[Copyedited version after the initial publication as an Epub ahead of print onOct 18, 2022 at www.fluorideresearch.online/epub/files/204.pdf]

COMPUTATION OF STRUCTURAL, ELECTRONIC, ELASTIC, AND OPTICAL PROPERTIES OF $BATF_3$ (T = HF AND TA) TERNARY FLUORIDE PEROVSKITES USING DFT APPROACH

Gohar Ayub,[a1], Mudasser Husain[1], Nasir Rahman[1*], Rajwali Khan[1], Imen Bejaoui[2], Tahir Zaman[3], Mohammad Sohail[1], Abid Ali Khan[4], Anwar Iqbal[4], Aurangzeb Khan[5,6]

Lakki Marwat, Karak, and Mardan, Pakistan and Serat Abida, Saudi Arabia

ABSTRACT: In the current research, we focus on the computation of some physical properties including structural, electronic elastic, and optical properties of barium-based $BaXF_3$ (X= Hf, and Ta) fluoroperovskites using the DFT approach within the wien2k simulation package. Structurally it is found that these cubic crystal compounds are stable having a tolerance factor of 0.93 for $BaHfF_3$ and 0.954 for $BaTlF_3$. The most accurate exchange-correlation potential that is TB-mBJ is for the accurate measurement of electronic properties and the computations of electronic properties, i.e., from the band's structures and density of states (DOS) depict that these materials are metallic with having overlapping valence and conduction bands. Elastic properties are computed for both the selected compounds using the IRelast cubic elastic package and it is found that the compounds of interest are mechanically stable, anisotropic, ductile, and possess hardness for scratching. The optical properties within 0 eV to 40 eV incident photon energy were measured and we concluded that these materials are optically active at low energy ranges because they are metallic. In addition to that, high optical conductivity, absorption, and high reflectivity are observed for $BaTF_3$ (T = Hf, and Ta) fluoroperovskite compounds. Herein we report for the first time the computational DFT-based precise results for both the compounds and from the reported work we deem the applications of selected fluoroperovskites will be relevant in many modern electronic and metallic industries.

Keywords: DFT; Fluoroperovskites; IRelast package; Structural, electronic, optical, and elastic properties; WIEN2K.

INTRODUCTION

The Perovskite compounds with higher reliability are now an attractive area for researchers. The perovskite structure, which is important in many types of functional ceramics, is a typical natural crystalline structure named after the mineral calcium titanate ($CaTiO_3$). Perovskite with the ABX_3 formula is important due to its technological application in the lenses nd semiconductor industries.[1-3] The fluoroperovskite structure can also be encountered in most ABF_3 compounds. A symbolizes a larger cation, whereas B indicates a smaller cation, and F indicates an anion. Fluoroperoskites are used in the medical field to monitor dose during radiation therapy.[4-6] The compound $BaXF_3$ (X=Li, Na, K, Rb) was investigated by Mubarak[7] and his research fellow, and they reported a large energy band gap in $BaXF_3$. These compounds can be utilized in high-frequency optical, lenses, optoelectronic instruments, and transparent coating. Ouenzerfi et al.[8] investigated the $BaLiF_3$ ternary fluoroperovskite and showed that it had a variety of instrumental applications due to its large energy band gaps. They also modified the design of the VUV light-

[a]Department of Physics, University of Lakki Marwat, 28420, Lakki Marwat, Khyber Pukhtunkhwa, Pakistan; [b]Department of Chemistry, College of Sciences and Art, King Khalid University, Serat Abida, Saudi Arabia; [c]Department of Mathematics, Govt Post Graduate College, Karak, Khyber Pukhtunkhwa, Pakistan; [d]Department of Chemical Sciences, University of Lakki Marwat, 28420, Lakki Marwat, Khyber Pukhtunkhwa, Pakistan; [e]Department of Physics, Abdul Wali Khan University, Mardan, Pakistan; [f]University of Lakki Marwat, 28420, Lakki Marwat, Khyber Pukhtunkhwa, Pakistan. For correspondence: Nasir Rahman, Department of Physics, University of Lakki Marwat, 28420, Lakki Marwat, Khyber Pukhtunkhwa, Pakistan. Email: nasir@ulm.edu.pk

emitting diode by using *ab-initio* band calculation. $BaLiF_3$ was also studied by Horsch et al.[9] for different practical applications like optical lithography steppers. Neupane et al.[10] theoretically examined $BaLiF_3$ and found that the compound has insulating behavior with a band gap of 6.8 eV. The Perovskite crystal family has a capacity for integrating physical properties such as large magneto-resistance and laser properties.[11,12] The temperature coefficient of resistivity which was calculated by Chi et al. in 2001 was nearly zero.[13] The fluoroperoskite crystal structure was investigated by Nishimatsu et al. and they found that there is a reduction in the transmittance of VUV because of impurities (Fe, Ni).[14] Several researchers studied the behavior of cubic Perovskite compounds, and most of the Perovskites were found to be elastic and mechanically stable.[15-18] The stable fluoroperovskites can be obtained by mixing fluorine with organic, inorganic, and TM (transition metals). Wide band-gap fluoroperovskites are the most promising candidates. They can be combined to produce complex lattice materials with wide band gaps, allowing these materials for band engineering and lattice fitting.[9] As far as we know, experimentation is not enough for the theoretical study of basic electronic and optical properties linked to $BaTF_3$ (T = Hf, and Ta) fluoroperovskite compounds. To fully use the properties of these compounds, theoretical research for the optimal technology application is necessary to have structural, electronic, and optical properties. The first principle method was used for computational investigations of the $BaTF_3$ (T= Hf, and Ta) using the DFT approach within WIEN2K.

RESEARCH METHODOLOGY

$BaXF_3$ (X=Hf and Ta) has a space group of pm-3m, which is a Perovskite structural compound. The research work is done by using the FP-LAPW method[19] incorporated within the WIEN2K package.[20] The different properties, like band structure, optical, and elastic, were obtained by using the most advanced and accurate Becke-Johson potential (TB-mBJ).[21] To estimate the structural features, the energy versus volume curve is approximated by using the Murnaghan equation of a state.[22] The muffin tin radius [RMT] value is selected in such a range that there is no leakage of charge either from the total or from the core. The GGA (generalized gradient approximation) is often used to determine the electron exchange and correlation potential for compositional and elastic characteristics. The GGA potential slight the band gap of the material, however, and this error is removed by using TB-mBJ potential. The cohesive energies of both compounds are estimated to verify the structural strength. The IRelast package[23] is used for the investigations of elastic properties and the software intends to provide researchers with a computational tool for computing elastic calculation of unknown compounds and comparing them to ECs of compounds that have been experimentally observed.

RESULTS AND DISCUSSION

This section describes in detail the investigated different results of the studied $BaTF_3$ (T = Hf and Ta) ternary fluorides compounds.

1. Structural properties

The ABF_3 fluoroperovskites possess a cubic crystalline structure with "A" and "B" elements being metallic cations and where the "F" is an anion.

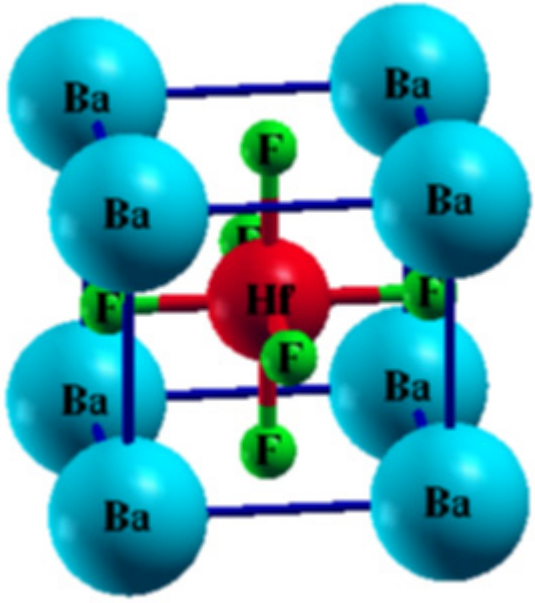
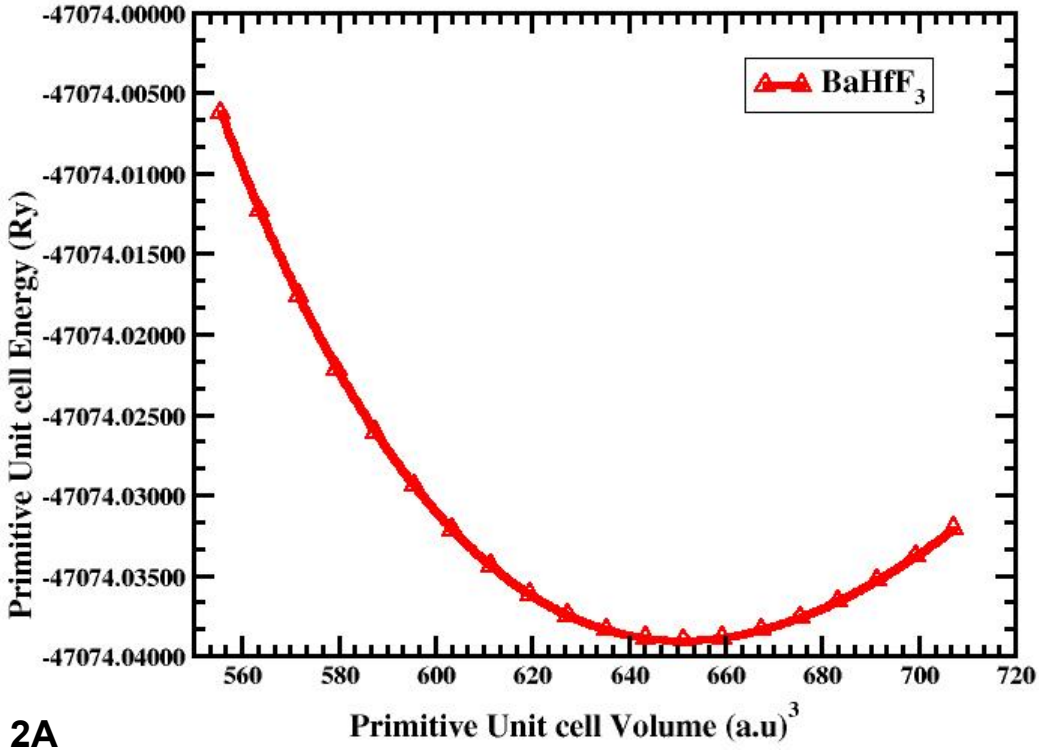
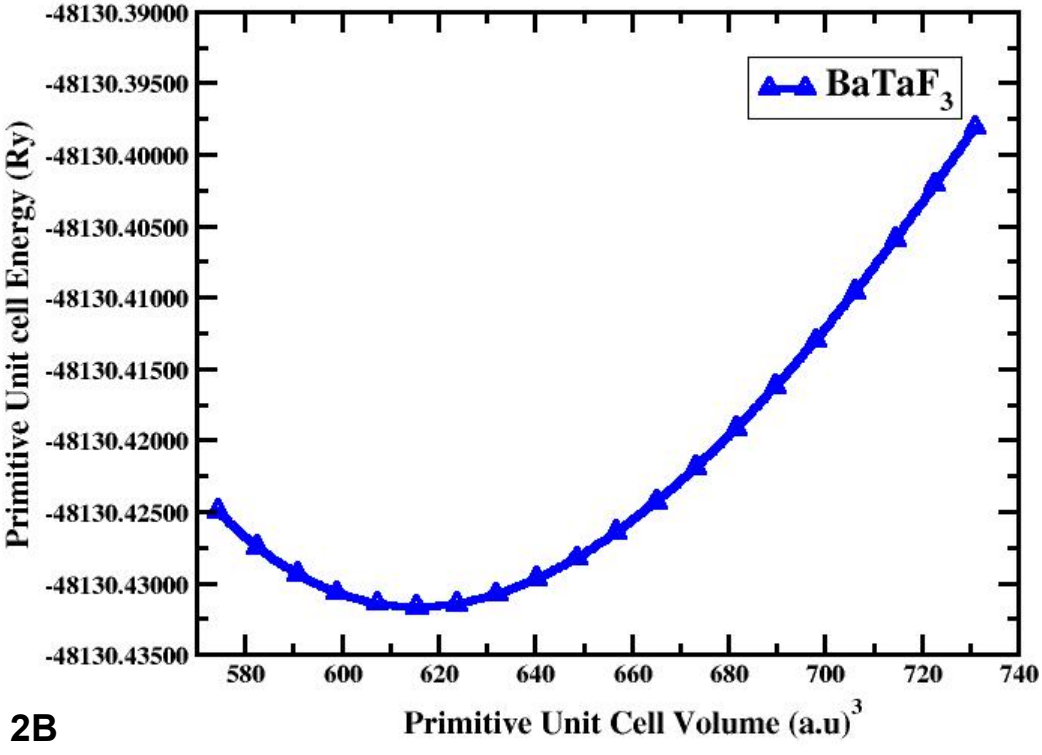


Figure 1. The prototype primitive unit cell crystal structure of fluoroperovskites BaTF3 (T = Hf and Ta) was obtained using the xcrysden package.

The cubical structure of fluoroperovskites $BaTF_3$ (T = Hf and Ta) with a space group of 221(pm-3m) is characterized by three atoms in the unit cell. The atomic positions of Ba are (0, 0, 0), T =Hf, and Ta lies at (0.5, 0.5, 0.5) and F is at (0, 0.5, 0.5) sites of the atoms in $BaTF_3$ and (0, 0, 0) is selected as the origin as shown in Figure.1. Figure.1 depicts the ideal cubic structure of fluoroperovskites compound which are studied here. We will compute in this segment the overall energy in response to unit-cell volume near V_0 (the equilibrium cell volume). The Birch-Murnaghan equation of state can also be used to identify the physical properties through the method of volume optimization. By executing an empirical approximation of our estimated values from the Birch-Murnaghan fit, we evaluate the ground state parameters, such as equilibrium lattice constant a_0, the bulk modulus B, and its pressure component. The optimization graph illustrates that the unit cell's least energy and may be obtained by reducing the unit cell's total energy with the appropriate volume. The ideal or Fermi energy E_0 and the volume V_0 are known as the total lowest energy against volume. The structural stability of the compound with the finest energy is estimated. The larger lattice constant has a smaller bulk modulus as usually observed, suggesting that the simulated values are much more accurate and practical. $BaTaF_3$ seems to have a slim optimized fit shape than $BaHfF_3$, implying that it is structurally better reliable. The structural optimization curves of primitive unit cell volume vs. the corresponding volume for fluoroperovskites BaTF3 (T=Hf and Ta) are shown in Figures 2A and 2B. Table.1 can be used to evaluate the stability of the compound.



2A



2B

Figures 2A and 2B. Structural optimization curves of primitive unit cell volume vs. the corresponding volume for fluoroperovskites $BaTF_3$ (T = Hf and Ta). 2A: $BaHfF_3$; 2B: $BaTaF_3$.

The computed values of optimized structural parameters are reported in the table.1 and from the tabulated values for both the compounds it is observed and concluded that $BaTaF_3$ is structurally more stable compared to $BaHfF_3$.

Table.1 Computed optimized structural parameters of fluoroperovskites $BaTF_3$ (T=Hf and Ta) ternary compounds. The "a_0" is the optimized lattice constant in Å, V_0 is the optimized volume in $(a.u)^3$, τ is the tolerance factor, B shows the bulk modulus in GPa, $B^/$ is the derivative of bulk modulus in GPa while E_0 represents the ground state energy in Ry

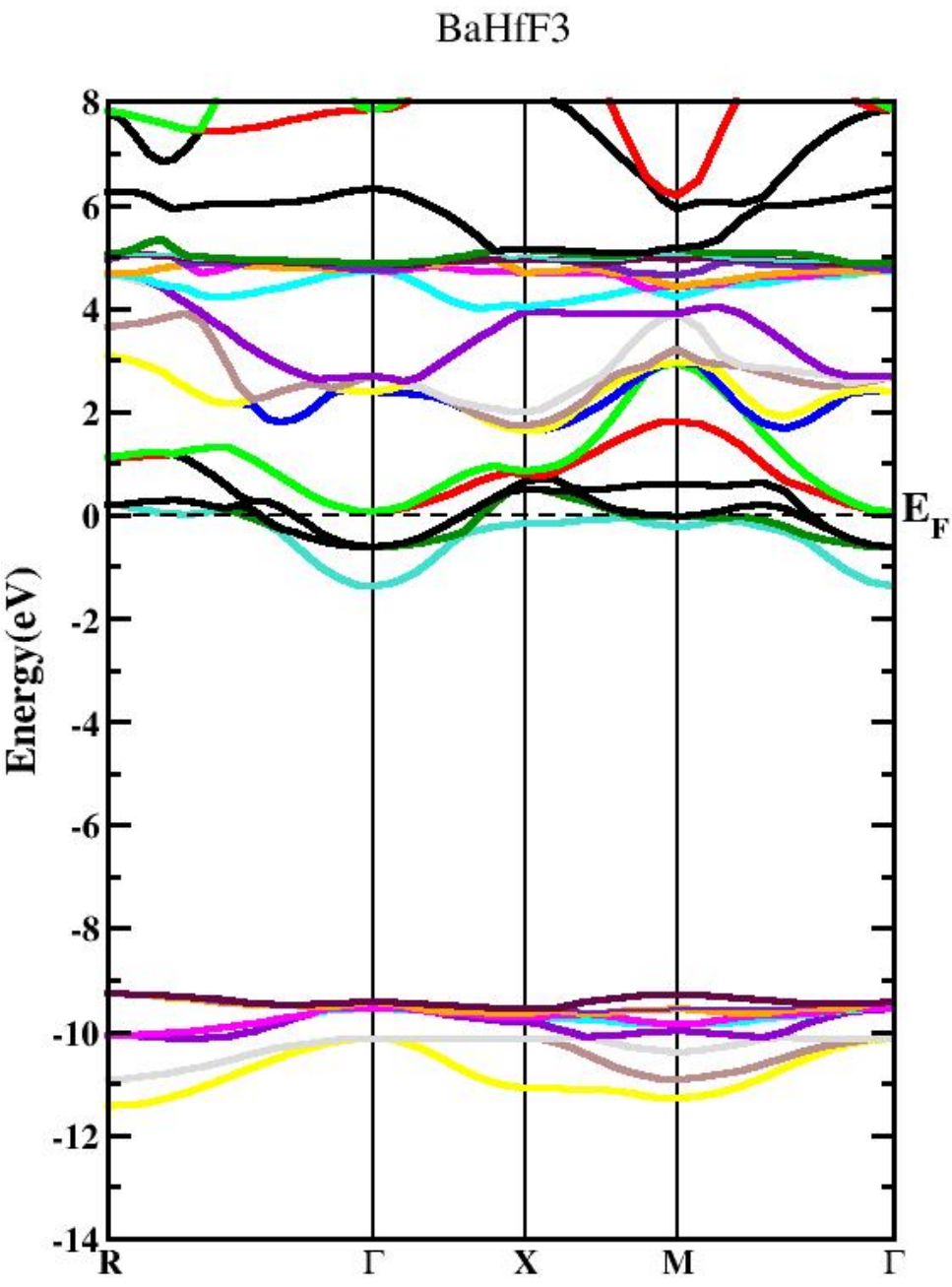
Structural parameters	$BaTaF_3$	$BaHfF_3$
a_0	4.501 A°	4.586 A°
V_0	615.557 $a.u^3$	651.082 $a.u^3$
τ	1.036	1.009
B	62.799 GPa	49.847 GPa
$B^/$	4.571 GPa	5.145 GPa
E_0 (in Ry)	-48130.432	-47047.039

2. Electronic properties

The electronic characteristics of the $BaTF_3$ (T = Hf and Ta) compound were calculated and examined using real energy band structure, DOS, and charge distribution in this section. LDA and GGA analysis undervalue the actual band gap of metals. The majority of this is related to their primary structures, which are poorly functional to stable recreate both the exchange-correlation and its current. The observed energy band patterns for the stable configuration of $BaTF_3$ (T=Hf and Ta) in the Brillion zone are presented in Figures 3A and 3B along with high symmetry axes. In metals, there is no band gap between the conduction and valance bands both the bands partially overlap as represented in Figures 3A and 3B. Simply the electrons are free to move in the conduction and valance band.

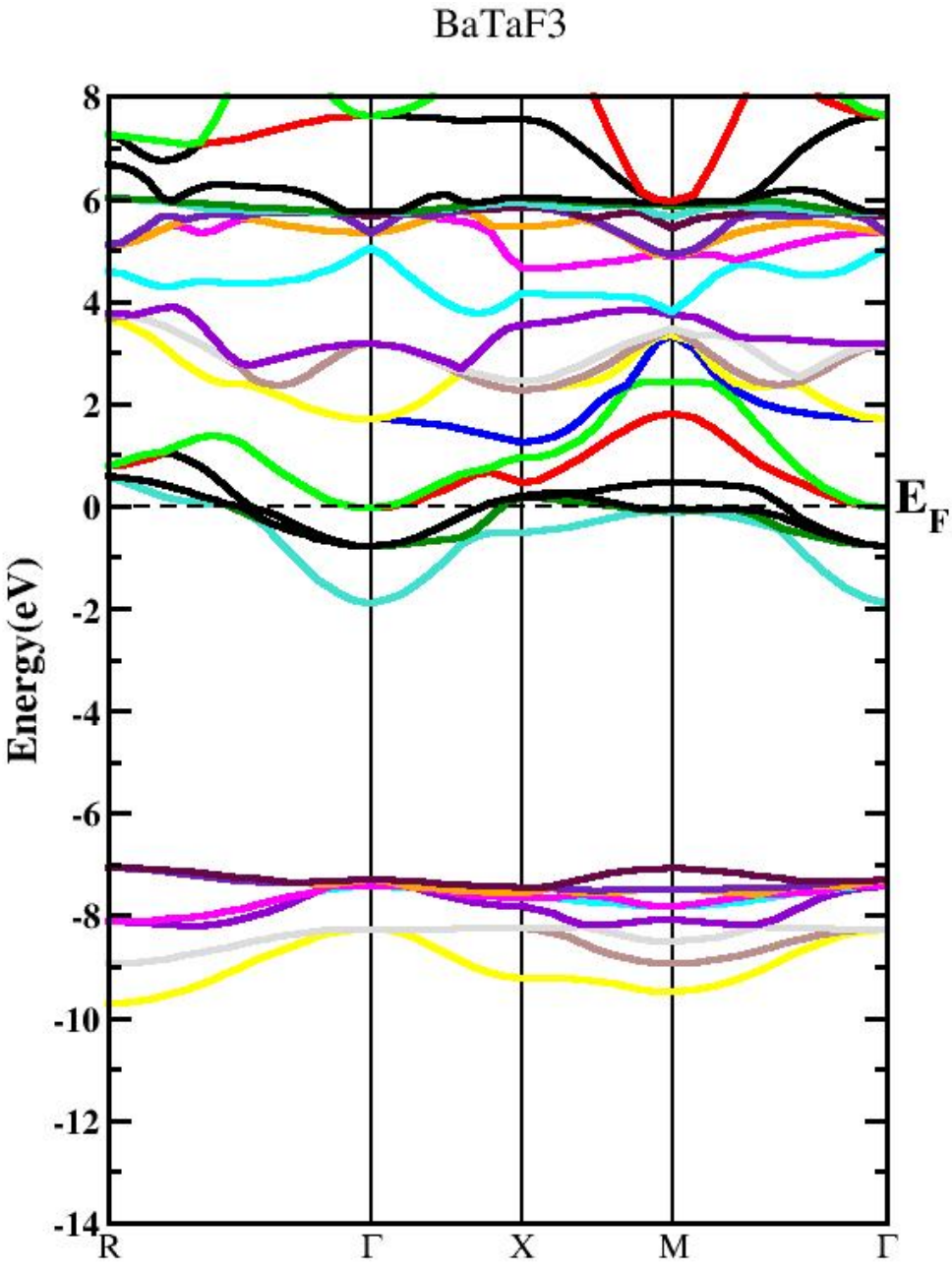
To acquire a good sense of the electronic properties we have shown in Figure 4 the PDOS and TDOS for said compounds. The influence of various electronic states on the valance and conduction bands can be seen in the DOS plot. As illustrated in Figure 4, the TDOS and PDOS (total DOS and partial DOS) provide a details understanding of the electrical structure.

The density of states (DOS) shows the contribution of different atomic states to the valance and conduction bands. The dotted line lies at 0 eV energy level showing the Fermi line. The portion to the right of this Fermi level is known as the conduction band whereas to the left is the valence band. It is very clearly depicted in Figures.4A and 4B of DOS that both the valence and conduction bands overlap at 0 eV energy level which results in the metallic nature.



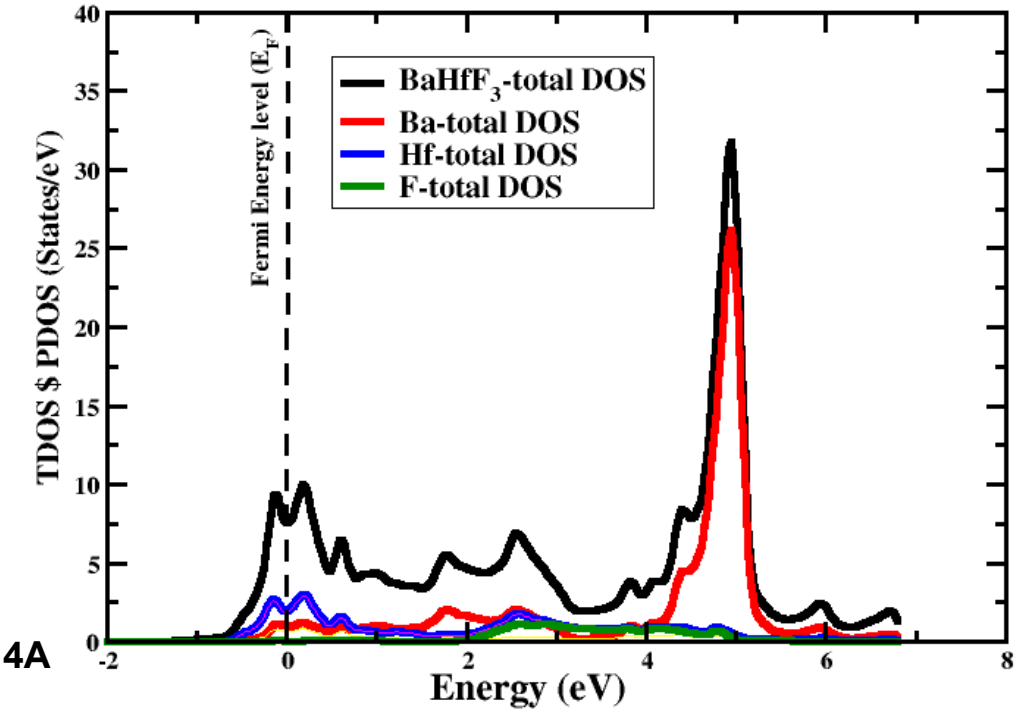
3A

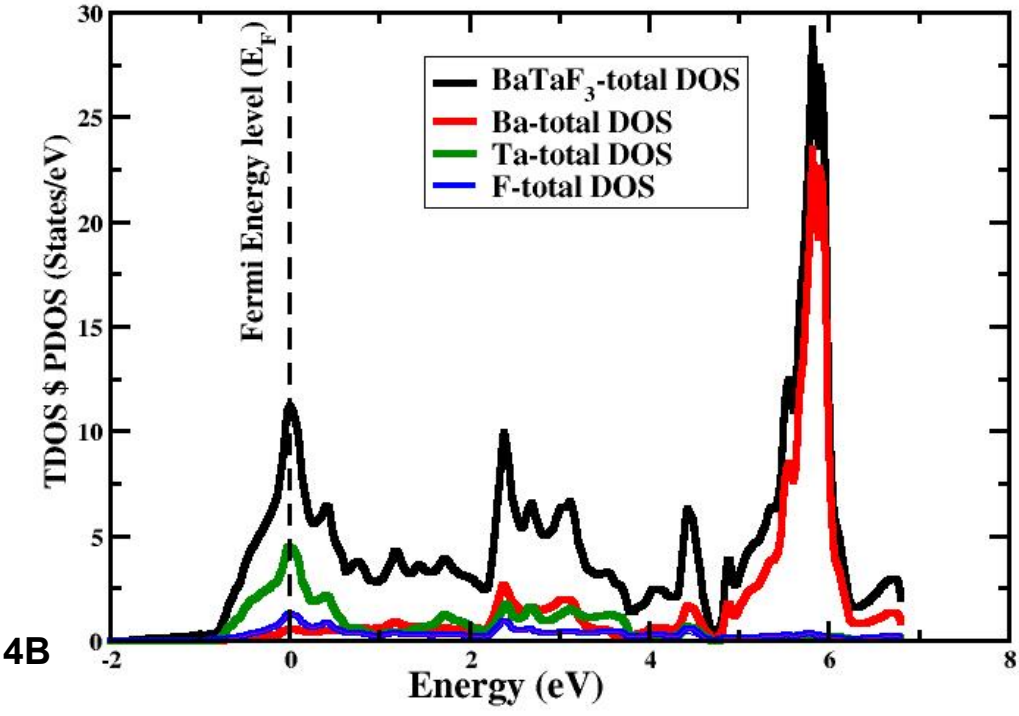
Figure 3A. The computed electronic band structures for BaTF3 (T=Hf) ternary fluoroperovskites.



3B

Figure 3B. The computed electronic band structures for BaTF3 (T=Ta) ternary fluoroperovskites.





Figures 4A and 4B. The computed TDOS and PDOS of $BaTF_3$ (T= Hf and Ta) ternary fluoroperovskites. 4A: $BaHfF_3$; 4B: $BaTaF_3$.

3. Elastic properties

The elastic properties influence the crystal behavior to external stimuli and are important in assessing material elastic modulus. The elastic constant data gives valuable information about structure consistency and strength. The elastic parameter of the studied compound at zero pressure was calculated by computing the variable of the bulk modulus for low strain and transferring energy following the lattice parameters that maintained volume. Elastic constants were estimated using the IRelast package, which is integrated into WIEN2K and is specifically designed for cubic systems (ECs). Due to the obvious cubic crystallite symmetry, the total number of distinct elastic constants C_{ij} is reduced to only three: C_{11}, C_{12}, and C_{44}. Table.2 highlights the predicted elastic moduli as well as other elastic parameters computed from the theoretical elastic modulus. The mechanical stability requirements[24] in a cubic structure sets limits on the elastic constants are $C_{11} - C_{12} > 0$, $C_{11} > 0$, $C_{44} > 0$, $C_{11} + 2\ C_{12} > 0$, and also $B > 0$. Our observed C_{ij} values meet these stability requirements, showing that these materials are elastically stable. From the reported data of elastic constants, we computed the A (anisotropy factor) to evaluate the elastic deformations of various materials as:

$$A = 2C_{44} / C_{11} - C_{12}) \quad (1)$$

The "A" value for isotropic material is "1" whereas "A" value for anisotropy material is greater or less than "1". The other elastic parameters such as "G" (shear modulus), "E" (Young's modulus), and "ν" (Poisson ratio) are to be found from the stated elastic constants by using the following equations:

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

$$V = \frac{3B - 2G}{2(3B + G)} \quad (3)$$

$$G_V = \frac{1}{5}(C_{11} - C_{12} + 3C_{44}) \quad (4)$$

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

Table 2. Shows the values of cubic elastic constants (C_{11}, C_{12}, and C_{44} in GPa), "A" is the anisotropy factor, "G" shows the shear modulus, "E" is Young's modulus, and "ν" is the Poisson ratio, "B" represent Bulk modulus, "G_v" is the Voigot shear modulus and "G_R"depicts Ruess shear modulus and the Pugh ratio (B/G) which are computed for $BaTF_3$ (T=Hf and Ta) ternary fluoroperovskites

Elastic parameters	$BaHfF_3$	$BaTaF_3$
C_{11} (GPa)	87.237	46.802
C_{12} (GPa)	43.225	48.337
C_{14} (GPa)	-24.049	-73.530
G_v	-5.955	-43.773
G_R	0.42	2.197
G	-2.764	-20.788
B	55.442	46.738
ν	0.795	1.250
A	0.56	0.68
B/G	20.058	2.66

4. Optical properties

Complex dielectric function:

The FP-LAPW is a significant computational approach for calculating optical characteristics of a compound $BaTF_3$ (T= Hf and Ta) fluoroperovskites by using the complex dielectric function equation:[25]

$$\varepsilon_1(\omega) = \varepsilon_1(\omega) + \iota\varepsilon_2(\omega)$$

We studied the optical parameters of the said compound ($BaTF_3$). The optical response is completely described for various compounds in different photon energy ranges (–2 to 14 eV). In the above mentioned equation the real and imaginary part of the dielectric function are represented by "$\varepsilon_1(\omega)$" and "$\varepsilon_2(\omega)$", respectively. This term is used to describe absorptive processes and is closely connected to a material's electronic band structure. The dispersive behavior of the structure is described by the real part and on the other hand, the light absorption action of the material is represented by the imaginary part. Figure 5 illustrates the optical activities of the compounds within the energy ranges of –2 to 14 eV, with some clear peaks at nearly 1 eV to 2 eV.

Reflectivity:

Measurement of reflectivity was done by using the imaginary part of the dielectric function ε(ω), as shown in Figure 6. The contribution in the valance band from F-p states, along with X-s and p-states in a conduction band, is used to construct the reflectivity "R(ω)" spectrum. From figure.6 it is clear that the high reflectivity peak is obtained for $BaHfF_3$ and $BaTaF_3$ at 1 eV and 3 eV respectively.

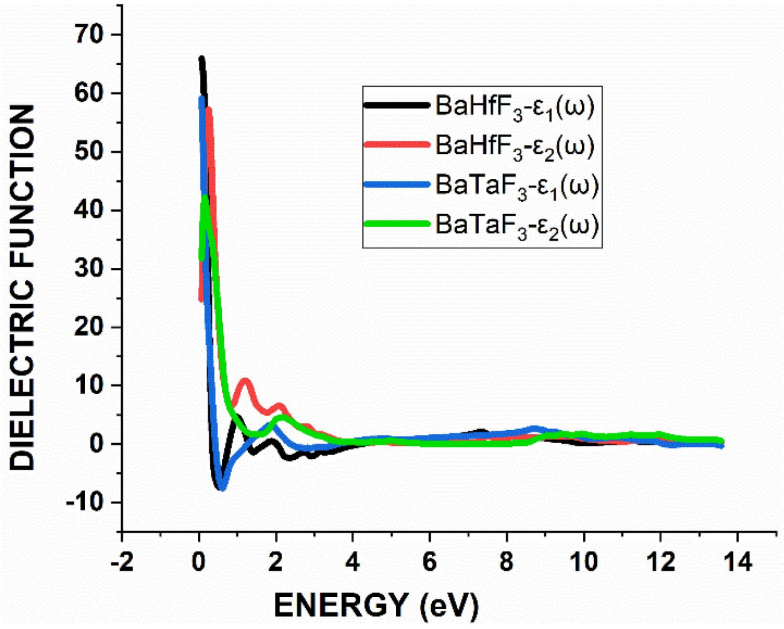


Figure 5. The computed complex dielectric functions for $BaTF_3$ (T= Hf and Ta) fluoroperovskites.

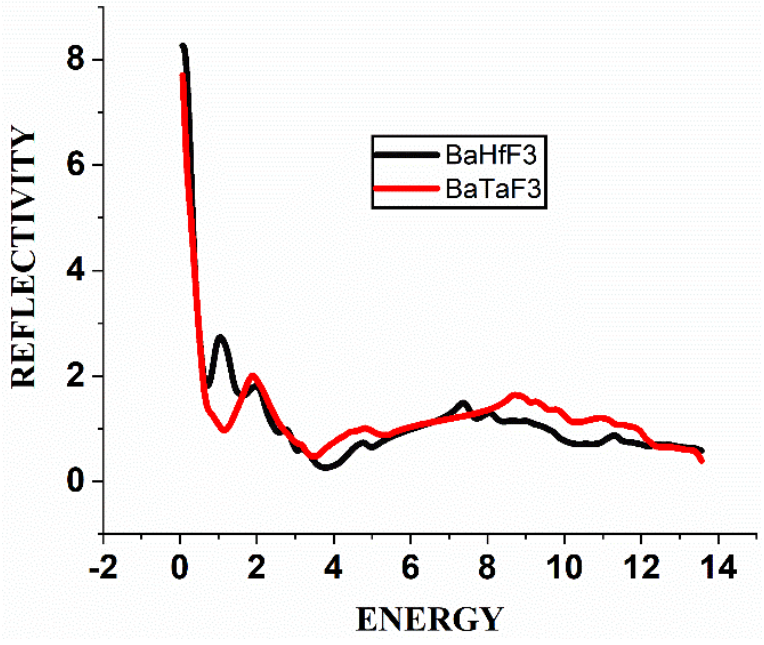


Figure 6. The computed optical reflectivity for $BaTF_3$ (T= Hf and Ta) fluoroperovskites.

4. Optical conductivity:

The conduction of electrons generated by an external electromagnetic field is referred to as optical conductivity. The examined conductivity of our compound $BaTF_3$ (T= Hf and Ta) is shown in Figure.7 and from the optical conductivity graph it is seen that this value sharply increases at a critical value of energy around 0.5 eV and reaches to highest values for $BaTaF_3$ and $BaHfF_3$ are 7 eV and 9 eV accordingly.

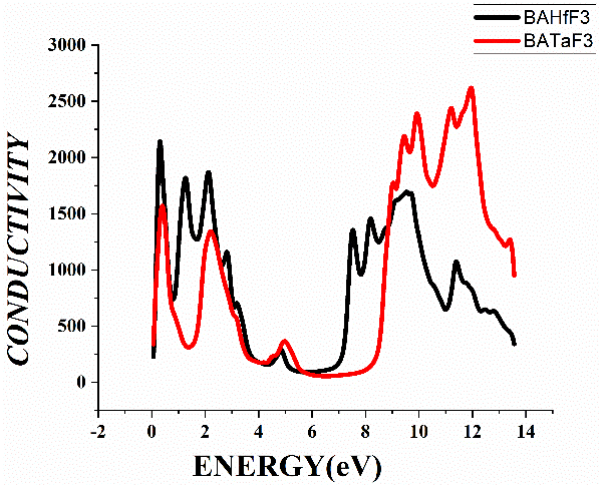


Figure 7. The computed optical conductivity for $BaTF_3$ (T= Hf and Ta) fluoroperovskites.

5. Absorption coefficient:

The absorption coefficient is influenced by both the real and imaginary parts of the dielectric function. The absorption coefficient means to measure how much light is absorbed by an optical device per unit length. Various interactions and transitions, like the interaction between electron-proton, inter-band, and intra-band transition generate absorption. The substances which are under consideration have a significant absorption as depicted in Figure 8.

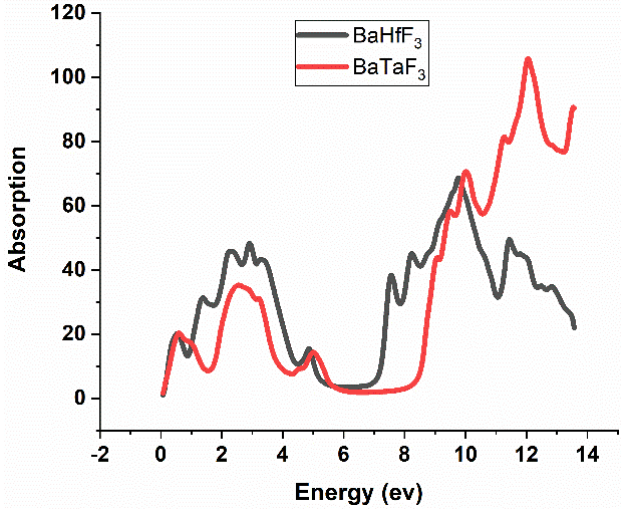


Figure 8. The computed absorption coefficient for $BaTF_3$ (T= Hf and Ta) fluoroperovskites.

The compound absorbs electromagnetic radiation at its threshold point. The active absorption for $BaTaF_3$ is 220 at 20 while for $BaHfF_3$ is 221 at 17.

In summary, the investigations of optical properties show that these materials possess a high absorption and optical conduction at high energy ranges.

CONCLUSIONS

This research work was successfully and precisely done by investigating the basic structural, elastic, electronic, and optical properties of ternary $BaTF_3$ (T=Hf and Ta) fluoroperovskite compounds. The conclusions dawn from the novel and precise results were:

❖ The ternary $BaTF_3$ (T=Hf and Ta) fluoroperovskites compounds are found to be cubic crystals and are structurally stable.

❖ From the investigations of the electronic properties, i.e., from the band's structure and the DOS, it was observed that both the materials are metallic with overlapping valence and conduction bands.

❖ The calculations of different elastic parameters for the elastic properties using the IRelast package show that the ternary $BaTF_3$ (T=Hf and Ta) fluoroperovskite compounds are mechanically stable, anisotropic, ductile, and possess hardness to scratch.

❖ The optical properties were investigated within the incident photon energy range of –2 to 14 eV and it was concluded that these compounds possess high optical conductivity, optical absorption, and high reflectivity at low energy ranges.

Therefore based on the above-investigated results we deem the application of these ternary fluoroperovskites will be relevant in many modern electronic devices and metallic industries.

ACKNOWLEDGMENT

The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University, Saudi Arabia for funding this work through the Research Groups Program under grant number R.G.P.1: 255/43.

REFERENCES

[1] Benmhidi H, Rached H, Rached D, Benkabou M. *Ab initio* study of electronic structure, elastic and transport properties of fluoroperovskite $LiBeF_3$. J Electron Mater 2017;46(4): 2205-10.

[2] Mousa AA, Mahmoud NT, Khalifeh JM. The electronic and optical properties of the fluoroperovskite $XLiF_3$ (X= Ca, Sr, and Ba) compounds. Comput Mater Sci 2013;79:201-5.

[3] Erum N, Iqbal MA. Effect of hydrostatic pressure on physical properties of strontium based fluoroperovskites for novel applications. Mater Res Express 2018;5(2):25904.

[4] Schuyt JJ. The effect of ionising radiation on the luminescence properties of fluoroperovskites [thesis]. Wellington, New Zealand: Victoria University of Wellington; 2020.

[5] Wang X, Hu Y, Wang R, Zhao P, Gu W, Ye L, Albumin-mediated synthesis of fluoroperovskite $KMnF_3$ nanocrystals for T1-T2 dual-modal magnetic resonance imaging of brain gliomas with improved sensitivity. Chem Eng J 2020;395:125066.

[6] Donaldson J, Williams GVM, Raymond SG. Characterization of a fluoroperovskite based fiber-coupled optical dosimeter for radiotherapy. In: Söhnel R, editor. Proceedings of the 38th annual condensed matter and materials meeting, Australia, 2014. p.147.

[7] Mubarak AA. *Ab initio* study of the structural, electronic and optical properties of the fluoropervskite $SrXF_3$ (X= Li, Na, K, and Rb) compounds. Comput Mater Sci 2014;81:478-82.

[8] Voigt W. Lehrbuch der Kristallphysik (Textbook of crystal physics). Leipzig and Berlin: BG Teubner; 1928.

[9] Hörsch G, Paus HJ. A new color center laser on the basis of lead-doped $KMgF_3$. Opt Commun 1986;60(1-2):69-73.

[10] Neupane K, Thapa RK., Study of electronic properties of fluoride Perovskite $BaLiF_3$ using FP-LAPW method. J Mater Sci Eng A 2017;7(11-12):311-4.

[11] Kim WS, Chi EO, Kim JC, Choi HS, Hur NH. Close correlation among lattice, spin, and charge in the manganese-based antiperovskite material. Solid State Commun 2001;119(8-9):507-10.

[12] Bloomstein TM, Liberman V, Rothschild M, D. Hardy DE, Goodman RB. Optical materials and coatings at 157 nm. Emerging Lithographic Technologies III 1999;3676:342-9.

[13] Chi EO, Kim WS, Hur NH. Nearly zero temperature coefficient of resistivity in antiperovskite compound $CuNMn_3$. Solid State Commun 2001;120(7-8):307-10.

[14] Korba SA, Meradji H, Schmid S, Bouhafs B. First-principles calculations of structural, electronic and optical properties of $BaLiF_3$. Comput Mater Sci 2009;44(4):1265-71.

[15] Husain M, et al. Structural, electronic, elastic, and magnetic properties of $NaQF_3$ (Q= ag, Pb, Rh, and Ru) fluoroperovskites A first-principle outcomes. Int J Energy Res 2022;46(3):2446-53.

[16] Sohail M, et al. First-principal investigations of electronic, structural, elastic and optical properties of the fluoroperovskite $TlLF_3$ (L= Ca, Cd) compound for optoelectronic applications. RSC Adv 2022;12(12):7002-8.

[17] Habib A, et al. Insight into the exemplary physical properties of Zn-based fluoroperovskite compounds $XZnF_3$ (X= Al, Cs, Ga, In) employing accurate GGA approach: A first-principles study. Materials (Basel) 2022;15(7):2669.

[18] Saddique J, et al. ìModeling structural, elastic, electronic and optical properties of ternary cubic barium based fluoroperovskites $MBaF_3$ (M= Ga and In) compounds based on DFT. Mater Sci Semicond Process 202*2;139:*106345.

[19] Petersen M, Wagner F, Hufnagel L, Scheffler M, Blaha P, Schwarz K., Improving the efficiency of FP-LAPW calculations. Comput. Phys. Commun 2000;126(3):294-309.

[20] Blaha P, Schwarz K, Madsen GKH, Kvasnicka D, Luitz J. Wien2k. An augmented plane wave plus local orbitals program for calculating crystal properties. Revised edition WIEN2k.17.1. [release 07/03/2017]. 2017.

[21] Kadim G, Masrour R, Jabar A. A comparative study between GGA, WC-GGA, TB-mBJ and GGA+ U approximations on magnetocaloric effect, electronic, optic and magnetic properties of BaMnS2 compound: DFT calculations and Monte Carlo simulations. Phys Sr 2021;96(4):45804.

[22] Jeanloz R. Universal equation of state. Phys Rev B 1988;38(1):805.

[23] Jamal M, Bilal M, Ahmad I, Jalali-Asadabadi S. IRelast package. J Alloys Compd 2018;735:569-79.

[24] Gao X, Jiang Y, Zhou R, Feng J. Stability and elastic properties of Y–C binary compounds investigated by first-principles calculations. J Alloys Compd 2014;587:819-26.

[25] Hilfiker JN, Tiwald T. Dielectric function modeling. In: Fujiwara H, Collins RW, editors. Spectroscopic ellipsometry for photovoltaics. Vol 1. Fundamental principles and solar cell characteristics. Cham, Switzerland: Springer International; 2018. pp. 115-53.