite solar cells with...
21% power conversion efficiency have increased interest to attain the reported 31% efficiency [5].

Although perovskites are reported to containing oxygen, with chemical formula ABO₃, a few perovskites such as fluoro-perovskites are found in ABF₃, where A and B are alkalies and alkaline earth elements, respectively, and F is fluorine characterized as the highest electro-negative element. Fluorine has shown its ability to form a great variety of fluorides of the high-level chemical stability, in particular, containing low electro-negative alkali metals plus alkaline earth metals. Complex metal fluorides have attracted a considerable attention caused by ferromagnetic [6], nonmagnetic insulating [7], piezoelectric [8] and photoluminescence properties [9]. Moreover, the fluoro-perovskite crystals, namely KMgF₃ [10], NaSrF₃, NaBaF₃, LiBaF₃ [11] have displayed their promise for “UV-Deep UV wave bands” in different studies [12] which can be exploited for different applications as highly transparent and low loss optical windows, lenses, and prisms. However, no one from the existing crystals completely fulfills all the obligatory requirements needed for the practical applications. Therefore, further studies at all levels are necessary to explore their potential in the existed crystals or search for new one which can fulfill all the necessary requirements for the practical applications, particularly for “UV-Deep UV wave bands”. Also, halide-based perovskites have emerged as an interesting and promising class of low-cost and highly efficient materials for solar cells [13]. Although over a longer period of time their efficiency and fabrication were too low owing to assorted structural instabilities and using conventional methods [14–16]. Fabrication of new halide-based perovskites is interesting due to ever revealing the variety of amazing properties, their possible applications in technology and have ability to involve more or less all elements of the periodic table [17–20].

Here, we investigate the structural, electronic, optical and thermodynamics properties of the NaCaF₃ and NaSrF₃ compounds. The total energy calculations are performed within FP-LAPW method embodied in WIEN2k code and structured within the DFT. The organization of the paper is; Section 2 briefs a description of computational method, while Section 3 presents results and discussion. Conclusions are summarized in Section 4.
2. Computational method

All the calculations have been carried out using the full potential linearized augmented plane wave (FP-LAPW) method [21] based on DFT [22,23] by means of WIEN2k code [24]. The description of exchange and correlation effects was considered here within generalized gradient approximation (GGA) [25], and local density approximation (LDA) [26]. In this scheme, the partition of the simulated crystal unit cell is divided into two parts; non-overlapping muffin-tin (MT) spheres considered around the atomic positions, and an interstitial region. In this approach, different basis sets are used for the both regions of crystal unit cell. Inside the non-overlapping MT spheres, the wave function is described using a “linear combination of radial functions times spherical harmonics”, whereas, in the interstitial region, expansion is achieved in terms of plane waves. To achieve a reasonable level of the convergence, value of the quantum number, \( l = 10 \) is used to expand the wave function inside the sphere, where the value of \( R_{\text{MT}} K_{\text{max}} = 8 \) (\( R_{\text{MT}} \) represents the minimum atomic sphere radii whereas \( K_{\text{max}} \) is used for the largest value of \( k \)-vector in the plane wave expansion) is chosen. Similarly, the charge density and potential, inside the atomic spheres are expanded in lattice harmonics and Fourier expansion in the interstitial region. Fourier expanded charge density is truncated at \( G_{\text{max}} = 12 \) (a.u.) \(^{-1} \). The Monkhorst–Pack \( k \)-mesh of \( 17 \times 17 \times 17 \) was used for integration over the Brillouin zone [27]. The convergence criterion for the total energy about 0.1 mRy was achieved.

The thermodynamic properties for the interested compounds were derived by employing “the quasi-harmonic Debye model” based on the Helmholtz free energy. The authentication of this approach has been well justified already by many previous studies.

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<th>X–X</th>
<th>M–M</th>
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<td><strong>NaCaF(_3)</strong></td>
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<td>LDA</td>
<td>8.67</td>
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<td>GGA</td>
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<td><strong>NaSrF(_3)</strong></td>
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<tr>
<td>LDA</td>
<td>7.46</td>
<td>4.48</td>
<td>6.36</td>
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<tr>
<td>GGA</td>
<td>7.28</td>
<td>4.32</td>
<td>6.19</td>
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\(^{a}\) [37].

Fig. 2. Calculated electronic band structure of NaCaF\(_3\) and NaSrF\(_3\).
The calculation of bulk modulus $B$ can also be done with “quasi-harmonic Debye model” at different temperatures and pressures. The type of non-equilibrium Gibbs function, $G^*$ used in this model is [30];

$$G^*(V; P, T) = E(V) + PV + Vib(V; T)$$  \hspace{1cm} (1)

where $E(V)$ represents total energy values with respect to unit cell volume, $PV$ is to signify the constant hydrostatic pressure condition and $A_{ vib}$ stands for the "vibrational Helmholtz free energy" and expressed as [31,32];

$$A_{ vib} (\theta_D; T) = nkT \left[ \frac{9}{8} \frac{\theta_D^2}{T^2} \ln(1-e^{-\theta_D/T}) - D(\theta_D/T) \right]$$  \hspace{1cm} (2)

In Eq. (2), $\theta_D$, $D(\theta_D/T)$ and $n$ refer to Debye temperature, Debye integral and number of atoms per formula unit, respectively. By minimizing the $G^*$ with respect to volume and solving corresponding equation, following relation is obtained;
From this, one can obtain relations for the isothermal bulk modulus $B$, heat capacity $C_v$ and thermal expansion coefficient $\alpha$ as:

$$
\left. \left( \frac{\partial G^*(V; pT)}{\partial V} \right) \right|_{p, T} = 0
$$

(3)

From this, one can obtain relations for the isothermal bulk modulus $B$, heat capacity $C_v$ and thermal expansion coefficient $\alpha$ as:

$$
B_T(P, T) = -V \left( \frac{\partial p}{\partial V} \right)_T = V \left( \frac{\partial^2 G^*(V; p, T)}{\partial V^2} \right)_{p, T}
$$

(4)

$$
C_v = 3nk \left[ 4D(\partial_H/T) - \frac{3\nu p/T}{e^{\nu T} - 1} \right]
$$

(5)

Fig. 4. Calculated imaginary part of the dielectric function $\varepsilon_2(\omega)$ of NaCaF$_3$ and NaSrF$_3$.

Fig. 5. Calculated real part of the dielectric function $\varepsilon_1(\omega)$ of NaCaF$_3$ and NaSrF$_3$. 
where $\gamma$ is the Grüneisen parameter. The more detailed explanation can be seen in Refs. [33,34]. From the above equations, the thermodynamic properties of NaCaF$_3$ and NaSrF$_3$ can be obtained.

3. Results and discussion

3.1. Structural properties

The simulated crystal unit cell with Wyckoff atomic sites, Na at 1b (0.5, 0.5, 0.5), X at 1a (0, 0, 0) and F at 3d (0.5, 0, 0) where X = (Ca, Sr), were optimized. The total energy is calculated as a function of unit-cell volume around the equilibrium cell volume $V_0$. 

$$\alpha = \frac{\gamma C_v}{B_1 V'}$$

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Fig. 6. The calculated refractive index $n(\omega)$ of NaCaF$_3$ and NaSrF$_3$.

Fig. 7. The calculated extinction coefficient $k(\omega)$ of NaCaF$_3$ and NaSrF$_3$. 

$$\alpha = \frac{\gamma C_v}{B_1 V'}$$
The total energies versus volume presented in Fig. 1 are obtained by fitting the obtained data to the Birch–Murnaghan equation of state [35]. The corresponding equilibrium lattice constant $a_0$, bulk modulus $B$, and its pressure derivative $B'$, together with other theoretical values, evaluated within LDA and GGA are given in Table 1. As can be seen, the calculated lattice constants are in agreement with other results [36–38]. It can also be seen that the computed results of NaCaF$_3$ have smaller values of lattice constants than that of NaSrF$_3$. The bulk modulus is a measure of the crystal rigidity (where the rigidity of a material is a measure of its resistance against any change to its permanent shape). Thus, we can say that NaCaF$_3$ is more rigid than NaSrF$_3$ owing to the fact that bulk modulus of NaCaF$_3$ is higher than NaSrF$_3$.

3.2. Electronic properties

The calculated electronic energy bands profile of NaCaF$_3$ and NaSrF$_3$ along with high symmetry points X, R, M and $\Gamma$ inside the
first Brillouin zone at zero pressure, within the GGA are illustrated in Fig. 2. From the band structure, it is clear that the valence band maximum (VBM) of NaCaF$_3$ compound is located at point R, whereas in case of NaSrF$_3$, it is located at point $\Gamma$. However, their conduction band minimum (CBM) is found at the same point for both compounds i.e. at the point $\Gamma$, showing that NaSrF$_3$ is a direct band gap at ($\Gamma - \Gamma$) compound and NaCaF$_3$ is an indirect band gap at (R-$\Gamma$), similar to other reported fluoride perovskites in the literature [39–42]. As seen in Table 2, our calculated band gaps for NaCaF$_3$ and NaSrF$_3$ equal 5.16 (4.88) eV and 4.50 (4.26) eV, respectively. For the sake of meaningful comparison, unfortunately, no theoretical or experimental data about energy band gap values of these compound are found in the literature. It should be noted that LDA (GGA) approximations for the exchange correlation usually underestimate the energy band gap calculated within DFT formalism [43, 44]. This is due to the solutions of Kohn-Sham equation, at the level of LDA or GGA, do not correspond to the quasi-particle excitations. Therefore, it can be said that, our calculated results predict insulators.

Seeking to have more comprehensive picture of electronic structure, the profile of the total density of states (TDOS) as well as the partial density of states (PDOS) for both NaCaF$_3$ and NaSrF$_3$ compounds are also shown in Fig. 3 over an energy range from $-20 \text{ eV}$ to 15 eV at GGA. From Fig. 3, it can be seen that the valence band close to Fermi level is mainly formed by F-2p states with a very small contribution from Na-s and p states. Whereas in low-energy valence band, the deep electronic states localized in the vicinity of $-20 \text{ eV}$, below the Fermi energy for both NaCaF$_3$ and NaSrF$_3$ compounds are populated by F-2s states. The structure situated at around $-15 \text{ eV}$ for NaCaF$_3$ and $-12 \text{ eV}$ for NaSrF$_3$ consists of Ca-p and Sr-p states, respectively. On the other hand, in the conduction band of both compounds, Na-s and p states are primarily presented, with a noticeable part from Ca-p and Sr-p states.

3.3. Optical properties

To evaluate the optical properties, complex dielectric function, $\varepsilon(\omega)$ is used. It is expressed as [45,46]:

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

(7)

where $\varepsilon_1(\omega)$ represents the real part, and $\varepsilon_2(\omega)$ represents the imaginary part. The imaginary part of the dielectric function of a solid is derived from its electronic band structure in accordance with the following relation [47]:

$$\varepsilon_2(\omega) = \frac{e^2 \hbar}{\pi m^* \omega^2} \sum_{\nu\gamma} \int_{BZ} |M_{\nu\gamma}(k)|^2 \delta[\omega_{\nu\gamma}(k) - \omega]dk$$

(8)

Here, $M_{\nu\gamma}(k) = \langle u_{\nu\gamma} | \mathbf{\delta} \cdot \nabla | u_{\nu\gamma} \rangle$ is the momentum dipole elements (\mathbf{\delta} is used for potential vector which defines the electric field), which represents matrix elements for the direct transitions between conduction band $u_{\nu\gamma}(r)$ states and valence band, $u_{\nu\gamma}(r)$ is energy states, and $\hbar\omega_{\nu\gamma}(k) = E_{\nu\gamma} - E_{\nu\gamma}$ gives the related transition energy. By employing Kramers–Kronig relation, the real part of the complex dielectric function $\varepsilon_1(\omega)$ is calculated from the imaginary part $\varepsilon_2(\omega)$ as:

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

(9)

In the relation, $P$ entails the main value of the integral. In order to determine other optical parameters (refractive index $n(\omega)$,
extinction coefficient \( k(\omega) \), absorption coefficient \( I(\omega) \) and reflectivity \( R(\omega) \), the following expressions were applied [36]:

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

\[
k(\omega) = -\frac{\varepsilon_1(\omega)}{2} + \frac{\sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)}}{2} \right]^{1/2}
\]

\[
I(\omega) = \sqrt{2} \omega \left[ \sqrt{\varepsilon_1^2(\omega) + \varepsilon_2^2(\omega)} - \varepsilon_1(\omega) \right]^{1/2}
\]

\[
R(\omega) = \frac{n + ik - 1}{n + ik + 1}
\]

All the above mentioned optical parameters have been evaluated using calculated equilibrium lattice constants at the level of GGA over energy range up to 40 eV. The obtained results for both NaCaF\(_3\) and NaSrF\(_3\) compounds are presented in Figs. 4 and 5. The \( \varepsilon_2(\omega) \) part of \( \varepsilon(\omega) \) gives the total sum of all transitions. In Fig. 4, the structures of the optical response show a shift towards lower energies as we move from Ca to Sr, showing their agreement with other band structures. From the closer look at \( \varepsilon_2(\omega) \) dispersion curves, we see,
first critical point (fundamental absorption edge) for the NaCaF$_3$ and NaSrF$_3$ are approximately found at 4.96 eV and 4.20 eV, respectively. These values are in line with the indirect and direct transitions between VBM and CBM, at the points (R–Γ) and (Γ–Γ) for NaCaF$_3$ and NaSrF$_3$, respectively. The rise in the curve is too fast due to numbers of transitions contributing to $\varepsilon_2(\omega)$ which are suddenly increased.

The real part $\varepsilon_1(\omega)$ of frequency-dependent dielectric function evaluated from the Kramers–Kronig dispersion relation is shown in Fig. 5. The main peaks are located at 9.75 eV and 10.13 eV for NaCaF$_3$ and NaSrF$_3$, respectively. The curves for both compounds show an almost similar trend. From the curves, it can be seen first, the curves are fallen following by rising, then again fall followed by a slow rise at high energy value. The calculated static dielectric constant $\varepsilon_1 (0)$ is about 1.95 for both compounds. It can be seen from the plots, the zero's value of $\varepsilon_1 (\omega) (\varepsilon_1 = 0)$ shows non existence of the dispersion, which reflects its perfect coincidence with the absorption coefficient's maximum value $I(\omega)$ located at 13.56 eV.

From the Eqs. (10)–(13), it can be observed easily that with the simple knowledge of $\varepsilon_1(\omega)$ and $\varepsilon_2(\omega)$, one determines other optical parameters like refractive index $n(\omega)$, extinction coefficient $k(\omega)$, absorption coefficient $I(\omega)$, energy loss $L(\omega)$ and reflectivity $R(\omega)$. The calculated results of $n(\omega)$ and $k(\omega)$ are shown in Figs. 6 and 7, respectively. At zero photon energy, the value of static refractive index $n(0)$ is found to be approximately equal to 1.40 for both NaCaF$_3$ and NaSrF$_3$ compounds. All the maxima of the refractive index

Fig. 12. Temperature dependence of the Bulk modulus $B_0$ at various pressures for (a) NaCaF$_3$ and (b) NaSrF$_3$. 

and extinction coefficient are localized at nearly equal photon energy values.

The absorption coefficient $\alpha(\omega)$ depicted in Fig. 8, reveals the high absorption at high photon energies. Although NaCaF$_3$ shows higher value compared to NaSrF$_3$ for both NaCaF$_3$ and NaSrF$_3$ compounds, the values of absorption coefficient are at 25.67 and 21.62 eV. This shows that both materials exhibit considerable absorption. The frequency of plasma resonance can be estimated from the energy loss spectra, as shown in Fig. 9. The maximum resonant energy loss is found equal to 30.08 and 26.68 eV for NaCaF$_3$ and NaSrF$_3$, respectively. Fig. 10 shows the calculated reflectivity $R(\omega)$. From this curve, the zero-frequency limit of reflectivity for NaCaF$_3$ and NaSrF$_3$ is found to be 0.028 and 0.027, respectively. There are high reflection peaks at energies 10.78 eV, 25.02 eV, 28.94 eV for both compounds as well.

3.4. Thermodynamic properties

The thermal properties of NaCaF$_3$ and NaSrF$_3$ compounds under high temperature and pressure have been investigated within the quasi-harmonic Debye model. At a first stage, we have obtained the numerical total energy as a function of unit cell volume i.e., $E(V)$, in the static approximation approach. At a second stage, the equation of state (EOS) was derived by numerical fittings. And then by using the EOS, the structural parameters (at zero temperature and pressure) and corresponding macroscopic properties as a function of the pressure and temperature have been derived. Here, the investigation of thermal properties is carried out within temperature
range from 0 to 1000 K, assuming the quasi-harmonic model validity, and the pressure is considered a range 0–40 GPa. The equilibrium unit cell volume $V_0$ versus the temperature, for NaCaF$_3$ and NaSrF$_3$, at different pressures, is presented in Fig. 11. We can see that the volume $V_0$ (a, lattice constant) increases monotonically as temperature increases, and on another side, it decreases, at a given temperature, with pressure P. The lattice constants, obtained for NaCaF$_3$ and NaSrF$_3$, were found to have 4.46 and 4.76 Å, respectively, at zero pressure and room temperature. As noticed in Fig. 12, the bulk modulus is almost a constant at given pressure, within the temperature range from 0 to 120 K, and then it starts decreasing linearly for a temperature greater than 120 K at a given pressure. However, at a given temperature, it increases with pressure. The calculated values of bulk modulus, at 300 K and zero pressure, for both NaCaF$_3$ and NaSrF$_3$ are found to be 98 GPa and 77.7 GPa, respectively.

The vibration properties can be accessed through the heat capacity. Therefore, heat capacity at constant volume, $C_V$, was calculated as a function of temperature, at given pressure (0, 10, 20, 30 and 40 GPa). The results obtained for NaCaF$_3$ and NaSrF$_3$ are shown in Fig. 13. As can be seen from the presented diagram, initially the $C_V$ curve is sharply increased up to 300 K, but next to it, its increasing is very slow. At further high temperature $C_V$ tends to approach the limiting value $3R$, agreeing with the Dulong–Petit law [37]. The diagrams given in Fig. 13 clearly indicate that at $T < 500$ K, the heat capacity $C_V$ depends on both temperature and pressure ($C_V$ is proportional to $T^3$ [48]).

The Debye temperature ($\theta_D$) can also be obtained from the low temperature heat capacity measurements. $\theta_D$ is also accessible for the evaluation by means of elastic constants. It is a characteristic temperature that may be evaluated from the phonon spectrum of the crystal as well. Fig. 14 illustrates the temperature dependence of $\theta_D$, over the pressure range 0–40 GPa, for both NaCaF$_3$ and NaSrF$_3$. 

Fig. 14. Variation of the Debye temperature $\theta_D$ as function of temperature at various pressures for (a) NaCaF$_3$ and (b) NaSrF$_3$. 

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compounds. As can be observed from Fig. 14, ⁶θ is nearly constant from 0 to 200 K and decreases linearly with temperature. Our calculated ⁶θ at zero pressure and ambient temperature are 622.57 K and 491.36 K for NaCaF₃ and NaSrF₃, respectively. Probably, this indicates that the quasi-harmonic Debye model ensures the efficient account of contributions of thermal vibrations in the crystal thermodynamic functions.

4. Conclusions

The structural, electronic, optical and thermodynamic properties of NaXF₃ (X = Ca and Sr) compounds using FP-LAPW method within LDA and GGA, have been evaluated from first-principles calculations. The most notable results are represented as:

- The obtained basic ground-state properties such as equilibrium lattice constants and bulk moduli are in good agreement with other data. The lattice constants evaluated within GGA are larger, whereas the bulk moduli are smaller, compared to those found with LDA.
- The electronic structure calculations showed that both compounds follow a similar trend, with a wide indirect band gap (R–Γ) for NaCaF₃ and direct band gap (Γ–Γ) for NaSrF₃.
- Corresponding total and partial DOS are analyzed and the nature and structure of the relevant curves are identified.
- The materials have wide band gaps. Moreover, the dispersion of imaginary part of dielectric function reveals its transparency for a wide range of energies. Therefore, we conclude that they are promising candidates for application in optoelectronics to capture the ultraviolet region.
- The quasi-harmonic Debye model employed appeared to be effective for the description of the material properties, namely an equilibrium volume, bulk modulus, heat capacities and Debye temperature, at the temperature and pressure conditions, in which the anharmonicity not significantly affects the thermodynamic parameters.

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References