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THEORETICAL INVESTIGATION OF THE STRUCTURAL, ELECTRONIC, AND MECHANICAL PROPERTIES OF THE MAGNESIUM-BASED FLUOROPEROVSKITE COMPOUNDS $XMgF_3$ (X= Ga, Al, In)

Nasir Rahman,[a,]* Mudasser Husain,[b,] Juan Yang,[a,]* Muhammad Sajjad,[b]
Muhammad Salman Ahmad,[c] Anwar Habib,[b] Abdur Rauf,[d]
Mahmood Ul Haq,[e] Jaffer Saddique,[f] Mohammad Nisar,[e]
Sufaid Shah,[a] Zulfiqar,[a] Chanez Maouche,[a]
Mutee Ur Rehman,[e] Muhammad Imran[g]

Zhenjiang, Neijiang, and Zhejiang, People's Republic of China,
and Islamabad and Kohat, Pakistan.

ABSTRACT: *Ab initio* investigations of the Mg-based fluoroperovskite $XMgF_3$ (X = Ga, Al and In) compounds were calculated by using the full-potential linearized augmented plane wave method. The various physical properties were computed using the WIEN2k code. The structural parameters of these compounds agreed with previous predictions within acceptable limits.This study revealed that $GaMgF_3$ and $InMgF_3$ compounds were anisotropic, ductile, and mechanically stable, while $GaMgF_3$ was found to be more rigid and less compressible than $InMgF_3$. Furthermore, it was shown that the third compound investigated, $AlMgF_3$, was mechanically unstable. The electronic band structure of $AlMgF_3$ and $InMgF_3$ was of a semiconductor with an indirect (M – X) band gap with an energy of 2.49 eV and 2.98 eV, respectively, while $GaMgF_3$ was found to be an insulator with a direct (X–X) band gap with and energy of 3.86 eV. We found that the bonding force between the atoms was mostly ionic with just a little covalent nature. The understanding of these compounds gained from these computations can be applied in the design of electronic devices.

Keywords: Electronic properties; Fluoroperovskites; GGA approximation; Mechanical properties; Structural properties.

1. INTRODUCTION

Cubic perovskite compounds have received a great deal of attention due to their massive use in technology. Many groups of perovskite crystals, including fluoroperovskites (ABF_3), oxideperovskites (ABO_3), and nitrideperovskites (ABN_3), are found on earth. A stable fluoroperovskite is generated by the concoction of fluorine, organic or inorganic, and a transition metal (TM).[1] Owing to the importance of their technical applications in lenses and the semiconductor industry, there has been a focus of interest on the structural, electronic, and elastic properties of the fluoroperovskites.[2] Cubic perovskite compounds are usually preferred for the manufacture of lenses because the birefringence which occurs with most lens materials does not occur with them. Fluoroperovskites, with the structure of ABF_3, are one of the customary perovskite structures. The elements A and B are alkaline

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[a]School of Material Science & Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China; [b]Department of Physics, Kohat University of Science & Technology, Kohat 26000, Pakistan; [c]School of Political Science and Public administration, Neijiang Normal University, Sichuan, People's Republic of China; [d]School of Materials Science and Engineering, Nanjing University of Science & Technology, Nanjing 210094, People's Republic of China; [e]School of Material Science & Engineering, Zhejiang University, People's Republic of China; [f]College of Material Science and Technology, Nanjing University of Aeronautics and Astronautics, People's Republic of China; [g]Materials Science Laboratory, Department of Physics, Quaid-i-Azam University, Islamabad, Pakistan. *For correspondence: (i) Dr Nasir Rahman, School of Material Science & Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China; E-mail: 11626070@zju.edu.cn; (ii) Dr. Juan Yang, School of Material Science & Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China; E-mail: yangjuan6347@ujs.edu.cn

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metals (Li – Cs), and alkaline earth metals (Be – Ba), respectively. The perovskite crystal family is a vast area for investigating other physical properties, such as giant magnetoresistance,[3] an almost zero temperature resistivity coefficient,[4] and being a laser source.[5] Based on their chemical composition, these compounds may be expected to have various significant physical properties, ranging from semiconduction to magnetic and superconduction properties.[6,7] The fluoroperovskites have a wide band-gap energy. Because of their short absorption edges, they have a high potential as window materials in the ultraviolet (UV) and vacuum-ultraviolet (VUV) wavelength regions.[8,9] Husain et al. reported for the first time on the structural, electronic, and mechanical properties of cubic fluoroperovskites, ($ZnXF_3$, X = Y, Bi) using the density functional theory (DFT). It was observed that both of the compounds had a narrow band gap, were structurally stable, and were mechanically ductile.[10] Khan et al. investigated theoretically the thallium (Tl)-based fluoroperovskite compounds $TlXF_3$ (X = Ca, Cd, Hg, and Mg) and concluded that due to their wide band gap, in the insulator range, these compounds can be used as a scintillation detectors.[11] To the best of our knowledge, there have been insufficient experimental and theoretical studies devoted to the basic structural, electronic, and mechanical properties of $XMgF_3$ compounds, where X = gallium (Ga), aluminum (Al), and indium (In). Among these compounds $GaMgF_3$ was found to be an insulator electronically and was predicted to have Auger-Free luminescence (AFL), while $AlMgF_3$ and $InMgF_3$ were considered to have a semiconducting nature. The aim of the present research was to investigate systematically the structural, electronic, and elastic properties of $XMgF_3$ (X = Ga, Al and In) using the full-potential linearized augmented plane wave (FP-LAPW) method.

2. METHOD OF CALCULATIONS

For this study we used a methodology based on the density functional theory (DFT)[12] and the approach of the FP-LAPW method[13] to solve the Kohn–Sham equations as implemented in the WIEN2k code.[14] For many body problems, this approach is a universal quantum mechanical method and has proven to be one of the most reliable methods for determining physical properties. The generalized gradient approximation—developed by Perdew, Burke, and Ernzerhof—(GGA-PBE)[15] was used for estimating the potential for exchange–correlation. The valence and core electrons were considered as semi- and completely relativistic, respectively.

The compound's unit cell was subdivided into two regions where the first was the interstitial zone. In this zone the plane wave was generated with the cutoff value of $K_{max} = 8.0/R_{mt}$ in order to achieve convergence eigen values. The K_{max} and R_{mt} are the largest K vector of the expansion of the plane wave and the smallest radius of the non-overlapping atomic spheres, respectively. The R_{mt} for the atoms X= Ga, Al, and In are 2.5 for each one, and 1.77, 1.76, and 1.8 for Mg in the cases of $AlMgF_3$, $GaMgF_3$, and $InMgF_3$, respectively. The corresponding values for F are 1.86, 1.85, and 1.89 atomic units (a.u.) on going from Al to Ga and In, respectively.

The second region is the non-overlapping muffin-tin spheres, in which the spherical-harmonic wave generates around and within $l_{max} = 14$. The lattice constants for each compound are determined using Murnaghan's equation of states[16] to minimize the total energy of the unit cell with respect to its volume.

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3. RESULTS AND DISCUSSIONS

3.1 Structural properties: We evaluated the structural properties of the Mg-based fluoroperovskite compounds $XMgF_3$ (X= Ga, Al and In) in the ideal 0 K and 0 GPa cubic unit cell. Such compounds with a Pm-3m space group have the Wyckoff atomic positions at (0, 0, 0) for X, (0.5, 0.5, 0.5) for Mg, and (0.5, 0.5, 0) for F as shown in Figure 1.

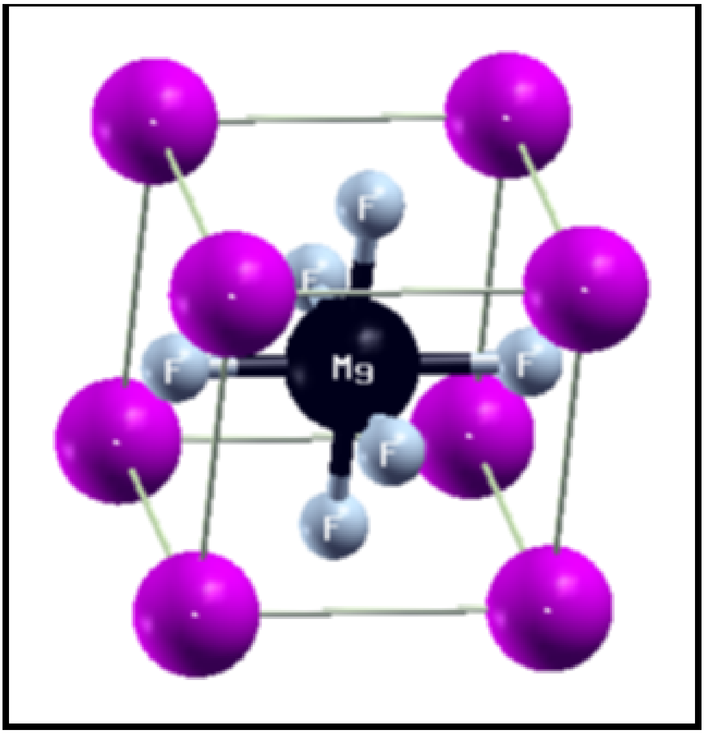

Figure 1. $XMgF_3$ prototype crystal structure unit cell obtained on (X-Window) Crystalline Structures and Densities (XCrysDen).

The structural properties, such as the lattice constants, the bulk modulus, the pressure derivative of the bulk modulus, the ground state energy, and the ground state volume, were calculated for the first time using first principles (*ab initio*) as shown in Table 1.

Table 1. The calculated lattice constant (a_0 in A), the bulk modulus (B_0 in GPa), the derivative of the bulk modulus (B'_0), the ground state energy (E_0 in Ry), and the ground state volume (V_0 in a.u.^{3}).

Compounds	Lattice constants (a_0)	Bulk modulus (B_0)	Derivative of bulk modulus (B'_0)	Ground state energy (E_0)	Ground state volume (V_0)
$GaMgF_3$	4.0576	69.7347	4.3626	–4888.770102	450.8312
$AlMgF_3$	4.1448	67.4351	4.5348	–12767.143154	480.5155
$InMgF_3$	4.0703	70.0005	4.2249	–1486.098732	455.0847

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The higher bulk modulus and absolute value of the cohesive energy suggest a high crystal rigidity. Thus, $AlMgF_3$ can be assumed to be harder and less compressible than $GaMgF_3$ and $InMgF_3$ based on the B_0 values as shown in Table 1.

The volume optimization method was used to analyze the structural properties of $XMgF_3$ (X = Ga, Al, and In). The volume optimization was conducted on each compound by reducing the unit cell's total energy with respect to the unit cell volume and was made to fit by the state equation of Birch–Murnaghan as shown in Figures 2A–2C.

From Figures 2A–2C it can be seen that energy of the unit cell at first decreases with the increase of the unit cell volume to a point where the system's minimum energy is obtained, which is the system's ground state energy E_0. The volume at this minimal energy is considered to be the ground state or optimum cell volume. After this optimized stage, the unit cell energy increases with the further increases in the unit cell volume and the system becomes un-relaxed again.

The energy of the unit cell was minimized by performing the volume optimization of the unit cell volume as shown in Figures 2A–2C.

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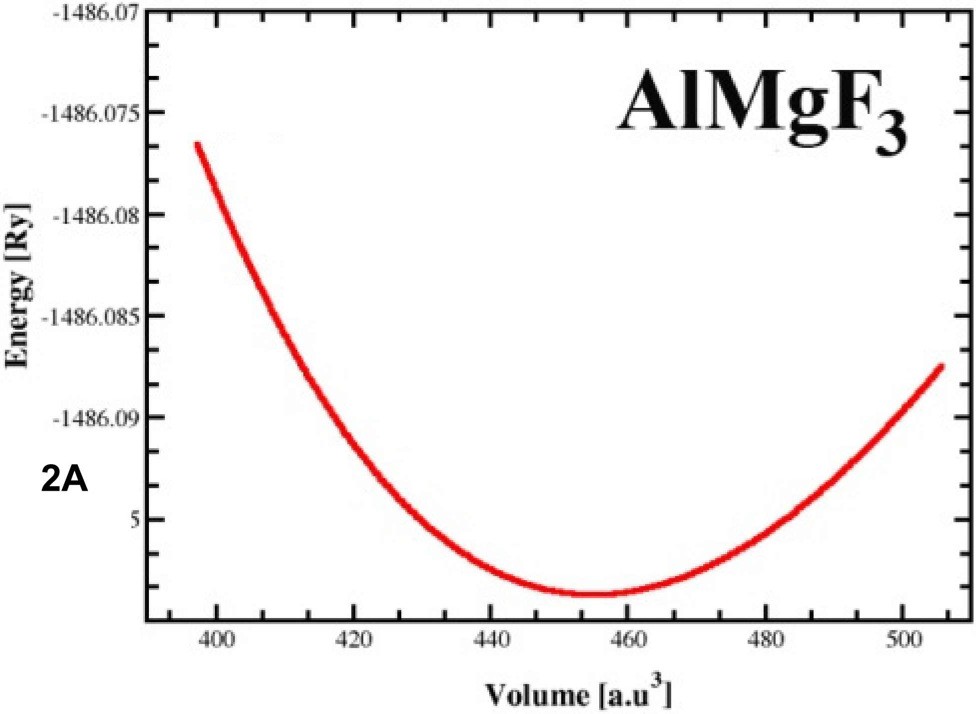

Figure 2A. Total energy dependency of the XMgF3 (X = Ga, Al, and In) crystal on the volume of the unit cells. 2A: $AlMgF_3$.

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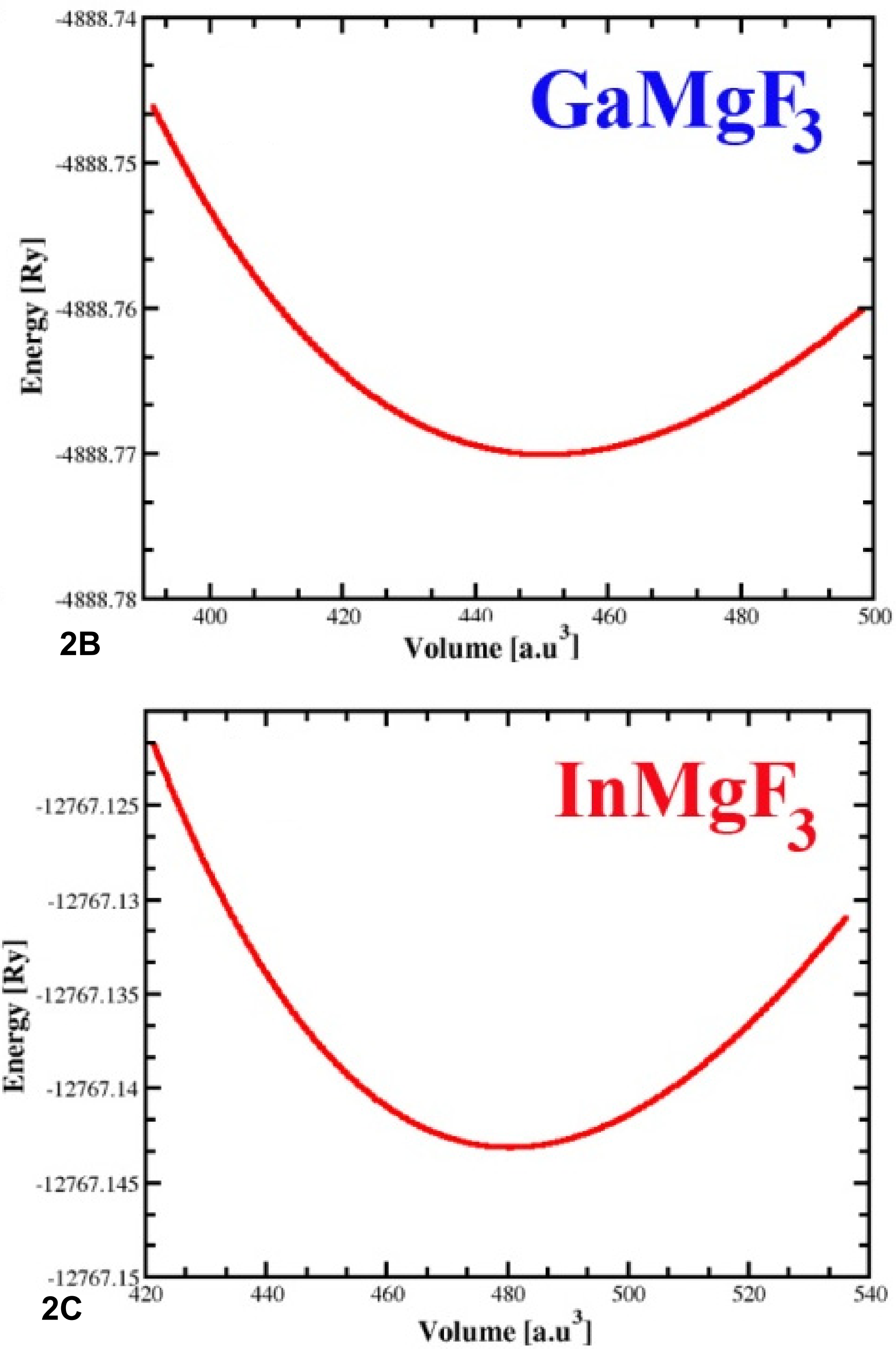

Figures 2B and 2C. Total energy dependency of the $XMgF_3$ (X = Ga, Al, and In) crystal on the volume of the unit cells. 2B: $GaMgF_3$, 2C: $InMgF_3$.

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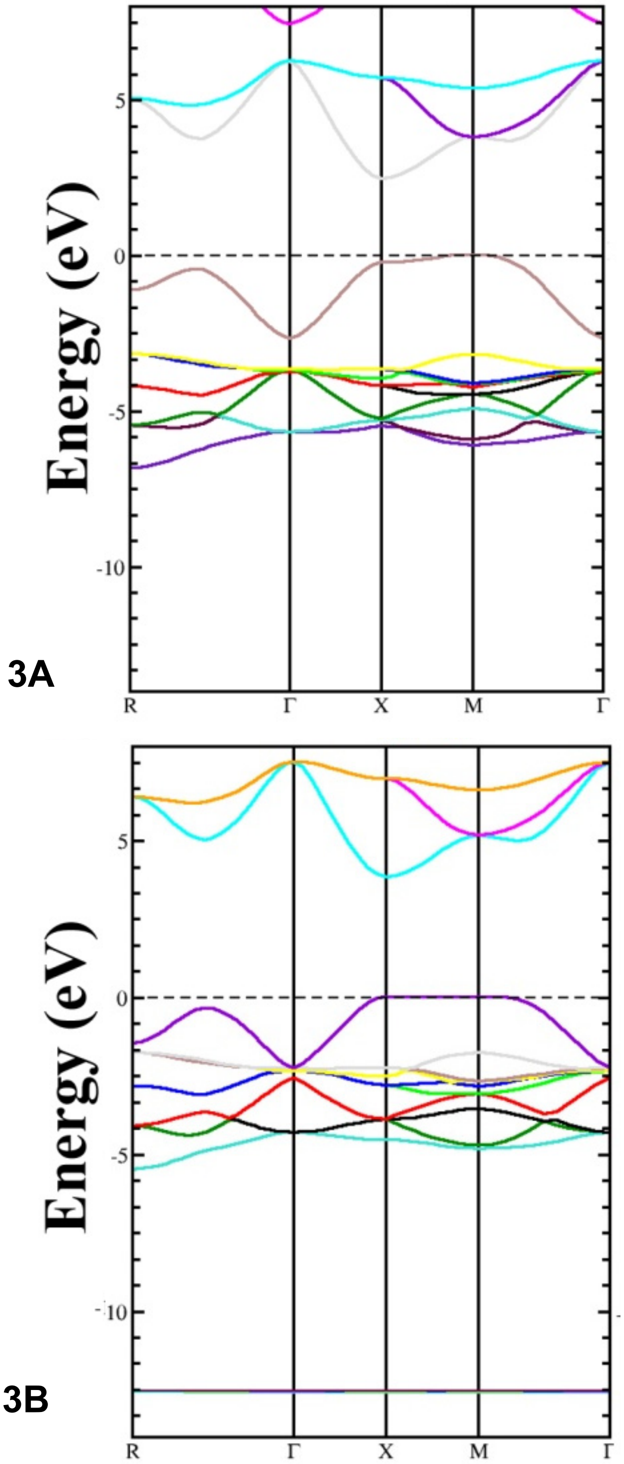
3.2 Electronic properties: The electronic properties of the compounds $GaMgF_3$, $AlMgF_3$, and $InMgF_3$ were examined at 0 K and 0 GPa using the electronic band structure and the full and partial state density spectrum as shown in Figures 3A–3C and 4A–4C.



Figures 3A and 3B. Electronic band structures of $XMgF_3$ where X= Ga, Al and In. 3A: Electronic band structures of $AlMgF_3$, 3B: $GaMgF_3$.

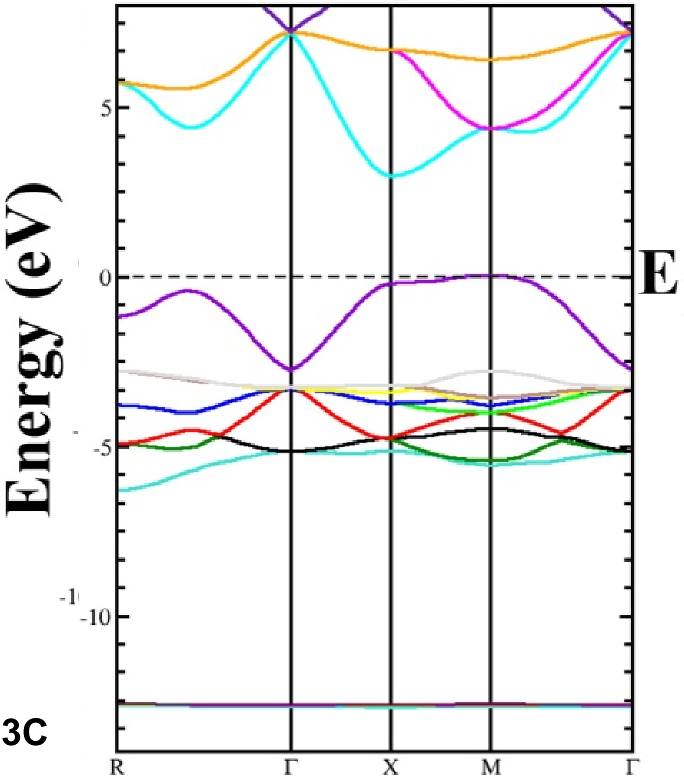
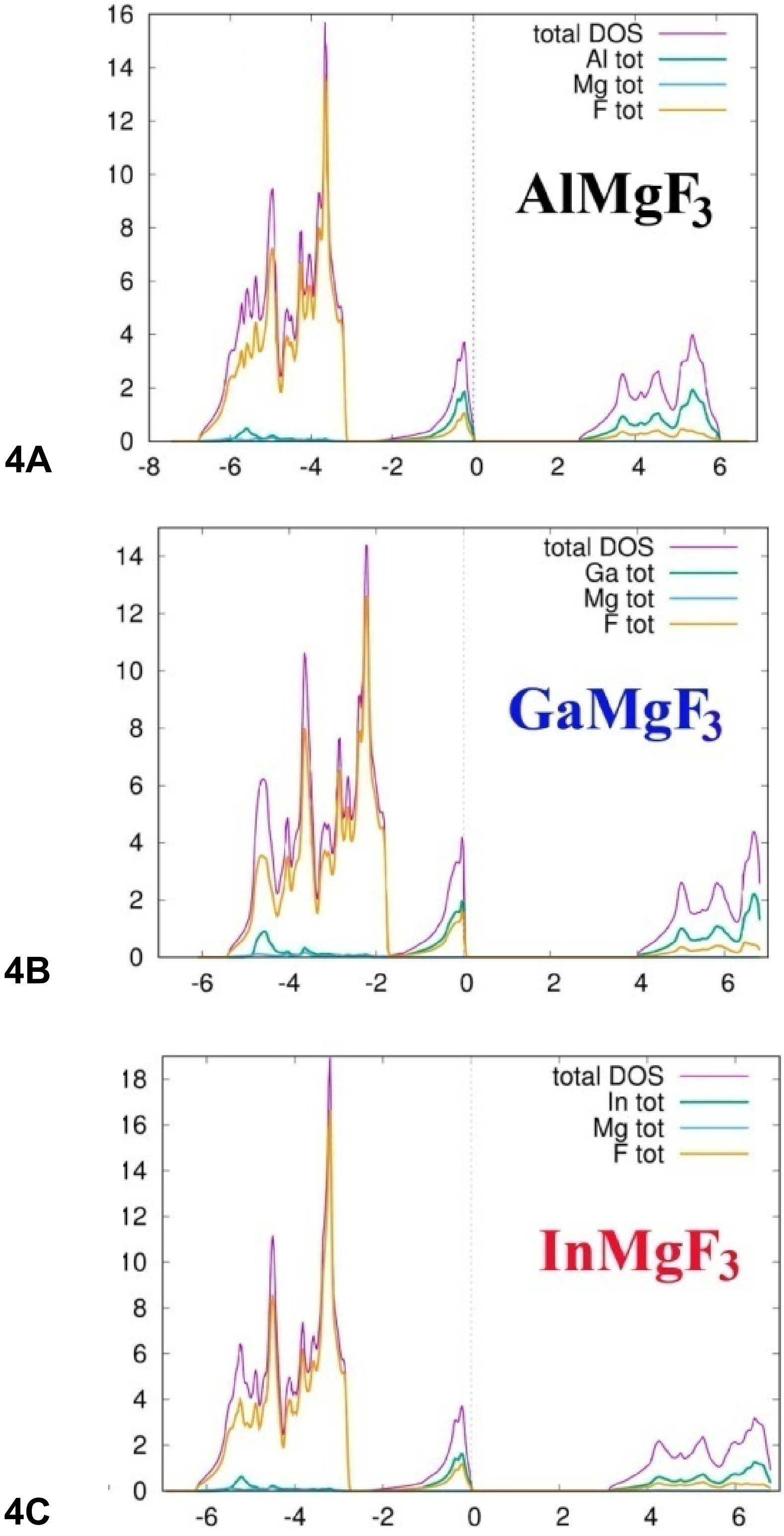


Figure 3C. Electronic band structures of $XMgF_3$ where X= Ga, Al, and In. 3C: Electronic band structures of $InMgF_3$,

From Figures 3A–3C, one can consider that both $AlMgF_3$ and $InMgF_3$ have a semiconducting nature while $GaMgF_3$ has a combination of insulators. The maxima of the valence and the minima of the conduction bands of $AlMgF_3$ and $InMgF_3$ were located at the M and X symmetry levels, respectively. Such bands create an indirect (M–X) band gap that has been found to be 0.49 eV for the former and 2.98 eV for the later compounds. Furthermore for $GaMgF_3$, both the valence band maxima and the conduction band minima lie at the same X symmetry points which form a direct (X–X) band gap of 3.86 eV. This gap in the energy band may serve as a reference for future research.

The total and partial state densities (TDOS and PDOS) of the compounds being studied were within the energy range of –7 to 7 eV as illustrated in Figures 4A–4C. The dominant hybridization in the TDOS valence band was linked to the F s-p states with a minor contribution from the X d-state (where X= Ga, Al, and In). The valence zone of the compounds was characterized by two bands. The first band near the Fermi scale was due to the hybridization of the d-state of X together with the p-state of F. In this region, the bonding states are connected to the spin-up X-d-state. The second band was linked to the actions of the d-state of X and the d-state of Mg with a major contribution from the p-state of F. The main contributions in the conduction band were from the s- and p-states of the X atom, the s- and d-states of the Mg atom, and the p-state of the F atom.



Figures 4A–4C. The total state density (TDOS) and the partial state densities (PDOS) of GaMgF$_3$, AlMgF$_3$, and InMgF$_3$. 4A: GaMgF$_3$, 4B: AlMgF$_3$, and 4C: InMgF$_3$.

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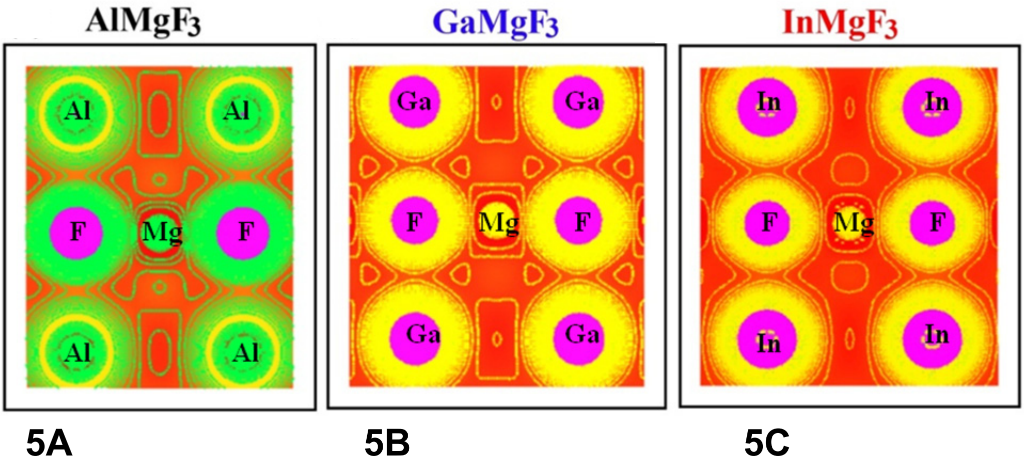
It should also be noted that the Mg atoms are positioned in $XMgF_3$ at the middle. The octahedrons of the MgF_6 bonds are formed because six F ions surround the central Mg atom. The transfer of electrons from the Mg atom to the F atom is due to the difference in the electro-negativity of these atoms. This difference in electro-negativity induces an attraction between the positively charged Mg atom and the negatively charged F atoms in the octahedron, and produces a dipole moment. The electrons are positioned in MgF_6 to partly fill the d-state of the Mg atom, while the p-state of the F atoms states is complete, which establishes the covalent Mg-F bond. The densities of electron charges along the (110) plane of the $XMgF_3$ compounds, $GaMgF_3$, $AlMgF_3$, and $InMgF_3$, are shown in Figures 5A–5C. Within the sphere, the form of Mg and X is not fully spherical, which shows that the d-state of the Mg is partially filled. It is known that the contours of the Mg-F bond are not completely isolated and that although the bond has some partially covalent characteristics it is mainly ionic in nature. In contrast however, the X-MgF_6 bond is strictly ionic since the X and MgF_6 contours are completely separated. One can infer that the compound $XMgF_3$ has some covalent bonding but is mainly ionic.



Figures 5A–5C. Electron densities of $GaMgF_3$, $AlMgF_3$, and $InMgF_3$. 5A: $GaMgF_3$, 5B: $AlMgF_3$, and 5C: $InMgF_3$.

3.3 Mechanical properties: The elastic constant parameters (Cij) were utilized to define the degree of the compound's reaction to the exerted macroscopic stress. These constants establish a connection between the mechanical and dynamic actions of the compound. In cubic arrangement crystals, three distinct elastic constants, C_{11}, C_{12}, and C_{44}, are needed to measure the mechanical properties such as stability and rigidity. The Cij values determined for the three compounds studied are shown in Table 2.

A compound can be described as mechanically stable when the restriction formulas in a cubic structure $[(C_{11}+2C_{12})/3$; $C_{44}> 0$; $(C_{11}–C_{12})> 2$; $C_{12}< B< C_{11}]$ are attained.[17] The uniaxial deformation along the (100) direction and the pure shear deformation on the (100) crystal plane are denoted by C_{11} and C_{44}. The calculated unidirectional elastic C_{11} is higher than C_{44} for all of our compounds $XMgF_3$ (X = Ga, Al and In). These compounds show a lower resistance to pure shear deformation compared with their resistance to unidirectional compression. From the measured

C_{44} values it can be concluded that $GaMgF_3$ is stiffer than $AlMgF_3$ and $InMgF_3$. To the best of our knowledge, there are no reported Cij values in the literature for $XMgF_3$ (X= Ga, Al and In) with which we can compare our findings,.

Table 2. The computed elastic constant (Cij in GPa), anisotropic factor (A), bulk modulus (B0 in GPa), shear modulus (G in GPa), Young's modulus (E in GPa), Kleinman parameter (f), Poisson's ratio (ν), and Pugh's index ratio (B/G) at equilibrium volume for $XMgF_3$ (X= Ga, Al, In)

Compound	C_{11}	C_{12}	C_{44}	B	A	G	E	ν	B/G
$GaMgF_3$	129.266	45.706	35.701	73.872	0.864	37.849	21.552	0.393	1.952
$AlMgF_3$	784.787	–284.544	27.564	72.069	0.052	137.358	251.985	–0.104	0.524
$InMgF_3$	99.217	53.357	34.139	68.720	1.496	29.221	76.780	0.443	2.352

The constant elastic anisotropy (A) is an important parameter in engineering science that describes the induction of microcracks in materials.[18]

$$A = \frac{2C_{44}}{C_{11}-C_{12}}, \tag{1}$$

This constant has been used to overcome the elastic anisotropy and to evaluate the degree. A compound is classified as isotropic where A = 1. Otherwise, it is known as anisotropic elastically. The present compounds can be classified as anisotropic based on the calculated A values in Table 2 which shows that $InMgF_3$ is more anisotropic than $GaMgF_3$ and $AlMgF_3$.

Table 2 also displays the elastic moduli results, such as the Young's modulus (E). The equations for the various factors are:

$$E = \frac{9GB}{3B+G}, \tag{2}$$

$$\upsilon = \frac{3B-2G}{2(2B+G)} \tag{3}$$

$$G = \frac{1}{2}(G_\upsilon + G_R) \tag{4}$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \tag{5}$$

$$G_R = \frac{5C_{44}(C_{11}-C_{12})}{4C_{44}+3(C_{11}-C_{12})} \tag{6}$$

The estimated B_0 values are in agreement, calculated by both the elastic constants and the state equation of Birch-Murnaghan. This may be due to the accuracy of the measurements of the elastic constants. The resistance to plastic dislocation and the

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degree of stiffness can be inferred, from the shear and Young's moduli, respectively. The measured values of G and E for $AlMgF_3$ were found to be higher than those for $GaMgF_3$ and $InMgF_3$ indicating that $AlMgF_3$ is stiffer than the other two.

A compound can be defined as ductile when Cauchy's pressure (C_{11}–C_{12}) has a positive value and Poisson's ratio (ν) and Pugh's index ductility (B/G) are higher than the critical values (ν_{crit} = 0.26 and B / G_{crit} = 1.75, respectively).[19-21] Similar work by Mubarak found that the Ag-based fluoroperovskite compounds $AgMF_3$ (M = Co and Ni) were ductile and mechanically stable.[22] Therefore, both $GaMgF_3$ and $InMgF_3$ can be considered to be ductile compounds according to the measurement values of the ductile parameters of the Poisson's ratio (ν) and the Pugh's index ductility (B/G).

Poisson's ratio can also be used to obtain the details on the bonding force behavior between atoms. The measured values of ν for the present compounds were located between the lower and upper limit values of the central force solids (0.25–0.5) indicating that the interatomic forces between the atoms are central.

4. CONCLUSIONS

The density functional theory with the GGA-PBE exchange correlation was used to examine the structural, electronic, and mechanical properties of $XMgF_3$ (X= Ga, Al, In). All the properties were calculated for the first time for these compounds and we are confident about the accuracy of the calculations. For the structural properties, the lattice constants, the bulk modulus, the ground state energy, and the ground state volume were investigated. $AlMgF_3$ and $InMgF_3$ were found to have a semi-conducting nature with an indirect (M–X) band gap of 0.49 eV for $AlMgF_3$ and 2.98 eV for $InMgF_3$, respectively, while $GaMgF_3$ was found to be an insulator with a direct (X–X) band gap of 3.86. All the compounds were found to be anisotropic with $GaMgF_3$ and $InMgF_3$ being ductile compounds and $AlMgF_3$ showing stiffness. The bonding force between the atoms was found to be predominantly ionic with only a little covalent nature. Our investigations indicate that compounds of this type can be used to create strong state electronic devices.

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