First-principles study of structural, elastic, electronic and optical properties of cubic perovskite LiMgF$_3$ for novel applications

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Abstract. Structural, elastic and optoelectronic properties of materials are important to identify their applications in technology. In the present paper LiMgF$_3$ is investigated to obtain these properties using the highly accurate full-potential linearized augmented plane wave (FP-LAPW) method. The exchange correlation effects are included through the generalized gradient approximation (GGA) and modified Becke-Johnson (mBJ) exchange potential. The structural optimization of LiMgF$_3$ is compared with previous results and is found to be in good agreement with those results. The predicted band structure shows an indirect (M-Г) bandgap of 6.1 eV. The elastic properties such as elastic constants, anisotropy factor, shear modulus, Young’s modulus, Poisson’s ratio are calculated and based on these calculations it is found that this compound is elastically stable and brittle in nature. The contribution of different bands to the band structure is analyzed from the total and partial density of states curves. Optical properties like real and imaginary parts of dielectric function, refractive index, extinction coefficient, reflectivity, energy loss function, conductivity and absorption coefficient are presented. Based on the optical properties of the compound, it is predicted that LiMgF$_3$ is suitable for optoelectronic devices

1. Introduction

LiMgF$_3$ crystal is a candidate for vacuum-ultraviolet-transparent (VUV-transparent) material for lenses in optical lithography that are useful in the semiconductor industry [1,2]. Lithography technology requires to write more accurate circuit with many challenges like polarized light system, laser lens system, stronger light source, immersion technique, etc. Ternary compounds belonging to the group of fluoroperovskites have the general formula ABF$_3$, where A is alkali metal (A=Li, Na, K
and Rb) and B is alkaline-earth metal (B=Be, Mg, Ca, Sr and Ba). In this structure, ion A has large size than ion B. Moreover, the fluoroperovskite compounds can be used in the medical field to measure the dose during radiation therapy, and they may also be used in the manufacture of radiation imaging plates for X-rays, gamma-rays and thermal neutrons for medical and non-destructive testing applications. Perovskite-like fluorides generally have the wide bandgaps and are therefore preferable materials for lenses and transparent optical coatings. Thermoluminescence properties of LiMgF$_3$ doped with Ce, Er and Dy impurities are reported and suggested that this material is very attractive for many dosimetric applications [3]. Thermoluminescence characteristics of LiMgF$_3$ are activated by Dy ions [4]. The thermoluminescence properties of LiMgF$_3$ doped with ErF$_3$ (1,2 and 4 mol%) are investigated by Munoz et al.[5]. From the literature it is found that LiMgF$_3$ doped with Ce, Er and Dy ions exhibit dosimetric applications. In the literature it is observed that KMgF$_3$ is also used for similar applications as reported in both experimental [6-9] and theoretical studies [10, 11]. It is well known that the materials with band gaps larger than 3.1 eV work well in the ultraviolet (UV) region of the spectrum [12-15]. Since LiMgF$_3$ is like the other fluoroperovskites and has a wide band gap larger than 6.1 eV, then it can be effectively used in UV based optoelectronic devices. However, its characteristics have not been investigated in detail till now [16]. In order to take full advantage of the properties of LiMgF$_3$ for more technological applications, it is necessary to investigate some of the physical properties. The aim of this work is to investigate the structural, elastic, electronic and optical properties of fluoro-perovskite LiMgF$_3$ by density functional theory (DFT) using the full potential linearized augmented plane wave (FP-LAPW) method, with LDA, GGA, and (mBJ) techniques.

2. Computational details
The crystal structure of the fluoroperovskite LiMgF$_3$ compound is cubic and it belongs to the space group Pm-3m (#221). The unit cell contains one molecule where the Li sits at the origin (0, 0, 0), the Mg at the body center (0.5, 0.5, 0.5) and the three fluorine atoms at the three face centers (0, 0.5, 0.5), (0.5, 0, 0.5) and (0.5, 0.5, 0). ‘Figure 1’ shows the crystal structure of LiMgF$_3$. In this paper, our calculations are performed using the full potential linearized augmented plane wave (FP-LAPW) method within density functional theory (DFT) [17,18] in the local density approximation (LDA)[19], generalized gradient approximation (GGA) of Wu-Cohen[20] and modified Becke-Johnson (mBJ) potentials[21] as utilized in the WIEN2K package [22]. A satisfactory degree of convergence was achieved by considering a number of FP-LAPW basis functions upto RM$_{MT}$K$_{max}$ = 8.0 (RM$_{MT}$ is the smallest muffin-tin radius). The muffin-tin sphere radii RM$_{MT}$ are taken to be 2.2, 1.8 and 1.6 atomic units (a.u.) for Li, Mg and F, respectively. The k-integration over the Brillouin zone is performed using a mesh of 35 k-points in the irreducible wedge of the Brillouin zone. The optical properties of the compound are calculated by using a denser mesh of 102 k-points. Within these spheres, the charge density and potential are expanded in terms of crystal harmonics upto angular momentum l$_{max}$ = 10. The self-consistent calculations are considered to be converged when the total energy is stable within 0.01 mRy.

Figure 1. Crystal structure of LiMgF$_3$ obtained with XCrysDen
3. Results and discussion

3.1. Structural properties

In this subsection we calculated important structural parameters of LiMgF$_3$ using the volume optimization process. These parameters are the lattice constant, bulk modulus, pressure derivative of the bulk modulus and ground state total unit cell energy. The volume versus energy curve fits well by the Birch-Murnaghan equation of state [23]. From this fit, we can get the equilibrium lattice constant ($a_0$), bulk modulus ($B_0$) and pressure derivative of the bulk modulus ($B'$). These values are shown in Table 1.

![Figure 2. Dependence of total energy of cubic perovskite LiMgF$_3$ crystal on unit cell volume using GGA-WC.](image)

We performed our calculations by using LDA[19], GGA-WC[20] approximations. The total energy per unit cell of LiMgF$_3$ in the cubic perovskite structure is shown in ‘Figure 2’. Our calculated equilibrium lattice parameter ($a_0$) is in reasonable agreement with the experimental value. The bulk modulus ($B_0$) is a measure of the crystal rigidity, thus a large value of $B_0$ indicates high crystal rigidity. No previous experimental or theoretical result for this parameter is available for the LiMgF$_3$ compound for comparison with the present calculation.

| Method   | Lattice Constant $a_0$ (Å) | $B_0$ (GPa) | $B'$    | $E_0$ (Ry)     |
|----------|---------------------------|------------|---------|----------------|
| LDA      | 3.8057                    | 85.7465    | 4.2453  | -1010.6576     |
| GGA-WC   | 3.8757                    | 73.6252    | 4.3796  | -1014.4261     |
| Expt.    | 3.807$^a$                 |            |         |                |

$^a$ Ref. [2], Experimental value

3.2. Elastic Properties

We further estimated the elastic constants $C_{ij}$ of LiMgF$_3$ to characterize the elastic nature. The elastic constants $C_{ij}$ are fundamental and indispensable for describing the mechanical properties of materials. The elastic constants of solids provide a link between the mechanical and dynamical behaviour of crystals, and define how a material undergoes stress deformations and then recovers and return to its original shape after stress ceases [24]. The elastic constants can provide valuable information about the structural stability, the bonding character between adjacent atomic planes, and anisotropic character. For cubic system, we have three independent elastic constants $C_{11}$, $C_{12}$ and $C_{44}$. In order to determine them, the cubic unit cell is deformed using an appropriate strain tensor to yield an energy-strain relation. In this work, we have used the method developed by T. Charpin and implemented in the WIEN2K package [22]. The most interesting elastic constants such as the anisotropy factor (A), Young’s modulus (E), Shear modulus (G) and Poisson’s ratio $\nu$ are calculated by using the relations from references [25-27]. In Table 2, we listed the calculated elastic constants, the bulk modulus ($B_0$),
anisotropy factor \( A \), shear modulus \( G \) (in GPa), Young’s modulus \( E \) (in GPa) and Poisson’s ratio \( \nu \) of the selected material.

| \( C_{11} \) | \( C_{12} \) | \( C_{44} \) | \( B_0 \) | \( A \) | \( G \) | \( E \) | \( \nu \) | \( B/G \) |
|---------|---------|---------|---------|--------|--------|--------|--------|--------|
| LiMgF\(_3\) | 161.573 | 29.877  | 35.361  | 73.7756 | 0.5370 | 45.3981 | 84.3124 | 0.1825 | 1.6250 |

For calculating elastic constants of LiMgF\(_3\) we followed the method of GGA-WC. The calculated elastic constants \( C_{ij} \) are positive and satisfy the mechanical stability criteria [28] in a cubic crystal: \((C_{11} - C_{12}) > 0; (C_{11}+2C_{12}) > 0; C_{11} > 0; C_{44} > 0\), and the bulk modulus \( B_0 \) also satisfies the criterion: \( C_{12} < B < C_{11} \).

The bulk modulus calculated from the elastic constants using the formula \( B_0 = (1/3) (C_{11}+2C_{12}) \) within GGA-WC approximation is in good agreement with that obtained from the total energy minimization calculations (Table 1). To the best of our knowledge no experimental or theoretical values for the elastic constants of this material have been published and hence our results can serve as a reference for future investigations. Similar work to calculate elastic properties of the other materials has been reported in the literature [10, 29]. The anisotropy factor \( (A) \) is equal to one for an isotropic material, while any value smaller or larger than one indicates anisotropy. The magnitude of the deviation from 1 is a measure of the degree of elastic anisotropy possessed by the crystal. We obtain the value of the anisotropy factor \( A \) as 0.5370 for this compound. This indicates that our compound is anisotropic.

Young’s modulus \( (E) \) is a good indicator about the stiffness of the material. When it is higher for a given material, the material is stiffer. Poisson’s ratio provides more information about the bonding forces than any other elastic property. The value of the Poisson’s ratio \((\nu)\) for covalent materials is small \((\nu < 0.1)\), whereas for ionic materials a typical value of \( \nu \) is 0.25 [30]. In our calculations \( \nu \) is 0.1825. Hence, a higher ionic contribution in an intra-atomic bonding for this compound is assumed. Mechanical properties such as ductility and brittleness of materials can be explained from the proposed relationship in Pugh’s criteria. The shear modulus \( G \) represents the resistance to plastic deformation, while the bulk modulus \( B_0 \) represents the resistance to fracture. There exists a criterion for \( B_0/G \) ratio which separates the ductility and brittleness of materials. According to Pugh’s criteria [31], the critical value is 1.75 i.e., if \( B_0/G > 1.75 \) the material is ductile, otherwise it is brittle. Thus according to Pugh’s criteria, the material LiMgF\(_3\) is brittle. Based on the experimental results, we find that KMgF\(_3\) compound shows brittle nature [6]. Our theoretical results for LiMgF\(_3\) also show similar nature.

### 3.3. Band Structure and Density of States (DOS)

Our theoretical results for LiMgF\(_3\) also show similar nature. The calculated energy bands along the high symmetry lines in the Brillouin zone and total as well as partial density of states of LiMgF\(_3\) are shown in Figures 3 and 4 respectively. We discuss our results for the electronic properties of LiMgF\(_3\) via the energy band, the total and partial density of states. The mBJ-GGA potential \( V_{xc} \) uses the mBJ exchange potential plus the GGA correlation potential and performs the calculations of bandgap precisely. This method provides the bandgaps almost equal to the experimental values [21]. The zero of energy is chosen to coincide with the valence band maximum (VBM), which occurs at M point, and the conduction band minimum (CBM) occurs at the \( \Gamma \) point resulting in an indirect band gap of 6.1 eV. On the basis of different bands; the total density of states (TDOS) could be grouped into four regions and the contribution of different states in these bands can be seen from the partial density of states (PDOS). In the first region around \(-4.5\) eV to the Fermi energy level, the majority contribution is given by \( F 2p \) states and minority contribution is given by \( Mg 3s, Mg 2p \) and \( Mg 3d \) states, as seen in figure 4.(d) and 4.(c). There is hybridization observed between \( F 2p \) with \( Mg 3s \) and \( Mg 2p \) states. In the second region around \( 6\) eV to \( 10\) eV, an equal contribution is given by \( Li 2s \) and
Li 2p states as seen in Figure 4 (b). In the region around 12 eV, a sharp peak is observed. The majority contribution due to Li 2p states and minority contribution due to Li 2s states are observed in this region. The contribution at 15 eV is mainly due to Mg 3s states and partially due to Li 2p states. In the region around 15 eV to 20 eV, majority contribution is by Mg 2p states and minority contribution is given by Mg 3d and F 2p states. The first region within the range of −4.5 to 0 eV comprises the valence band. The second region above the Fermi level is the conduction band. In the conduction band from 6.0 eV to 12 eV majority contributions is from Li 2p and Li 2s states. From 12 to 20 eV the contribution is due to the Mg 3s, Mg 2p, Mg 3d and Li 2p states in the conduction band.

The calculated band gap of LiMgF$_3$ is shown in Table 3. Our calculated indirect band gap is 6.11 eV, while the calculated value reported by others is 5.97 eV [2].

Table 3. Energy gap (eV) at high symmetry points for LiMgF$_3$

| Method      | M–Γ | Γ–Γ | R–X | R–M | M–M | R–R | R–Γ | X–X |
|-------------|-----|-----|-----|-----|-----|-----|-----|-----|
| mBJ-GGA     | 6.11| 6.52| 8.50| 10.05| 10.50| 10.05| 6.11| 8.81|

3.4. Charge Density
The charge density distributions are shown in Fig. 5. Charge density maps serve as a complementary tool for achieving a proper understanding of the electronic structure of the system being studied. The ionic character of any material can be related to the charge transfer between the cation and anion while covalent character is related to the sharing of the charge among the cation and anion. The covalent behaviour is due to hybridization of F 2p with Mg 3s and Mg 2p states in the valence band near the Fermi Energy level. From the figures it is clear that the highest charge density occurs in the immediate vicinity of the nuclei. The near spherical charge distribution around Li indicates that the bond between Li and F is strong ionic, with no charge sharing among the contours of the respective atoms. It can be seen that most of the charge is populated in the Mg-F bond direction, while the maximum charge resides on the Mg and F sites. The corresponding contour maps of the charge density distributions are shown in Figure 5. (a) along (1 0 0) plane in 2D representation, Figure. 5.(b) along (1 0 0) plane in 3D representation and Fig. 5. (c) along (1 1 0) plane in 2D representation. Hence, we conclude that there exists a strong ionic bonding in Li-Mg and a mixture of ionic and weak covalent bonding in Mg-F.
3.5. Dielectric and Optical Properties

The dielectric function $\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$ is known to describe the optical response of the medium at all photon energies. The imaginary part $\varepsilon_2(\omega)$ is directly related to the electronic band structure of a material and describes the absorptive behaviour. The imaginary part of the dielectric function $\varepsilon_2(\omega)$ is given [32,33] by

$$
\varepsilon_2(\omega) = \left(\frac{4\pi^2 e^2}{m^2 \omega^2}\right) \sum_{i,j} \left| i M j \right|^2 f_i (1 - f_j) \delta(E_{j,k} - E_{i,k} - \omega) d^3k
$$

where $M$ is the dipole matrix, $i$ and $j$ are the initial and final states respectively, $f_i$ is the Fermi distribution function for the $i$-th state, and $E_i$ is the energy of electron in the $i$-th state with crystal wavevector $k$. The real part $\varepsilon_1(\omega)$ of the dielectric function can be extracted from the imaginary part using the Kramers-Kronig relation in the form [34-36]:

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

where $P$ implies the principal value of the integral.

The FP-LAPW is a good theoretical tool for the calculation of the optical properties of a compound. The optical properties give useful information about the internal structure of the LiMgF$_3$ compound. The GGA method is used to calculate the optical properties of this compound. The calculated optical properties of LiMgF$_3$ are shown in Figure 6. The imaginary part $\varepsilon_2(\omega)$ and the real part $\varepsilon_1(\omega)$ of the dielectric function, refractive index $n(\omega)$, extinction coefficient $k(\omega)$, Reflectivity $R(\omega)$, energy loss function $L(\omega)$, optical conductivity $\sigma(\omega)$ and absorption coefficient $\alpha(\omega)$ of LiMgF$_3$ are shown in Fig. 6, as functions of the photon energy in the range of 0-30 eV.

![Figure 6. Optical spectra as a function of photon energy for cubic perovskite LiMgF$_3$](image-url)
(a) Imaginary part $\varepsilon_2(\omega)$ and (b) real part $\varepsilon_1(\omega)$ of dielectric function (c) refractive index $n(\omega)$ (d) extinction coefficient $k(\omega)$, (e) reflectivity $R(\omega)$, (f) energy loss function $L(\omega)$, (g) optical conductivity $\sigma(\omega)$ and (h) absorption coefficient $\alpha(\omega)$ of LiMgF$_3$.

The imaginary part $\varepsilon_2(\omega)$ gives the information of absorption behaviour of LiMgF$_3$. In the imaginary part $\varepsilon_2(\omega)$, the threshold energy of the dielectric function occurs at $E_0 = 6.14$ eV, which corresponds to the fundamental gap at equilibrium. The real part of the dielectric function $\varepsilon_1(\omega)$ is displayed in Figure 6 (b). This function $\varepsilon_1(\omega)$ gives us information about the electronic polarizability of a material. The static dielectric constant at zero is obtained as $\varepsilon_1(0) = 1.88$. From its zero frequency limit, it starts increasing and reaches the maximum value of 2.60 at 6.63 eV, and goes below 0 in negative scale for the range of 18.54 – 18.75 eV. The refractive index and extinction coefficient are displayed in Figures 6 (c) and 6 (d).

When we look at the behaviour of imaginary part of dielectric function $\varepsilon_2(\omega)$ and extinction coefficient $k(\omega)$, a similar trend is observed from Figures 6 (a) and 6 (d). The extinction coefficient $k(\omega)$ reaches the maximum absorption in the medium at $18.48$ eV. Frequency dependent refractive index $n(\omega)$, reflectivity $R(\omega)$, and optical conductivity $\sigma(\omega)$ are also calculated and the salient features of the spectra are presented in Table 4.

**Table 4.** Calculated zero frequency limits of refractive index $n(0)$, reflectivity $R(0)$, energy range for $n(\omega) < 1$, maximum values of refractive index $n(\omega)$, reflectivity $R(\omega)$ and optical conductivity $\sigma(\omega)$ of LiMgF$_3$.

| LiMgF$_3$ | n (0) | Maximum n (ω) | Energy range (in eV) for n (ω) < 1 | R (0) % | Maximum R (ω) | Maximum $\sigma(\omega)$ (in $\Omega$-1 cm-1) |
|-----------|-------|---------------|-----------------------------------|--------|--------------|----------------------------------|
| This work | 1.37  | 1.61          | 18.54-30                          | 2.43   | 18.59        | 5137.33                          |

4. **Conclusion**

In summary, the structural, elastic, electronic and optical properties of the cubic perovskite LiMgF$_3$ are investigated using the full-potential linearized augmented plane wave method. The exchange correlation effects are included through the generalized gradient approximation and modified Becke-Johnson exchange potential. The lattice parameter at equilibrium is in reasonable agreement with previous calculations. Cubic perovskite LiMgF$_3$ is brittle and elastically anisotropic. The analysis of partial density of states revealed that the valence bonding region shows hybridization of F 2p with Mg 3s and Mg 2p states. The energy band structure clearly demonstrates that LiMgF$_3$ is an indirect band gap (M- $\Gamma$) material. The optical properties such as dielectric function, reflectivity, absorption coefficient, optical conductivity, refractive index, extinction coefficient and electron energy loss function are studied in the energy range of 0-30 eV. The high absorption power of the compound in the visible and ultraviolet energy range predicts its usefulness in optical and optoelectronic devices in this range.

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