



# Theoretical Study of Rhombohedral NaCaF<sub>3</sub> Crystal in the Predicted Ferroelectric Phase

B. ERDINC<sup>1,\*</sup>, M. AYCIBIN<sup>1</sup>, M. N. SECUK<sup>1</sup>, S. E. GULEBAGLAN<sup>1</sup>,  
E. K. DOGAN<sup>1</sup>, H. AKKUS<sup>1</sup>

<sup>1</sup>Physics Department, Faculty of Science, Yuzuncu Yil University, 65080, Van, Turkey

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## ABSTRACT

The calculated results for structural optimization, electronic band structure, total density of states and optical properties of a rhombohedral NaCaF<sub>3</sub> compound were discussed using generalized gradient approximation under the density functional theory. According to our calculation, NaCaF<sub>3</sub> crystal has a direct band transition. Moreover, optical properties of NaCaF<sub>3</sub> were investigated using scissor approximation. This is the first theoretical study of rhombohedral crystal structure of NaCaF<sub>3</sub> as far as we know.

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**Keywords:** Density functional theory; Electronic band structure; Optical properties.

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## 1. INTRODUCTION

Ferroelectric materials have been investigated intensively by physicists. The ferroelectricity was first observed in insulator materials having hydrogen bonds. However, the observation of ferroelectricity in some insulator materials not having hydrogen bonds and semiconductors has increased the interest and speeded up the idea of using these ferroelectric materials in industrial areas. The investigation of such materials and determination of their physical properties gave opportunities to understand ferroelectric properties being used in various fields such as sonar detectors, memory devices and audio converters.

Many of halide based perovskite-like compounds having chemical formula ABF<sub>3</sub> show ferroelectric behaviors. Due to simplicity of the crystal structures, the halide based perovskite-like crystals are intensively investigated ferroelectric materials. Moreover, they are very important because of their technological uses and there is fundamental interest in their phase transition phenomena. Depending on temperature values, many ABF<sub>3</sub> compounds undergo a phase transition from ferroelectric to anti-ferroelectric. At zero pressure, the ideal structure of ABF<sub>3</sub> compound is a simple cubic,

where cation A ion is located at the corner, the cation B ion lies in the center, while anion F ions are in the face centers of the cube.

Among these important ABF<sub>3</sub> compounds, the NaCaF<sub>3</sub> was estimated to have a ferroelectric state [1-9]. In the estimated ferroelectric phase of NaCaF<sub>3</sub>, the compound has rhombohedral structure with two NaCaF<sub>3</sub> molecules per unit cell and every molecule has five atoms. The space group of rhombohedral NaCaF<sub>3</sub> structure is R3c [2]. The calculated positions of the atoms and the calculated lattice constants in its unit cell are given in Table 1 [2].

As a result of our research, we concluded that neither experimental study nor theoretical study of electronic structure and optical properties of NaCaF<sub>3</sub> crystal have been reported using first-principles calculations yet. The electronic structure of NaCdF<sub>3</sub> having the same symmetry of NaCaF<sub>3</sub> was studied using the first-principle total energy calculations [2, 3]. The electronic and linear optical properties of NaCdF<sub>3</sub> crystal in the rhombohedral phase were investigated using density functional method [3]. The calculated energy band gap of this crystal is 6.6 eV [2] at the  $\Gamma$  symmetry point in the Brillouin zone. Also, the predicted experimental

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\*Corresponding author, e-mail: [bahattinerdinc@yyu.edu.tr](mailto:bahattinerdinc@yyu.edu.tr)

energy gap of NaCaF<sub>3</sub> compound is about 8-9 eV [2]. NaCaF<sub>3</sub> can be a good candidate for a frequency conversion material working in the region of ultraviolet light [2]. A thorough study of instabilities in NaCaF<sub>3</sub> was made using Gordon Kim potentials [4] and found that NaCaF<sub>3</sub> were good candidates for ferroelectric phase [5]. Molecular dynamic simulations for NaCaF<sub>3</sub> was performed and predicted that ferroelectric transition occurs at 550 K [1]. The electronic and vibrational properties for NaCaF<sub>3</sub> were calculated using the self consistent atomic deformation method [6, 7]. The effect of structural phase transitions in NaCaF<sub>3</sub> was investigated using lattice statics and molecular dynamics [8]. The ferroelectric behavior of NaCaF<sub>3</sub> was demonstrated using a constant pressure Monte Carlo simulation [9]. The molten salt solution of NaCaF<sub>3</sub>, Na<sub>2</sub>CaF<sub>4</sub> and Na<sub>3</sub>CaF<sub>5</sub> was studied using molecular dynamics simulation [10].

The wide energy band gap of NaCaF<sub>3</sub> compound has received considerable attention for device applications in the ultraviolet wavelengths and scientific, technological areas due to their interesting nonlinearities, electro-mechanic and electro-optic properties and phase transitions. In the present study, the physical properties of rhombohedral NaCaF<sub>3</sub> compound were calculated using generalized gradient approximation based on density functional theory.

## 2. COMPUTATIONAL DETAILS

The structural optimization, electronic band structure, total density of states and optical properties of rhombohedral NaCaF<sub>3</sub> were calculated by using self-consistent norm-conserving Troullier-Martins [11] pseudo-potentials written in FHI98PP software [12]. Plane wave basis sets were used for electronic wave functions. Kohn-Sham equations [13] were solved by using conjugate gradient minimization method [14] with ABINIT software [15]. Both production of pseudo-potential and calculation of band structure were investigated under the generalized gradient approximation [16]. The 3s electrons of Na atom, 4s electrons of Ca atom and 2s and 2p electrons of F atom were taken as a real valance electrons. All the calculations included two molecules per unit cell. A good convergence for the bulk total energy calculation was performed when cut-off energies were taken as 50 Hartree with 6×6×6 Monk-Horst-Pack mesh grid [17]. On the other hand, the irreducible Brillouin zone was sampled with 8×8×8 k-points for calculating optical properties of NaCaF<sub>3</sub>.

Frequency dependent complex dielectric function for a material is usually defined as  $\epsilon(\omega) = \epsilon_1 + i\epsilon_2(\omega)$ . In general, this equation describes optical response of

material. The frequency dependent complex dielectric function's real ( $\epsilon_1(\omega)$ ) and imaginary ( $\epsilon_2(\omega)$ ) parts contain all required response information. Here, imaginary part can be given by calculation of momentum matrix elements between occupied and unoccupied wave functions with selection rule. If the imaginary component of dielectric function is known, Kramer-Kronig relations let us calculate real component of the dielectric function. After calculating complex dielectric function, the rest of optical constants such as energy loss function, refraction index, extinction coefficient, reflection coefficient and absorption coefficient of a solid can be calculated [18].

Kohn-Sham equations, based on the density functional theory, are used to determine properties of ground state and unoccupied conduction band states having no physical meaning. If these bands are used in calculation of optical properties for single particle case, the optical absorption will start at low energy states [19]. For this reason, the application of self consistent ground state energies on the excited spectrum requires the correction of eigenenergies. One of the approximations to calculate self-energy effects is Scissors approximation [19]. Scissors shift was taken as 2.5 eV for adjusting experimental and theoretical band gaps to the same value by Chun-gang Duan *et al* [2].

## 3. RESULTS AND DISCUSSION

The crystalline structure of rhombohedral NaCaF<sub>3</sub> was investigated using various techniques such as [1, 10]. NaCaF<sub>3</sub> compound has rhombohedral crystal structure with the space groups *R3c*. The obtained crystal data from first-principles calculations using lattice constant values of Gordon and Kim (GK) are presented in Table 1. Using generalized gradient approximation under the density functional theory in ABINIT code, the total energy calculations of crystal were done. All physical properties of a material depend on either total energy or differences of total energies. Calculating total energy lets us to obtain a physical property linked to total energy.

To calculate lattice constant corresponding to ground state energy value theoretically, the ground state energy of rhombohedral NaCaF<sub>3</sub> was calculated for different theoretical lattice constants using experimental lattice constant. The total energy as a function of volume is shown in Figure 1. As given in Table 1, the calculated and previously obtained theoretical volume values were compared and found to be in good agreement. Moreover, the optimized atomic positions are given in Table 1.

Table 1 Crystal data of NaCaF<sub>3</sub> compound.

NaCaF <sub>3</sub>	Wycoff	Space group			R3c –Rhombohedral			GK [4]
		Calculated			Theoretical [2]			
		x	y	z	x	y	z	
Na	2a	0.292	0.292	0.292	0.289	0.289	0.289	
Ca	2a	0.002	0.002	0.002	0.000	0.000	0.000	
F	6b	0.881	0.614	0.210	0.879	0.617	0.212	
a (Å)		6.248			6.212			6.022
E <sub>g</sub> (eV)		6.31			6.6			-
Vol.(Å <sup>3</sup> )		160.053			157.302			143.305

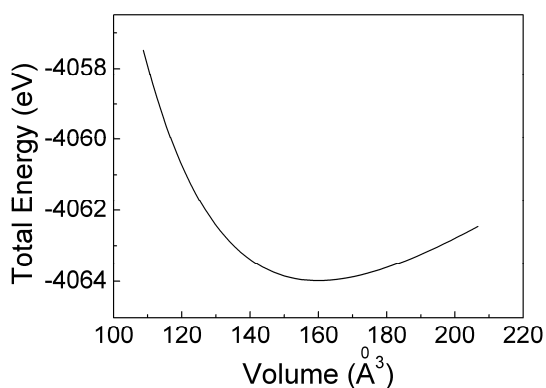


Figure 1. Total energy-volume dependence for NaCaF<sub>3</sub>.

Investigating electronic band structure can be helpful in better understanding electronic structure, density of states and optical properties of rhombohedral NaCaF<sub>3</sub>.

The calculation of electronic structure, density of states and optical properties of NaCaF<sub>3</sub> are shown in Figure 2 and 3. As can be seen in the Figure 2, we set the Fermi level as a zero level. The obtained band structure of this compound has a direct band gap, 6.31 eV, at the  $\Gamma$  symmetry point of the Brillouin zone. The calculated band gap is congruent with the obtained theoretical band structure [2]. From experimental study, the estimated band gap of this compound is around 8-9 eV. Due to imperfection of the method, band gap values calculated by pseudopotential method are smaller compared to those obtained from experimental ones. To adapt theoretical calculation with measured value of band gap, we need to apply scissors operator approximation which is utilized in calculating optical parameters.

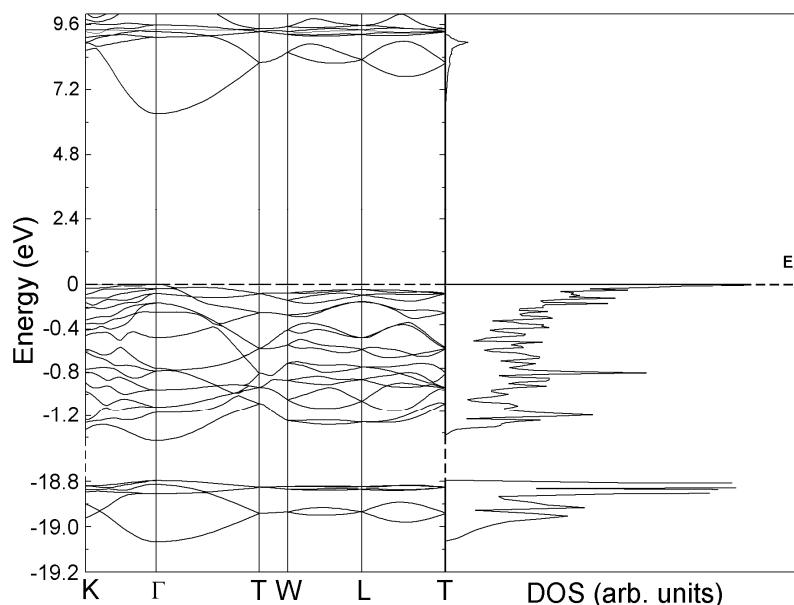


Figure 2. Calculated band structure for rhombohedral NaCaF<sub>3</sub> crystal.

The calculated optical properties of NaCaF<sub>3</sub> are investigated and plotted in Figure 3. In all calculations, vibrational effects of lattice are neglected and only electronic transitions are counted. We choose an energy

range of 0-30 eV for photons in calculation of the optical response and found that 0-20 eV range is sufficient. Then, we have derived values of real and

imaginary parts of the dielectric function and the optical constants.

We can investigate the frequency dependent behavior of NaCaF<sub>3</sub> compound. The frequency-dependent real and the imaginary parts are calculated and plotted in Figure 3a. The imaginary part,  $\epsilon_2(\omega)$ , shows peaks at 9.13, 9.57, 9.96, 10.65, 11.28, 12.16, 13.03, 13.47 and 15.62 eV. Given peaks correspond to transitions from valance to conduction band. Region I in Figure 3a is characterized by high transparency. No absorption is observed in 0-9 eV photon-energy range but a small reflection can be detected and transparency is high in this range. Although there is no absorption in region I in Figure 3a, the reflectivity can be noticeable. That simply means that the polarization current corresponding to oscillation of valance electrons causes the reflectivity. Region II in Figure 3a has a strong absorption and noticeable reflectivity in the photon energy range between 9.00 - 12.00 eV. In this region, optical absorption increases rapidly. Region II in Figure 3a indicates that the values of refractive index and extinction coefficient may be high. This means that the light on material is strongly absorbed and not reflected. Region III in Figure 3a is characterized by high reflectivity in the 12 to 15 eV photon-energy range. As if photon energy in this region is much greater than the binding energy of the electron, the electrons of NaCaF<sub>3</sub> compound can response. Region IV in Figure 3a is characterized by high transparency in the 15 to 20 eV

photon-energy range. The real part,  $\epsilon_1(\omega)$ , is also shown in Figure 3a. The calculated static dielectric constant is 1.91. Figure 3a shows that the real part becomes zero at values of 13.57 and 17.38 eV. These points mostly consist of plasmon excitations and scattering probabilities of the volume and surface losses are directly related to the energy loss function peaks.

The obtained energy-loss functions for volume and surface are plotted in Figure 3b and Figure 3c, respectively. Energy loss of fast electrons, making transitions in material, is described by energy-loss functions. The calculated energy-loss functions for the volume and the surface show mainly intense maxima, one peak at 17.40, and two peaks 15.00 and 16.30 eV values, respectively. The peak value for volume loss, 17.40, coincides with a zero value of dielectric function's real part. These sharp maxima are related with the existence of plasma oscillation.

For calculating refractive index, the 0 – 1  $\mu\text{m}$  photon-wavelength range was taken and shown in Figure 4a. In Figure 4a, it obvious that maximum value of refractive index depending on wavelength was obtained as 2.23. The calculated refractive index value is 1.36. Effective number of valance electrons ( $N_{eff}$ ) can be calculated using means of the sum rule [20]. As seen from Fig. 4b, up to 8.80 eV the effective electron number is zero and saturates above 17.50 eV.

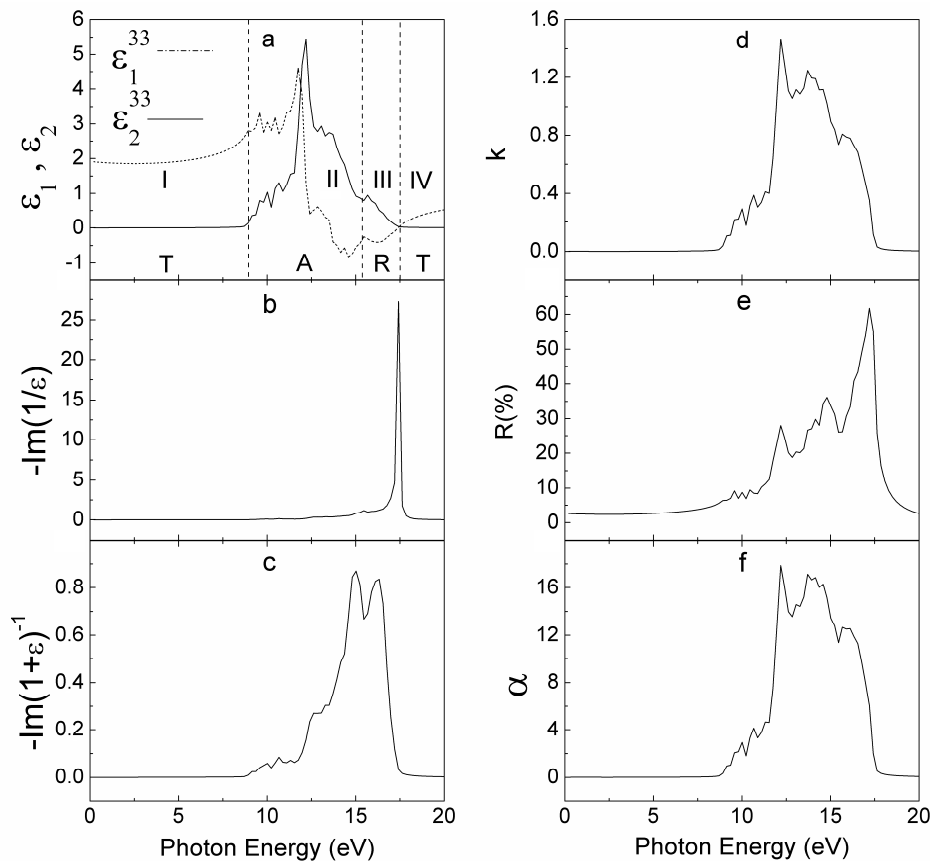


Figure 3. Optical properties of NaCaF<sub>3</sub> crystal

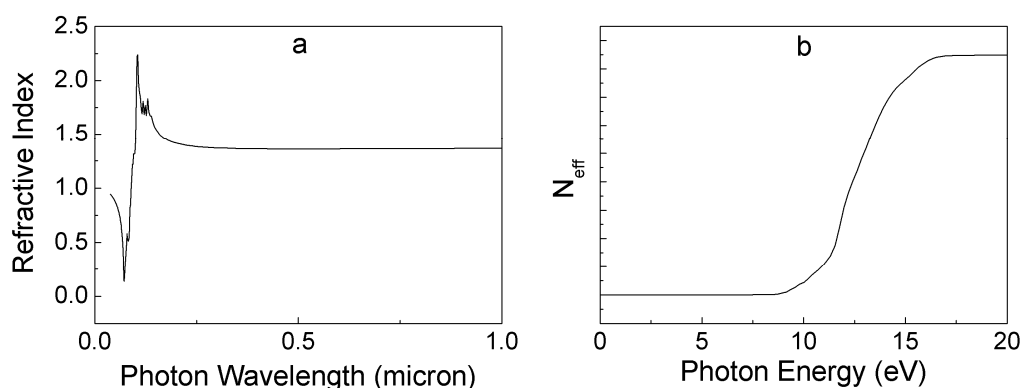


Figure 4. Refractive index dispersion and effective number of valence electrons for NaCaF<sub>3</sub> crystal.

#### 4. CONCLUSIONS

In this article, the structural optimization, electronic structure, total density of states and optical properties of rhombohedral NaCaF<sub>3</sub> crystal structure have been investigated in details using the density functional methods under the generalized gradient approximation. The calculated structure optimization of NaCaF<sub>3</sub> was compared with the previous experimental and theoretical results and found in a good agreement. As a result of calculations, it is seen that the fundamental gap of NaCaF<sub>3</sub> crystal structure is a direct transition at the gamma point in the Brillouin zone and in a good agreement with the previous theoretical values. The linear dielectric function was examined as a function of photonic energy. For the first time, the electronic band structure and optical properties of NaCaF<sub>3</sub> have been examined, calculated and discussed in detail.

#### CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

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