

# Incommensurate Phase Transition and Electronic Properties of BaMnF<sub>4</sub>

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**Abstract.** We present the ab initio study the electronic, mechanical and structural properties of BaMnF<sub>4</sub>. We discuss the trends in the electronic and mechanical properties of BaMnF<sub>4</sub> under pressure up to 80 GPa. BaMnF<sub>4</sub> belongs to the family of BaMF<sub>4</sub>-type fluorides (M = Mn, Fe, Co, Ni, Mg, Zn) which share the same orthorhombic structure. The main focus of this study is to elaborate the changes brought about in the electronic and the structural properties by applied pressure. The calculated lattice parameters have been in agreement with the available experimental and theoretical value. Band gap of BaMnF<sub>4</sub> in our calculation is about 2.0 eV, separating the empty upper-Hubbard t<sub>2g</sub> bands and occupied lower-Hubbard e<sub>g</sub> bands. The total and partial DOS corresponding to the electronic band structure are calculated. Comparative analysis of the results of these calculations shows that the band-gap energy of BaMnF<sub>4</sub> decreases with increasing pressure and has a minima value at a critical pressure (appr. 65 GPa), after which it increases again. Some fundamental physical parameters such as elastic constants, bulk modulus, Poisson's ratio, sound velocities and Debye temperature were calculated and interpreted, too.

**Keywords:** BaMnF<sub>4</sub>, multiferroic, incommensurate phase transition, band structure

## 1. Introduction

One of the very promising approaches to create novel materials is to combine in one material different physical properties to achieve rich functionality. The attempts to combine in one system both the ferromagnetic and ferroelectric properties started in 1960's [1], Materials combining these different "ferroic" [2] properties were later on called "multiferroics" [3].

Barium manganese fluoride BaMnF<sub>4</sub> one of the most favorite compound of the barium fluorides BaMF<sub>4</sub>, where M is Mn, Fe, Co, or Ni. This series of multiferroic compounds presents numerous interesting physical properties and has been the subject of experimental or theoretical studies [3]. It also presents interesting structural properties and, in particular, a structural transition at 250 K from a high-temperature (HT) phase to an incommensurate modulated phase which has already been widely investigated.



We hope that our work will inspire further research in this interesting class of multiferroic materials, with the goal of exploring a broader range of non-oxide-based materials as candidates for magnetoelectric device applications.

Here we present a comprehensive computational study of the structural, electronic, mechanical, and optical properties of BaMnF<sub>4</sub> using first principles electronic structure calculations. The goal is to elucidate the origin of ferroelectricity in these materials. We have determined that there is not much work in our literature research about these compounds that exhibit interesting physical properties. Spaldin et al. [3], using the DFT-GGA(+U) approach, calculated the density of states for BaMF<sub>4</sub> compounds and tried to explain the origin of ferroelectricity in these compounds. Our aim in this study is to fill this emptiness by examining the mechanical and optical properties of BaMnF<sub>4</sub> multiferroic compound under pressure which have not been studied theoretically as far as we know.

This paper is organized as follows. We first describe the methods we use in our calculations, together with some technical details. We then present the results of our calculations for the structural, electronic, and mechanical properties of BaMnF<sub>4</sub>. Finally, we analyze the mechanism underlying the polar structural distortions in this compound. We end with a discussion and summary.

## 2. Method of calculation

In all of our calculations that were performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) [4-7] that was developed within the density functional theory (DFT) [8], the exchange-correlation energy function is treated within a spin polarized GGA (generalized gradient approximation) by the density functional of Perdew et al. [9]. The potentials used for the GGA calculations take into account the 5s<sup>2</sup>5p<sup>6</sup>6s<sup>2</sup> electrons for Ba-atom, the 3p<sup>6</sup>4s<sup>2</sup>3d<sup>5</sup> electrons for Mn-atom and the 2s<sup>2</sup>2p<sup>5</sup> electrons for F-atom as valence states. To get good convergence, the kinetic energy cutoff for the total energy calculation is found to be 554 eV for BaMnF<sub>4</sub> compound. The Brillouin-zone integration was performed using special k points sampled within the Monkhorst-Pack scheme [10]. We found that the mesh of 5x5x4 and 9x9x9 k points was required to describe well of structural, electronic, and elastic properties. This k-point mesh guarantees a violation of charge neutrality less than 0.008e. Such a low value is a good indicator for an adequate convergence of the calculations.

## 3. Results and discussion

### 3.1. Structural properties

BaMnF<sub>4</sub> compound have the orthorhombic symmetry with space group Cmc2<sub>1</sub> (No:36). There are four molecules with 24 atoms in the unit cell of BaMnF<sub>4</sub> compound. As a first step of our calculations, we obtained equilibrium lattice parameters and atomic positions of BaMnF<sub>4</sub> using experimental data given in Ref. [11]. These obtained results were used in all subsequent calculations. The obtained results are given in Table 1. We see that the results of our structural optimizations are in very good agreement with the experiment data.

**Table 1.** The calculated and experimental lattice parameters for BaMnF<sub>4</sub> compound.

Material	Reference	a (Å)	b (Å)	c (Å)
BaMnF <sub>4</sub>	Present	4.285	15.355	6.086
	Exp. [11]	4.221	15.107	5.998
	Exp. [12]	4.22	15.08	5.99
	Exp. [13]	4.221	15.098	5.984
	Exp. [14]	4.211	14.853	5.924
	Exp. [15]	4.23	15.1	6.0
	Exp. [16]	4.215	15.096	5.966
	Exp. [17]	4.221	15.098	5.984
	Exp. [18]	4.220	15.100	6.00

### 3.2. Elastic properties

Elastic constants are vital in determining physical properties of solids, such as their mechanical stability, stiffness, the brittle and ductile behaviours, Debye temperature, thermal expansion coefficient and bonding nature between atoms. The elastic constants of orthorhombic crystals are characterized with nine independent elastic constants, that is,  $C_{11}$ ,  $C_{22}$ ,  $C_{33}$ ,  $C_{44}$ ,  $C_{55}$ ,  $C_{66}$ ,  $C_{12}$ ,  $C_{13}$  and  $C_{23}$  [19,20]. The elastic constants of  $\text{BaMnF}_4$  compound were calculated using the strain–stress method [21] as implemented in the VASP [6,7]. Mechanical stability criteria for orthorhombic crystals [22],

$$C_{11}>0, C_{22}>0, C_{33}>0, C_{44}>0, C_{55}>0, C_{66}>0, [C_{11}+C_{22}+C_{33}+2(C_{12}+C_{13}+C_{23})]>0, (C_{11}+C_{22}-2C_{12})>0, (C_{11}+C_{33}-2C_{13})>0, (C_{22}+C_{33}-2C_{23})>0,$$

The bulk modulus (B), shear modulus (G), Young's modulus (E) and Poisson ratios ( $\nu$ ) for orthorhombic crystals can be calculated using the Voigt-Reuss-Hill (VRH) method [23]. The transverse, longitudinal, average elastic wave velocities ( $\mathcal{V}_t$ ,  $\mathcal{V}_l$  and  $\mathcal{V}_m$ ) and Debye temperatures ( $\Theta_D$ ) of  $\text{BaMnF}_4$  compound have been calculated using the common relations given in Ref. [24,25].

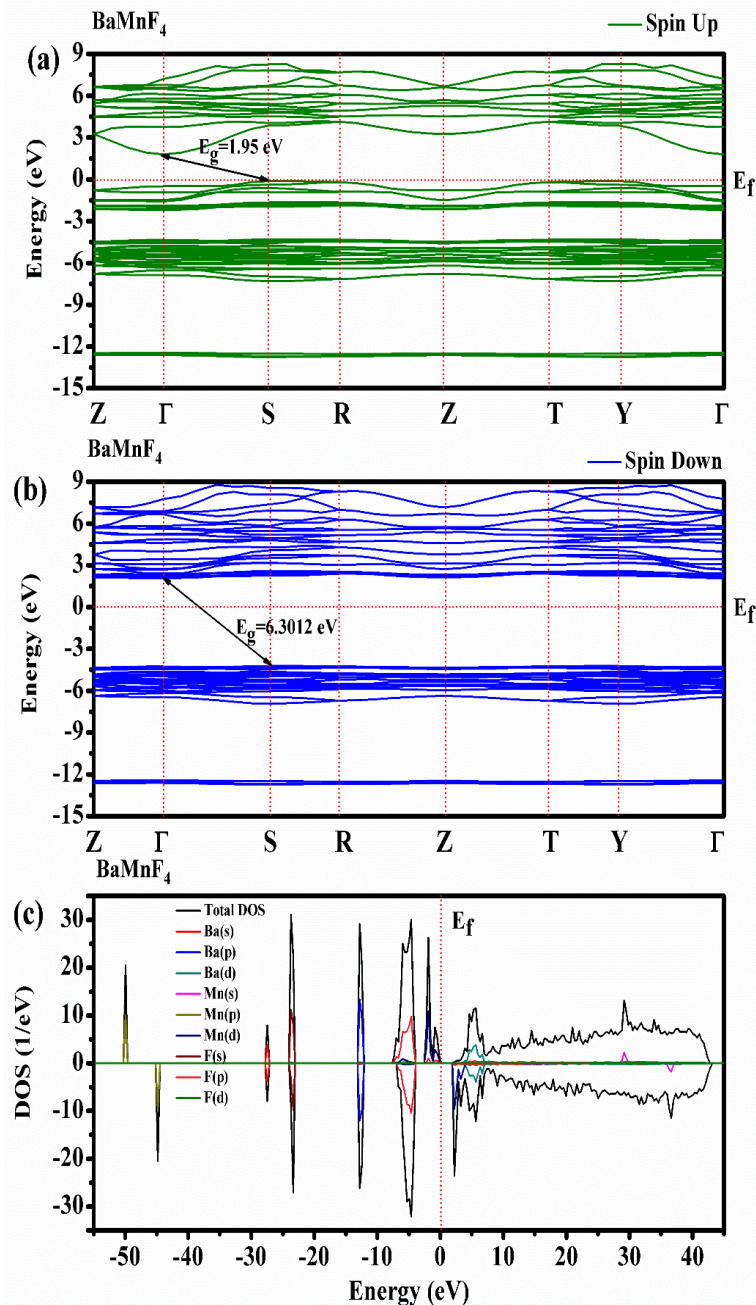
**Table 2.** The Poisson's ratio ( $\nu$ ), density ( $\rho$  in  $\text{g/cm}^3$ ), transverse, longitudinal, average elastic wave velocities ( $\mathcal{V}_t$ ,  $\mathcal{V}_l$  and  $\mathcal{V}_m$ , in m/s) and Debye temperature ( $\Theta_D$  in K) for  $\text{BaMnF}_4$  compound.

Pressure	$\nu$	B/G	$\rho$	$\mathcal{V}_t$	$\mathcal{V}_l$	$\mathcal{V}_m$	$\Theta_D(\text{K})$
0	0.316	2.387	4.449	2525	4872	2827	329.36
5	0.314	2.359	4.874	2040	3921	2283	274.28
30	0.324	2.518	6.374	3300	6477	3697	485.63
40	0.325	2.527	6.718	3451	6781	3867	516.95
60	0.324	2.517	7.275	3763	7385	4217	578.76
70	0.309	2.295	7.510	3791	7222	4240	588.18
80	0.326	2.543	7.728	3964	7806	4443	622.22

### 3.3. Electronic properties

The electronic structure plays an important role in determining the multiferroic properties of the  $\text{BaMnF}_4$ . The band structure of along the principal symmetry directions have been calculated by using the equilibrium lattice constants as shown in Table 1.

The majority spin (spin-up) (a) and minority spin (spin-down) (b) electronic band structures and partial and total DOS (c) of the  $\text{BaMnF}_4$  compound were calculated using GGA along the high symmetry directions in the first Brillouin zone (BZ) and, shown in Fig. 1. It is seen that for  $\text{BaMnF}_4$ , the majority spin states cross the Fermi level and thus have the semiconductor characters, while the minority spin states open the band gaps around the Fermi level and thus have the insulating nature with indirect transition between valence and conducting bands ( $\Gamma - S$ ).



**Figure 1.** The calculated electronic band structure and total density of states for the majority spin (spin-up) and minority spin (spin-down) of the BaMnF<sub>4</sub> compound.

The calculated total densities of states as well as the partial densities of the F p and Mn d states for BaMnF<sub>4</sub> is shown in Fig. 1. In the BaMnF<sub>4</sub> compound the gap is larger and is produced mainly by the strong exchange splitting between the two spin channels. In BaMnF<sub>4</sub> the forbidden gap is between occupied and unoccupied d states of the transition metal ion.

These results indicate that the use of the GGA is inadequate for the BaMF<sub>4</sub> systems, whereas the GGA method with an appropriate U value leads to a good description of the electronic structure. Since the overall features of the transition-metal d states in the present fluoride are very similar to the oxide cases. It can be seen from Fig. 1 that transition-metal cation are in a high-spin configuration,

where the local majority spin states are fully occupied, and the minority spin states are filled. In the case of the GGA, the transition-metal d states are energetically well separated from the fluorine p states, leading to only negligible hybridization between the two sets of states. The use of GGA lowers the energy of the filled transition-metal d states, leading to energetic overlap of these states with the fluorine p levels and a certain degree of hybridization. The evolution of the electronic structure of BaMnF<sub>4</sub> under compression was studied by employing DFT, too. Comparative analysis of the results of these calculations shows that the band-gap energy of BaMnF<sub>4</sub> decreases with increasing pressure and has a minima value at a critical pressure (appr. 65 GPa), after which it increases again.

#### 4. Conclusion

We have performed the structural, mechanical, and electronic properties of the BaMnF<sub>4</sub> multiferroic under pressure using density functional theory within the GGA approximation. The lattice parameters obtained as a result of geometric optimization are in good agreement with the experimental values. In the calculation of the calculated electronic band structure, BaMnF<sub>4</sub> compound is found as indirect band structured semiconductors in nature. The calculated elastic constants provide the mechanical stability. In addition, the calculated mechanical properties show that these compounds are ionic in character, less compressible, nearly rigid, low anisotropy, and dynamically stable.

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