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FIRST PRINCIPLE STUDY OF THE STRUCTURAL, ELECTRONIC, AND MECHANICAL PROPERTIES OF CUBIC FLUOROPEROVSKITES: (ZnXF$_3$, X = Y, Bi)

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ABSTRACT: In the scheme of density functional theory (DFT) and by means of the full-potential linearized augmented plane wave process within the generalized gradient approximation, the structural, electronic and elastic properties of ZnXF$_3$ (X = Y, Bi) were investigated for the first time. The structural parameters for each compound were observed to be consistent to those reported in the literature. It is observed that both of the compounds had a narrow band gap and that one of the compounds (ZnBiF$_3$) had a direct band gap of 0.5 eV from (M-M), while the other one (ZnYF$_3$) had an indirect band gap from (M-X) of 1.95 eV. The total electronic properties of ZnXF$_3$ (X = Y, Bi) were mainly controlled by the Zn atom, while in the partial electronic properties and the density of states the major contribution came from the Zn-d state and a minor contribution came from the F-p state. For the elastic properties, calculations were made of the elastic constants, the shear modulus, the anisotropy factor, Young's modulus, and the Poisson ratio was calculated. The results indicated that the present compounds were ductile and mechanically stable. The above investigations give a comprehensive insight into how these compounds may be used in designing high performance electronic devices.

Keywords: Cubic fluoroperovskites; Elastic properties; FP-LAPW method; Structural properties.

1. INTRODUCTION

Fluoroperovskite compounds have received an immense consideration owing to their remarkable physical and structural properties,[1] such as piezo-electricity,[2] ferromagnetism,[3] photoluminescence,[4,5] colossal magneto-resistivity, and high temperature superconductivity.[6] Fluoro-perovskites like AgMgF$_3$ and AgZnF$_3$ were investigated previously by focusing on their structural properties to calculate their lattice constants and tolerance factors, by means of various analytical approaches.[7-9] Other material properties, such as electronic, optical, and chemical bonding, were not given much attention. Murtaza et al. investigated the structural and opt-electronic properties of similar compounds, namely AgTF$_3$ (T = Mg, Zn), by the full-potential linearized augmented plane wave technique incorporated within the generalized gradient approximation.[10] The mechanical properties of such fluoroperovskite compounds still need to be investigated. Among these fluoroperovskite compounds, the structural, electronic, elastic, and other physical properties of ZnXF$_3$ (X = Y, Bi) have, so far, not been studied, either theoretically or experimentally.

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In the present work, therefore, we examined the structural, electronic, and mechanical/elastic properties of $ZnXF_3$ (X = Y, Bi) by means of the density functional theory (DFT): (i) the structural variables such as lattice constants, bulk moduli, and their derivatives, regarding pressure and bond lengths, were investigated; (ii) the electronic properties were predicted in stipulations of the band structures along with, at the same time, the density of the states of the compounds and the chemical bonding was studied from the electronic density distributions in various planes, and (iii) the elastic properties parameters, like the co-efficient of elasticity constants and the bulk modulus were also calculated.

2. COMPUTATIONAL DETAILS

This work was done using the density functional theory (DFT) framework. In the calculations for the compounds under investigation, the FP-LAPW method, inside the generalized gradient approximation (GGA) by Perdew Burke Ernzerhof (PBE)[11] as utilized in the WIEN2k package,[12] was applied to work out the Kohn-Sham equations[13]

The unit cell of a crystal compound is divided in different domains within the full potential scheme: (i) the atomic spheres and (ii) the interstitial region (outside the region of the atomic spheres). The wave function is split to two different basis sets and is extended in atomic-like functions (radial function time's spherical harmonics) in each atomic sphere, while it is extended into a plane wave basis in the interstitial region. In the expressions of spherical harmonics, the wave function is expanded to:

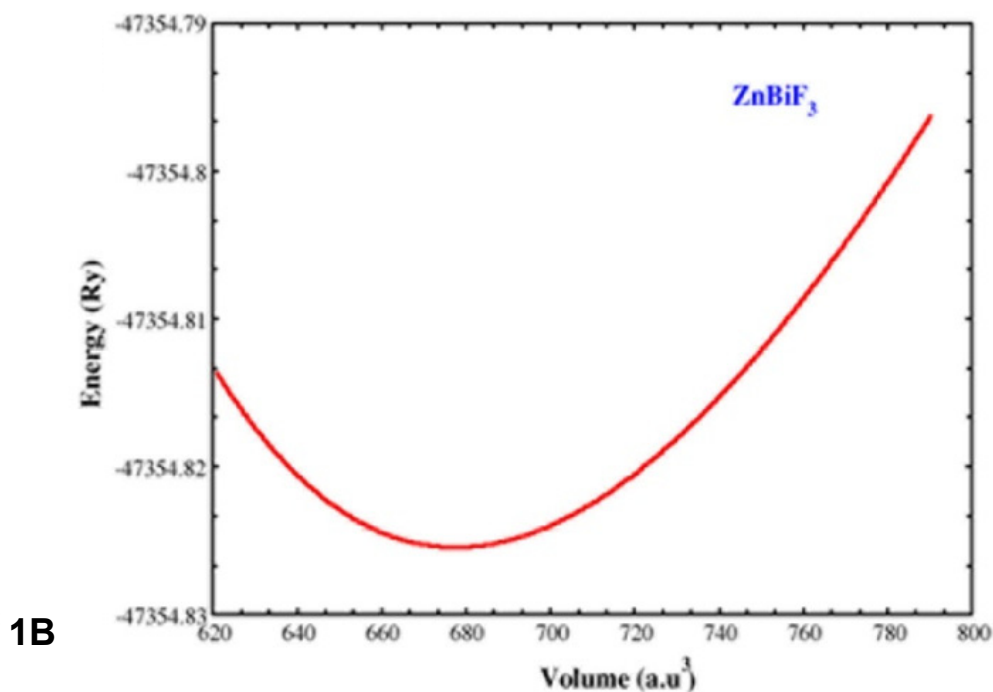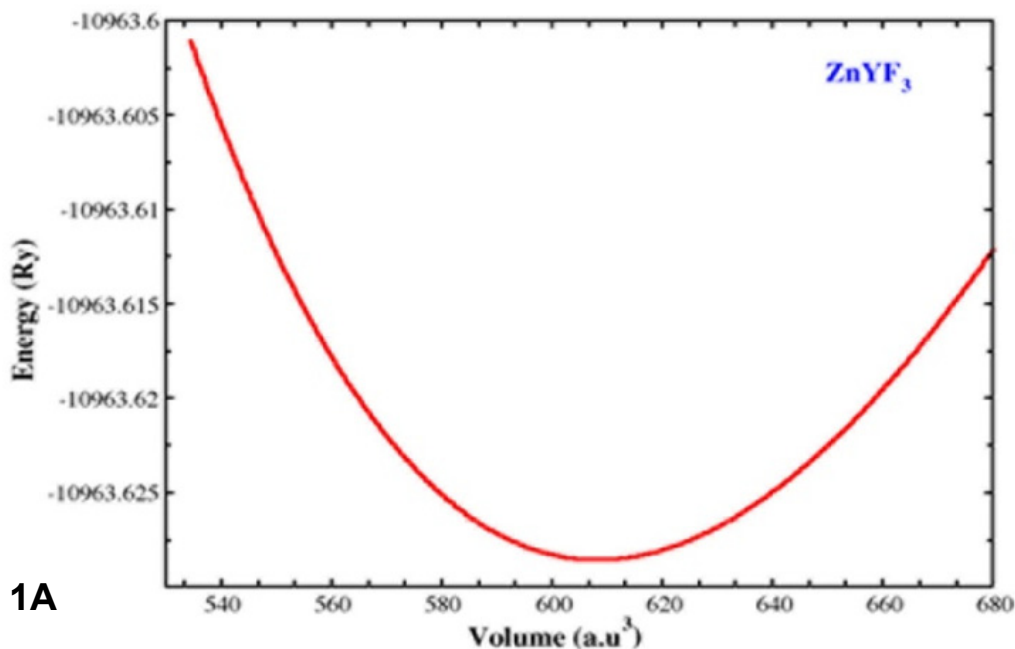$$l = 12$$

Similarly, the potential is extended as:

$$V(r) = \begin{cases} \sum_{lm} V_{lm}(r)Y_{lm}(\hat{r}) \\ \sum_{K} V_K e^{iKr} \end{cases} \quad (1a, 1b)$$

The inside of the sphere, represented by Equations 1a and 1b, is for the interstitial domain. In addition, the potential is considered to be spherically symmetrical within the atomic spheres and is constant somewhere else, in the old muffin-tin approximation. The potential has a common form in the full potential scheme. The core electrons act relativistically whereas the valence electrons act semi-relativistically. The R_{MT} values of 2.5, 2.05, 2.0, and 1.9 a.u were used for Zn, Y, Bi, and F, respectively. In the irreducible Brillion zone (IBZ), for the k-space incorporation, the modified tetrahedron method,[10] with 35 k-points was used in order to obtain self-consistency. With $R_{MT} K_{max}$ = 7.0 (the smallest muffin-tin radius is R_{MT} and K_{max} represents the plane wave cut-off), well converged solutions were obtained and the k-point sample was checked. The overall system was stable within the energy of 0.00001 Ry and the self-consistency calculations were considered to have converged at this point.

3. RESULTS AND DISCUSSION

3.1 Structural properties: To predict the structural properties of $ZnXF_3$ (X = Y, Bi), the volume optimization process was used. For each compound, the whole energy of

the unit cell concerning the unit cell volume was minimized by performing volume optimization and this was built-in by the Birch-Monahan equation as can be seen in Figures 1 (a, b). As illustrated in Figures 1A and 1B, the unit cell initial energy decreased as the unit cell volume increased.

Figures 1A and 1B. Unit cell energy as a function of unit cell volume. 1A: $ZnYF_3$, 1B: $ZnBiF_3$.

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The ground state energy E_0 is obtained at a point where the energy of the system is at a minimum. The corresponding volume consequent to this lowest energy is acknowledged as the ground state or optimal volume. After gaining a ground state, the system again becomes un-relaxed, as the energy increases further followed by the increase in unit cell volume. Table 1 demonstrates the structural parameters obtained at the ground state, for instance the lattice constant, a_0, the bulk modulus at zero pressure B_0, and its pressure derivative B_0'. The obtained lattice constants and other structure parameters were in excellent accord with the values reported in the literature (AFLOW).[14]

Table 1. Calculated structural parameters, (a_0), bulk modulus, (B_0), pressure derivative of bulk modulus (B'), and ground state energy (E_0) for $ZnYF_3$ and $ZnBiF_3$

Compound	a_0 (Å)	B_0 (GPA)	B'	E_0 (Ry)
$ZnYF_3$	4.4836	70.5912	4.6572	−10963.63
$ZnBiF_3$	4.6476	61.5862	4.7366	−47354.83

The B_0 of $ZnBiF_3$ is smaller than that of $ZnYF_3$, and therefore the former is more compressible and is less hard than the latter. It is also clear from the Table that the formation energy for a unit cell of the $ZnBiF_3$ is considerably more than that required for $ZnYF_3$. The B' value for fluoroperovskites is generally 5.0[15], but in the present case it was 4.66 for $ZnYF_3$ and 4.74 for $ZnBiF_3$.

3.2 Electronic properties: The electronic properties for $ZnYF_3$ and $ZnBiF_3$ were calculated concerning the energy band structure, along with the total and partial density states. We used the GGA approximation to compute these properties. For both these compounds the band structures along with the high symmetry direction were calculated in the first Brillion zone at the equilibrium volume are shown in Figures 2A and 2B.

The compound $ZnYF_3$ had an indirect band gap of 1.95 eV (Figure 2A). The maximum of the valence band (VB) was placed at the M symmetry point, whereas the bottom of the conduction band (CB) was located at the X symmetry point, resulting in an indirect (M-X) band gap.

The compound $ZnBiF_3$ had a direct energy band gap of 0.5 eV (Figure 2B). The maximum of the valence band and the minimum of the rgw conduction band were both situated at the M symmetry point and this resulted in a direct (M-M) band gap.

It is pertinent to note here that, to the best of our knowledge, there has not been any previous theoretical predictions or experimental results about the band gap of these perovskite compounds to compare our results with. However, we are in no doubt about the precision of our results as they were carried out using large k-points in the irreducible Brillion zones (IBZ) and the most precise Wu-Cohen GGA approach. Our work may provide a reference ground for further investigations of these compounds. Figures 2A and 2B show that the compounds studied had three bands in the range of

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–15 to 0 eV. In addition, for both the compounds, the trend of the band structure above the Fermi level was the same.
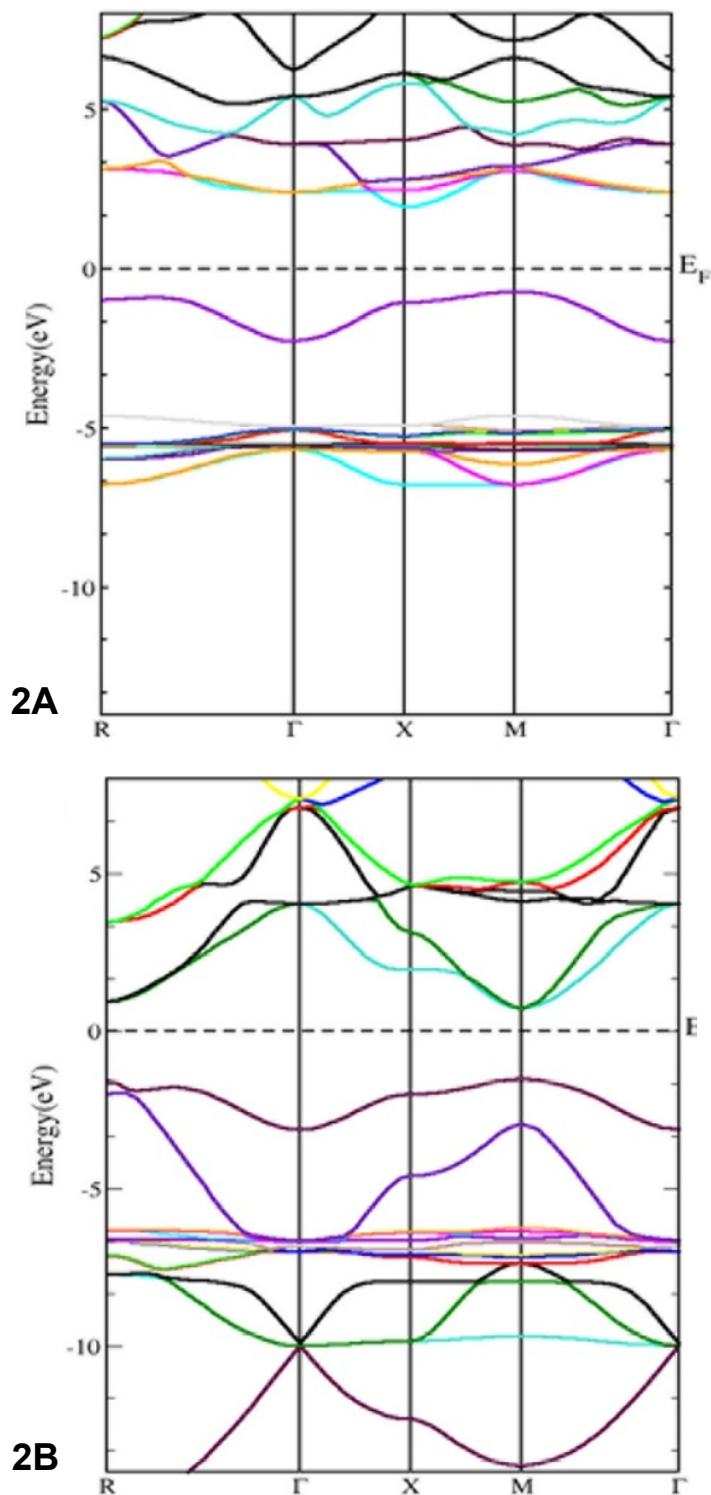
Figures 2A and 2B. 2A: Band structure of ZnYF$_3$ in the high symmetry direction. 2B: Band structure of ZnBiF$_3$ in the high symmetry direction.

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To understand and to explain the obtained band structures, some knowledge of the bonding characters of a compound and the electronic density of states (DOS) is required. So, in order to gain an understanding of these properties, we investigated the total (TDOS) and the partial (PDOS) density states for these compounds (Figures 3A and 3B).
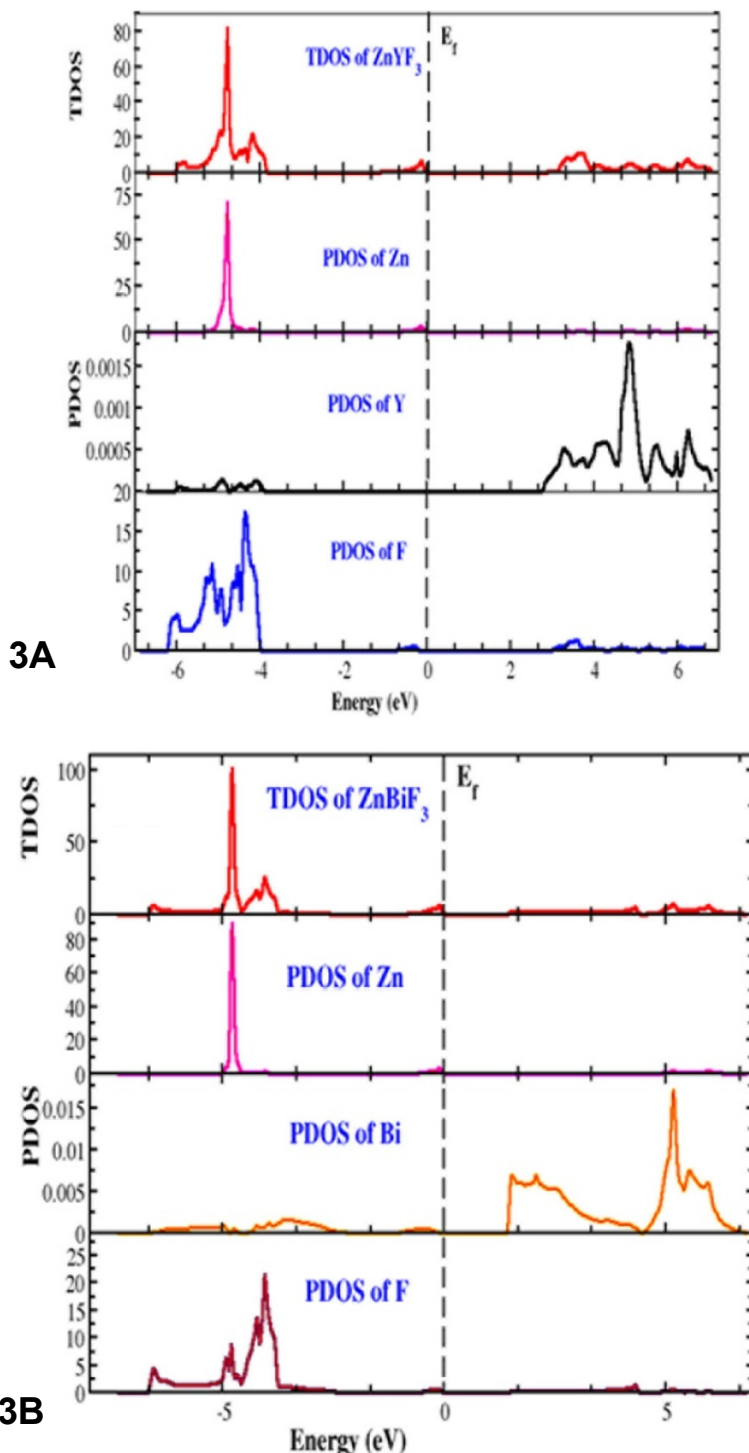
Figures 3A and 3B. The total and partial densities of the states of 3A: $ZnYF_3$ and 3B: $ZnBiF_3$.

The total and the partial densities of states for both of these compounds are illustrated in Figures 3A and 3B. The plots for the full and partial DOS for the compounds were split for analysis into three regions: (i) region I, ranging from –6 to –4 eV; (ii) region II, ranging from –1 to 0 eV; and (iii) region III, at the top of the Fermi level and in a conduction band, ranging from 3 to 7 eV.

For $ZnYF_3$ for region 1, the major contribution to the total density of states came from the Zn atom and there was a minor contribution from the F atom. For region II, there was only a small contribution to the density of states which came mainly from the Zn atom with a very small contribution from the F atom. For region III, the dominant contribution to the total density of states was from the Y atom and there was a small contribution from the F atom (Figure 3A).

For $ZnBiF_3$, for region I, the dominant contribution to the density of states came from the Zn-d state and there were small contributions from the F-p state and the Bi atom. For region II, the Zn atom, Bi-d, and F-p contributed a little to the density of states. For region III, above the Fermi level, the major contribution to the partial density of states was from Bi-d with only a little from the F-p state and the Zn atom.

The character of the bonding associated with the various atoms of a compound is explained by the charge density distribution. In particular, the ionic and covalent nature of a material can be associated with the charge transport involving cations and anions and the distribution of the charges surrounding the cations and anions.

The calculated electronic charge densities for both compounds, $ZnYF_3$ and $ZnBiF_3$, are illustrated in Figures 4A and 4B.

4A

4B
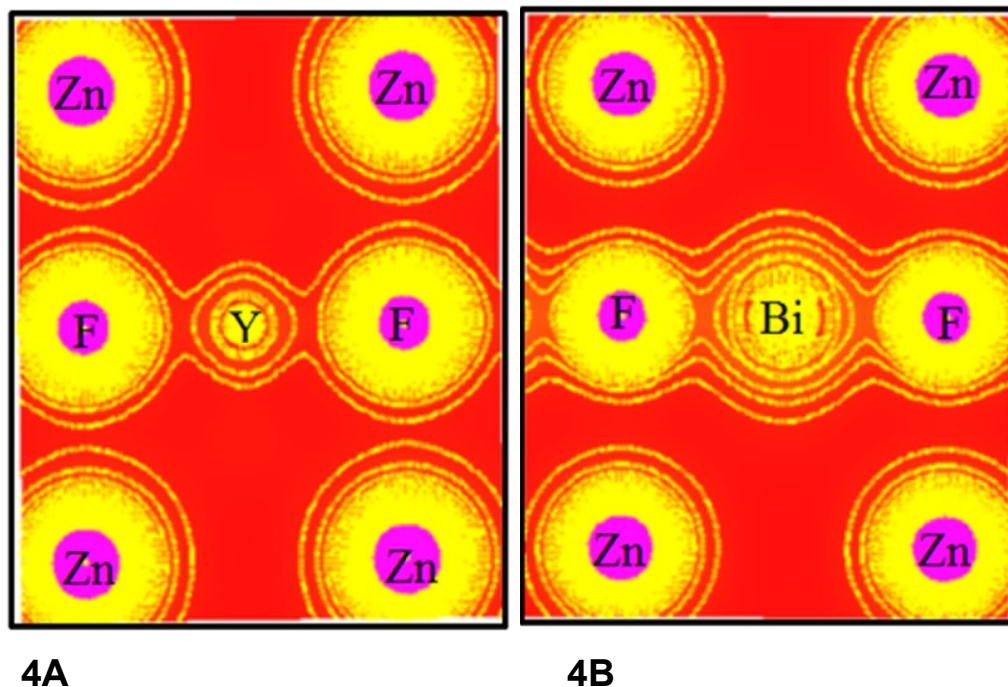
Figures 4A and 4B. Electron density of $ZnYF_3$ and $ZnBiF_3$. 4A: $ZnYF_3$ and 4B: $ZnBiF_3$.

It can be seen that the bonding character for both the compounds is somewhat ionic and somewhat covalent. The d orbital of Zn and p orbital of F contribute most to the density. Also it can be shown that the Y and B atoms are positioned at the center of $ZnYF_3$ and $ZnBiF_3$, respectively. The central atom is enclosed by six F atomic ions creating YF_6 octahedral bonds. Due to the electronegativity differences in the atoms of YF and BiF, the electrons transfer from Y and Bi to F, resulting in the attraction of the positively charged atoms of Y and Bi with the negatively charged atoms of F in the octahedron yielding an inward induced dipole moment and showing the covalent nature of the Y-F and Bi-F bonds. The shape of Zn, Y, and Bi is completely spherical which proves their ionic bonding nature. Because of the pd-hybridization surrounding Zn and F, there is a covalent character to these compounds. One can deduce that, for both $ZnYF_3$ and $ZnBiF_3$, the compounds are mainly ionic but have some covalent bonding.

3.3 Elastic properties: To understand the mechanical properties of a material, the elastic constants C_{ij} are investigated. The reaction to an applied macroscopic stress can be described by elastic constant parameters. The physical connection within the mechanical and active functioning of solids is provided by the elastic constants and further, they define how a deformation is caused by a stress and how the original form is regained following the ending of the stress.[16] The elastic constants are essential parameters for describing a material and provide valuable information about the structurural stability, the anisotropic character, and the bonding character within the adjoining atomic planes. Three self-sufficient elastic constants are used for describing cubic compounds: C_{11}, C_{12}, and C_{44}. These parameters are determined by deforming the cubic unit cell by applying a proper strain tensor and yield an energy strain connection. In this work, the elastic parameters were determined using the technique advanced by Charpin and put into practice in the WIEN2k package.[12] The obtained elastic constants and bulk modulus are summarized in Table 2.

Table 2. The calculated elastic constants C_{11}, C_{12}, and C_{44}, bulk modulus (B), anisotropy factor (A), shear modulus (G), Young's modulus (E in GPa), and Poisson's ratio (ν) for both $ZnYF_3$ and $ZnBiF_3$

Compound	Parameter								
	C_{11}	C_{12}	C_{44}	B	A	G	E	ν	B/G
$ZnYF_3$	165.590	23.534	14.905	70.932	0.210	29.561	77.866	0.298	2.399
$ZnBiF_3$	105.064	24.415	10.341	50.541	0.249	18.783	50.138	0.476	2.690

The investigated elastic constants Cij are positive and therefore the standard

$$(C_{11} - C_{12}) > 0$$
$$(C_{11} + 2C_{12}) > 0$$
$$C_{44} > 0$$

and the bulk modulus B should also persuade that the criterion $C_{12} < B < C_{11}$ for the mechanical stability[17] in a cubic crystal is satisfied.

Up until the present date, to the best our knowledge, no theoretical predictions and experimental results, for the elastic constants for the compounds $ZnYF_3$ and $ZnBiF_3$ have been reported, and thus our calculations for the elastic properties can be used as a reference for further succeeding study.

The investigation of similar elastic properties has been reported previously.[18,19] The parameters like the anisotropy factor (A), the shear modulus (G), Young's modulus (E), and Poison's ratio ν are determined by using the following relations.[20]

$$A = \frac{2C_{44}}{C_{11-C_{12}}}, \qquad (1)$$

$$E = \frac{9GB}{3B+G}, \qquad (2)$$

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

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

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

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

Where G is the shear modulus, G_v is Voigt's shear modulus subsequent to the upper limit of G values, and G_R is Reuss's shear modulus subsequent to the lower bound of G values.

For isotropic compounds, the anisotropy factor (A) is equal to one and it having a greater or smaller value would indicate anisotropy. The elastic anisotropy of crystals comes from the magnitude of the deviation from 1. As in our case, the value of the anisotropy factor was 0.210 for $ZnYF_3$ and 0.249 for $ZnBiF_3$, this indicates that both of the materials were anisotropic.

The material is stiffer if it possesses a higher Young's modulus (E), as the modulus is a fine marker concerning the stiffness of a material. Additional information on the bonding forces and the elastic properties is provided by the Poisson's ratio (ν), which is a measure of the Poisson effect that describes the expansion or contraction of a material in directions perpendicular to the direction of loading. For covalent material, the value of the Poisson's ratio (ν) is small (ν < 0.1). However, for ionic compounds its typical value is 0.25.[21] In the present investigation, ν was 0.298 for $ZnYF_3$ and 0.476 for $ZnBiF_3$. Therefore, for both of these compounds, it can be presumed that there is an excessive ionic participation in the intra-bonding.

The proposed relationship explains the mechanical properties such as the ductility and brittleness of materials. Both $ZnYF_3$ and $ZnBiF_3$ are ductile as these compounds

satisfy Pugh's criteria[22] which have a standard value for the B/G of 1.75. A material is known to be ductile if B/G > 1.75. In the present work, the B/G for $ZnYF_3$ was 2.399 and for $ZnBiF_3$ it is 2.690. Hence both $ZnYF_3$ and $ZnBiF_3$ are ductile.

The structural parameters of each compound were established to be consistent with those reported in the literature. It was established that both of the compounds had a narrow band gap. One of the compounds ($ZnBiF_3$) had a direct band gap (from M-M) while the other one ($ZnYF_3$) had an indirect band gap (from M-X).

The total electronic properties of $ZnXF_3$ (X = Y, Bi) are mainly controlled by the Zn atom, while in the partial electronic properties and the density of states the major contribution comes from the Zn-d state with only a minor contribution from the F-p state. The calculated elastic properties such as the elastic constants, the anisotropy factors, the shear moduli, Young's modulus, and Poison's ratio specify that these compounds are mechanically stable and ductile.

4. CONCLUSIONS

In the present work, we examined the structural, electronic, and elastic properties of $ZnXF_3$ (X = Y, Bi) compounds by means of the density functional theory (DFT). The lattice parameters such as the bulk modulus, the derivatives of the bulk modulus, and the ground state energy increase when the cation changes from Y to Bi. Both the compounds are narrow band gap materials. $ZnYF_3$ has a band gap energy of 1.95 eV and is indirect in nature as is evident from the (M-X) band points. $ZnBiF_3$ has a band gap energy of 0.5 eV and is direct in nature as shown by the (M-M) meeting points of the band diagram. The bonding nature for both compounds is a mixture of both covalent and ionic bonds. The characteristic peaks for both the compounds in the electronic density of states are due to the transition of electrons from Zn-d and F-d of the VB to the unoccupied state in CB. In addition, some of the elastic properties such as the elastic constants, the anisotropy factor, the shear modulus, Young's modulus and the Poisson ratio were investigated and showed that the compounds were mechanically stable, which is important for their applications in high performance electronic devices. It was also concluded, from the investigations of the elastic properties, that both the compounds were ductile in nature.

REFERENCES

1   Parhi P, Kramer J, Manivannan V, Microwave initiated hydrothermal synthesis of nano-sized complex fluorides, KMF_3 (K = Zn, Mn, Co, and Fe). J Mater Sci 2008;43:5540-5.

2   Eibschütz M, Guggenheim HJ. Antiferromagnetic-piezoelectric crystals: $BaMe_4$ (M = Mn, Fe, Co and Ni). Solid State Commun 1968;6:737-9.

3   Margadonna S, Karotsis G, Cooperative Jahn-Teller distortion, phase transitions, and weak ferromagnetism in the $KCrF_3$ perovskite. J Am Chem Soc 2006;128:16436-7.

4   Zhang F, Mao Y, Park T-J, Wong SS. Green synthesis and property characterization of single-crystalline perovskite fluoride nanorods. Adv Funct Mater 2008;18:103-12.

5   Gektin A, Krasovitskaya IM, Shiran NV. High-temperature thermoluminescence of $KMgF_3$-based crystals. J. Lumin 1997;72-74:664-6.

6   Rao CNR, Raveau B, editors. Transition metal oxides. New York: VCH Publishers; 1995.

7   Jiang LQ, Guo JK, Liu HB, Zhu M, Zhou X, Wu P, Li CH, Prediction of lattice constant in cubic perovskites. J Phys Chem Solids 2006;67:1531-6.

8   Moreira RL, Dias A, Comment on "Prediction of lattice constant in cubic perovskites." J Phys Chem Solids 2007;68:1617-22.

9   Verma AS, Kumar A, Bhardwaj SR. Correlation between ionic charge and the lattice constant of cubic perovskite solids. Phys Status Solidi (b) 2008;245:1520-6.

10   Murtaza G, Sadique G, Rahnamaye Aliabad HA, Khalid MN, Naeem S, Afaq A, et al. First principle study of cubic perovskites: $AgTF_3$ (T=Mg, Zn). Physica B: Condensed Matter 2011;406:4584-9.

11   Perdev JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. Phys Rev Lett 1996:77:3865-8.

12   Blaha P, Schwarz K, Madsen GKH, Kvasnicka D, Luitz J, Laskowski R, Tran F, Marks LD. WIEN2k: an augmented plane wave plus local orbitals program for calculating the crystal properties. Vienna, Austria: Vienna University of Technology, Institute of Materials Chemistry; 2001. [ISBN 3-9501031-1-2]. Available from: http://www.wien2k.at/reg_user/textbooks/usersguide.pdf

13   Kohn W, Sham LJ, Self-consistent equations including exchange and correlation effects. Phys Rev 1965;140:1133-8.

14   AFLOW automatic-flow for materials study. Available from: http://aflowlib.org/

15   Murtaza G, Ahmad I. First principle study of the structural and optoelectronic properties of cubic perovskites $CsPbM_3$ (M=Cl, Br, I). Physica B: Condensed Matter 2011;406:3222-9.

16   Reshak AH, Jamal M, DFT calculation for elastic constants of orthorhombic structure within WIEN2K code: A new package (*ortho-elastic*). J Alloys Comp 2012;543:147-51.

17   Grimvall G. Thermophysical properties of materials. Enlarged and revised ed. Amsterdam, The Netherlands: Elsevier; 1999.

18   Meziani A, Belkhir H. First-principles calculations of structural, elastic and electronic properties of $CsCaF_3$ compound. Comput Mater Sci 2012;61:67-70.

19   Ghbouli B, Ghebouli MA, Fatmi M, Bouhemadou A. First-principles study of the structural, elastic, electronic, optical and thermodynamic properties of the cubic perovskite $CsCdCl_3$ under high pressure. Solid State Commun 2010;150:1896-1901.

20   Mayer B, Anton H, Bott E, Methfessel M, Sticht J, Schmidt PC. *Ab-initio* calculation of the elastic constants and thermal expansion coefficients of Laves phases. Intermetallics 2003;11:23-32.

21   Haines J, Leger JM, Bocquillon G. Synthesis and design of superhard materials. Annu Rev Mater Res 2001;31:1-23.

22   Pugh SF. XCII. Relations between the elastic moduli and the plastic properties of polycrystalline pure metals. The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science 1954;45:823-43.