NIPES

Journal of Materials Engineering, Structures and Computation

Journal homepage: www.nipesjournals.org.ng

Ab Initio Calculation of Structural, Mechanical, and Electronic Properties of $BaSnO_3$ and $KCoF_3$ Perovskite Materials

I. E.Osawele [a], S. E. Ifada [b], B. E. Iyorzor [c]*

[a,b,c] Department of Physics, University of Benin, Nigeria.
*Corresponding author. E-mail address: beniyorzor@uniben.edu

ARTICLE INFORMATION

Article history:
Received 23 May 2023
Revised 26 May 2023
Accepted 28 May 2023
Available online 12 June 2023

Keywords:
Perovskites, Band Structure, Density of State, Density Functional Theory, Generalised Gradient Approximation (GGA).

https://doi.org/10.5281/zenodo.8028620

ISSN-2682-5821/

ABSTRACT

Ab initio calculation was carried out to investigate the Structural, Mechanical and Electronic Properties of $BaSnO_3$ and $KCoF_3$ Perovskite Materials using the Ultra Soft Pseudo Potential (USPP) from the Quantum Espresso (QE) software program. The Density Functional Theory (DFT) within the generalised gradient approximation (GGA) was used to optimize their crystal structure. The elastic constants, bulk modulus, shear modulus, and Young's modulus were computed to analyze their mechanical stability and resistance to deformation; Poisson's ratio was determined to elucidate the materials' response to external stress. Calculations on their band structures and electronic density of state suggests that both materials are metallic.

1. Introduction

Halide (KCoF3) as well as chalcogen (BaSnO3) perovskite materials have tremendous industrial applications, some of which include use in the production of sensors, batteries, fuel cells and photovoltaics. They have recently garnered rapid scientific growth. In 2016 [1] for example, perovskite solar cells were described as the fastest advancing solar technology, serving as better photovoltaic cells than the common silicon cells. Since then, perovskite materials have attracted even more research interest. Perovskite is generally a material with a crystal structure following the formula ABX3. From the chemical formula, atoms 'A' and 'B' are two cations that are often of very different sizes with the 'A' atoms larger than the 'B' atoms. At the same time, 'X' is an anion that generally can be an oxide, a chalcogen, a halide, a nitride, etc. that bonds to both cations. [20] There are 576 compounds experimentally characterized as perovskite materials at ambient conditions. Bartel et al (2019) [2] showed the different elements permissible within these compounds.

Barium Stannate (BSO or BaSnO3) have been researched recently because of its high electron mobility, excellent thermal stability, high transparency, structural versatility, and flexible doping controllability at room temperature hence it has potential use in the manufacturing of optoelectronic devices and experimenting on novel electronic quantum states [3]. Experimental results showed that barium stannate has a stable structure with a lattice parameter of 4.116Å. Using the PBE-GGA functional, the study suggests that BaSnO3 is a semiconductor with a band gap of 0.98eV. A comparative study of the cation effect on KCoF3 fluoride was investigated to examine its electromagnetic character in the cubic (Pm-3m) phase [4]. Using L(S)DA+U approach and

ferromagnetic configuration, results from the study showed that KCoF3 fluoride has a steady structure and a lattice parameter of 4.035Å. The fluoride's unique electronic properties allow it to be a potential candidate in optoelectronic, spintronic, and solar cell devices. Babalola *et al* (2019) [17] employed the ab initio calculation to investigate the physical and thermodynamic properties of XCrBi (X=Hf, Ti, and Zr) half-Heusler alloys. The alloys TiCrBi and ZrCrBi possess half-metallic characteristics; HfCrBi shows metallic behaviour in both up and down spin channels. Calculations showed that all three half- Heusler alloys considered were mechanically and thermodynamically stable and had a magnetic moment of 3μB. Iyorzor *et al* (2019) [18] carried out first-principle calculation of the structural, mechanical, electronic, lattice dynamic, and magnetic properties of LiO in Caesium Chloride, Rocksalt, and Zinc Blend structures in the cubic phases and determined that at the equilibrium lattice constants, LiO is ferromagnetic in the three phases and is chemically unstable. Also, in the Zinc Blend structure, LiO is brittle while ductile in others.

Based on the desire to advance the understanding of perovskite materials and contribute to the broader scientific knowledge of materials science as a field, considerations are given in this study to compute using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) formalism and verify that both BaSnO3 and KCoF3 are structurally stable in the simple cubic (SC) form, to examine if these materials are mechanically and electronically stable and confirm that computational results agree with other theoretical results. Accordingly, this study presents an ab initio computation of the structural, mechanical and electronic properties of BaSnO3 and KCoF3 perovskite structures.

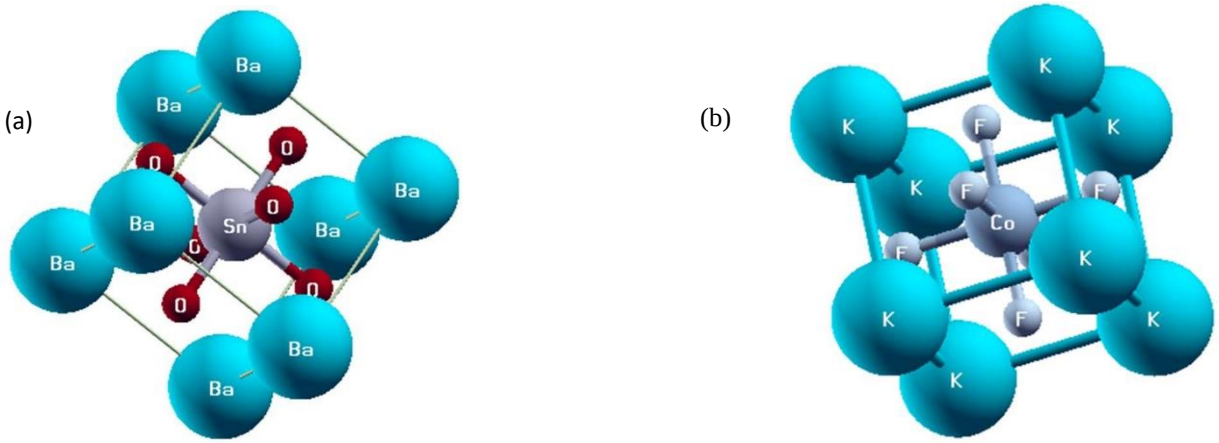

Figure 1. Crystallographic structures. (a). $BaSnO_3$ and (b). $KCoF_3$ Perovskite compound

2. Methodology

The structural optimization and prediction of properties of BaSnO3 and KCoF3 ternary compounds are performed by adopting the Quantum Espresso (QE) code similarly used in Gainnozi *et al* [5]. This calculation, based on the ultra-soft pseudopotential (USPP) method within the framework of the density-functional theory (DFT) and exchange-correlation was calculated using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA) formalism. [6] To achieve convergence, a plane-wave basis set with a kinetic energy cut-off (ecut) of 80 Ry, a charge density cut-off of 320 Ry, and a convergence threshold of 1.0 X 10-6 was applied in both BaSnO3 and KCoF3 structures. Lattice parameters of 4.1842Å and 4.0065Å were applied in BaSnO3 and KCoF3 structures respectively. The crystal structures used in this calculation are shown in Figure 1 above. The ground state properties of BaSnO3 and KCoF3 structures were obtained by performing the structural optimization for the lattice parameters through energy minimization as shown in Figure 2 below. Figure 2 shows that BaSnO3 is more structurally stable than the two structures in the simple

cubic form, the clear difference in the chemical composition of these structures accounts for their large energy separation on the graph.

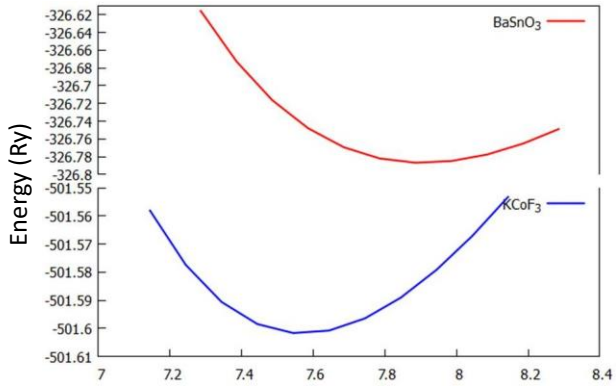

Figure 2. Total energies as functions of lattice parameters for $BaSnO_3$ and $KCrF_3$ perovskite structures.

3. Results and Discussion

3.1. Structural and mechanical properties

Calculations were performed on the total energy as a function of the lattice constant of both $BaSnO_3$ and $KCoF_3$ structures. Results obtained and other available literature results are summarized in Table 1. It was observed that a fair agreement exists between the present results and experimental results from other literature reports. [7, 8]. The elastic constants are functions of the stability and stiffness of both perovskite structures as recorded in the present calculation. The mechanical properties of both $BaSnO_3$ and $KCoF_3$ perovskite structures are computed and presented in Table 2.

Table 1. The structural properties: the lattice constant, a (Å), and bulk modulus, B (GPa) of $BaSnO_3$ and $KCoF_3$ perovskite compounds.

Perovskite structures	***a* (Å)**	***B* (GPa)**
$BaSnO_3$	4.18	276.6
$BaSnO_3^*$	4.12	–
$KCoF_3$	4.01	83.6
$KCoF_3^*$	4.01	90.7

*Results from experimental analysis on $BaSnO_3$ [7] and $KCoF_3$ [8] structures respectively.

The mechanical stability of a solid depends on the structural features and the corresponding elastic constants [9]. There are three independent elastic constants for cubic phases, $C11$, $C12$, and $C44$. The mechanical stability is measured by the following conditions: $C11 + 2C12 > 0$, $C11 - C12 > 0$, $C44 > 0$, and $C11 > 0$ [10]. The results in Table 2 show that both perovskite structures satisfy the necessary conditions hence, both compounds are mechanically stable. The bulk modulus B, Young modulus E, and shear modulus G are the parameters that are used to quantify the mechanical properties of solids. They show the extent of resistance of the alloys to volume and

shear deformation respectively. The higher their values, the stronger the deformation resistance offered by the alloys.

Table 2. Mechanical properties: The Young Modulus, *E* (GPa), the Shear Modulus, *G* (GPa), the Poisson ratio *n*, the ratio of the Bulk Modulus, *B* (Gpa) to the Shear Modulus, *G* (GPa), the Zener Anisotropy *A*, the Cauchy pressure C_p, and the Elastic constants C_{11}, C_{12}, C_{44} (GPa) of $BaSnO_3$ and $KCoF_3$ perovskite structures.

Mechanical property	**$BaSnO_3$**	**$KCoF_3$**
E	182.2	103.8
G	75.7	40.1
n	0.2	0.29
B/G	3.65	2.08
A	1.19	0.75
C_{11}	193.4	146.7
C_{12}	57.3	52.1
C_{44}	80.8	35.4
C_p	-23.5	16.7
$C_{11} + 2C_{12}$	308	250.9

From Tables 1 and 2, the results of the bulk, Young and shear moduli show that BaSnO3 have higher resistance to compressive deformation than KCoF3. An empirical relation to determining the plastic properties of materials is given by the ratio of the bulk modulus to the shear modulus B/G. The critical threshold value of the ratio for delineating ductile from brittle materials is about 1.75 [11]. From the results presented in Table 2, it is obvious that both BaSnO3 and KCoF3 perovskite structures are ductile with BaSnO3 having the higher ductility. The anisotropy factor, *A* is a measure of the degree of anisotropy in solid structures [12]. For perfectly anisotropic materials, the anisotropy factor is 1. If the value of *A* is zero, then the material is said to be isotropic. But when the values are deviating from zero and approaching unity it indicates high elastic anisotropy. The Zener anisotropy values as shown in Table 2 indicate that both BaSnO3 and KCoF3 perovskite compounds are very close to being perfectly isotropic i.e. they are both very close to being uniform in all orientations with KCoF3 having a higher variation. These results are obtained using the relation from equation (1), as recorded in [13],

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

The stability of the material against shear stress can be determined from the value of Poisson's ratio of the material. It also discloses the nature of the bonding forces. The value range is of the order $0 < n < 0.5$ [13]. The low value of Poisson's ratio indicates a large volume compression of the material and when $n = 0.5$ no volume change occurs. The higher the Poisson's ratio, the better the malleability. From the calculated results of the Poisson's ratio in Table 2, it is clear that both BaSnO3 and KCoF3 perovskite structures are positive showing that both structures have steady tensile deformation rather than compressive deformation with KCoF3 possessing a higher value of *n* than BaSnO3. The Cauchy pressure as described in the works of Niu *et al* (2012) [14], Xing *et al* (2017) [15], and Hu *et al* (2016) [16] is defined in terms of the single crystal elastic constants of a cubic material in equation (2).

$$C_p = C_{12} - C_{44} \tag{2}$$

A positive Cauchy pressure is considered to indicate ductile behaviour, while a negative pressure implies brittle behaviour. Table 2 shows that BaSnO3 possess brittleness while KCoF3 is observed to be ductile.

3.2 Electronic properties

Electronic properties of BaSnO3 and KCoF3 have been explained based on band structure and density of states using GGA. Figures 3 and 4 show the band structure and PDOS of BaSnO3 and KCoF3 materials respectively. There is no energy gap around the Fermi level in the band structure of both compounds suggesting metallic properties which implies that both BaSnO3 and KCoF3 materials are conductors. Regarding the PDOS, the Co-3d orbital in Figure 4 has the greatest contribution to its metallic nature around the Fermi level. Outside the Fermi level, it is observed that F-2p orbital plays a dominant role in the valence band. Also, at the conduction band, it is seen that there is a hybridization between the K-3s, K-4p, Co-5p, and F-1s orbitals suggesting high molecular stability. Considering Figure 3, the contribution of O-2p orbital at the Fermi level suggests semiconductor properties which are also indicated by some studies [19] but the contribution of Sn-2s orbital around and slightly on the Fermi-level indicates metallicity in BaSnO3. In the conduction band, there is an interplay of metallic orbitals showing strong hybridization with the Ba-3d orbital having the highest bonding contribution. There is also a relatively weaker hybridization of all 6 orbitals just below the Fermi level in the valence band.

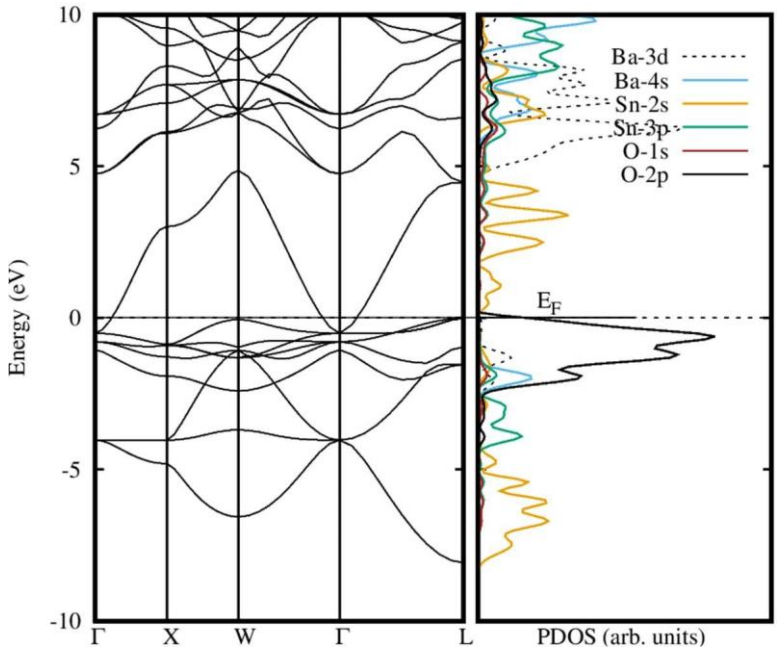

Figure 3. Electronic band structure and density of state for $BaSnO_3$ perovskite structure.

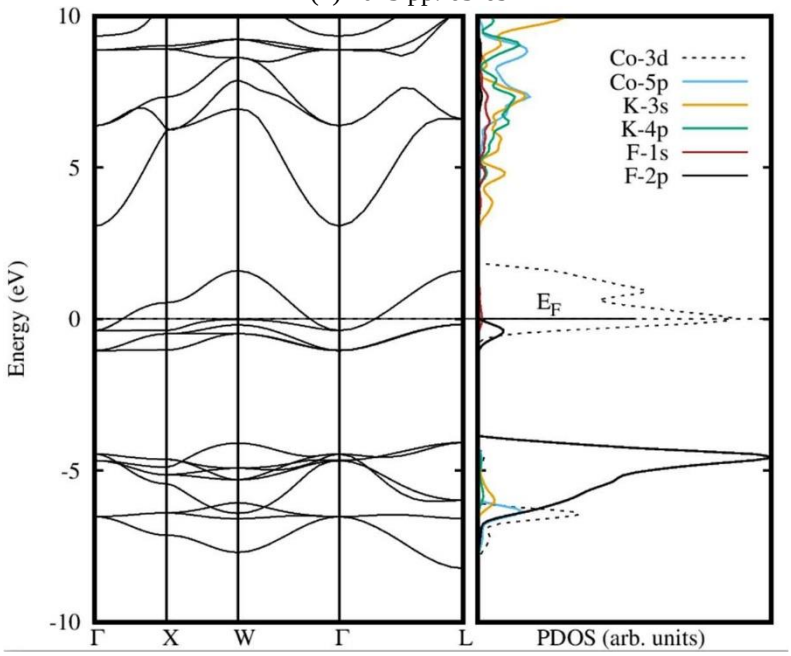

Figure 4. Electronic band structure and density of state for $KCoF_3$ perovskite structure.

4. Conclusion

In the present work, the structural, mechanical, and electronic properties of $BaSnO_3$ and $KCoF_3$ perovskite structures were examined, by performing ab initio calculations. The lattice parameter optimizations using energy minimization were reported in this study and suggests that $BaSnO_3$ is most structurally stable of the two compounds. It was observed that the lattice constants and the bulk modulus for both structures are in fair agreement with experimental studies. Calculations show that both compounds at their equilibrium lattice parameters have energy gaps of 0eV which implies that they both are metallic. It was found that both $BaSnO_3$ and $KCoF_3$ perovskite structures satisfied the mechanical stability conditions for cubic phases. Following calculations of the shear and Young moduli, the Poisson's ratio, and the Zener anisotropy, it was observed that $BaSnO_3$ and $KCoF_3$ structures are mechanically stable. The B/G ratio suggests that the two structures are ductile with $BaSnO_3$ having a higher ductility. The Cauchy ratio relation reveal that $KCoF_3$ is ductile while $BaSnO_3$ is brittle. The PDOS of both compounds confirm that Sn-2s orbital has the highest bonding contribution for $BaSnO_3$ being conductive while Co-3d orbital has the highest bonding contribution for $KCoF_3$ around the Fermi level. Finally, it was established from table 2 that the structures are isotropic and they are fairly plastic with $KCoF_3$ showing higher plasticity as observed from the Poisson's ratio calculations.

References

[1] Manser, J.S., Christians, J.A. and Kamat, P.V., 2016. Intriguing optoelectronic properties of metal halide perovskites. *Chemical reviews*, 116(21), pp.12956-13008.

[2] Bartel, C.J., Sutton, C., Goldsmith, B.R., Ouyang, R., Musgrave, C.B., Ghiringhelli, L.M. and Scheffler, M., 2019. New tolerance factor to predict the stability of perovskite oxides and halides. *Science advances*, 5(2), p. eaav0693.

[3] Yuwei Li, Lijun Zhang, Yanming Ma, David J. Singh (2015). Tuning optical properties of transparent conducting barium stannate by dimensional reduction. *APL Materials* Vol.3, (1), pp. 011102

[4] Sihem Filalli, and Noura Hamdad (2020). Electro-magnetic behavior of highly correlated fluorides $KFeF_3$, $KCoF_3$ and $KNiF_3$: a comparative ab-initio study of cation effect. *Annals of west university of Timisoara - Physics* Vol.62, pp. 23–51 DOI: https://doi.org/10.2478/awutp-2020-0003

[5] Giannozzi, P., Baroni, S., Bonini, N., Calandra, M., Car, R., Cavazzoni, C., Ceresoli, D., Chiarotti, G.L., Cococcioni, M., Dabo, I. and Dal Corso, A., 2009. QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of physics: Condensed matter*, 21(39), p.395502.
[6] John P. Perdew, Kieron Burke, and Matthias Ernzerhof (1996). Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* Vol. 77(18), pp. 3865-3868. doi = 10.1103/PhysRevLett.77.3865
[7] Licheron, M.; Jouan, G.; Husson, E. (1997), Characterization of BaSnO3 Powder Obtained by a Modified Sol-Gel Route. *J. Eur. Ceram. Soc.* Vol.17, pp. 1453−1457
[8] Margadonna, S. and Karotsis, G., 2007. High temperature orbital order melting in $KCrF_3$ perovskite. *Journal of Materials Chemistry*, 17(19), pp.2013-2020.
[9] Wu, Z., Hao, X., Liu, X. and Meng, J., 2007. Structures and elastic properties of OsN_2 investigated via first-principles density functional calculations. *Physical Review B*, 75(5), p.054115.
[10] Sin'Ko, G.V. and Smirnov, N.A., 2002. Ab initio calculations of elastic constants and thermodynamic properties of bcc, fcc, and hcp Al crystals under pressure. *Journal of Physics: Condensed Matter*, 14(29), p.6989.
[11] Pugh, S.F., 1954. 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*, 45(367), pp.823-843.
[12] Kittel, C., 2005. *Introduction to solid state physics*. John Wiley & sons, inc.
[13] Cheng, H.C., Yu, C.F. and Chen, W.H., 2013. First-principles density functional calculation of mechanical, thermodynamic and electronic properties of CuIn and Cu_2In crystals. *Journal of alloys and compounds*, 546, pp.286-295.
[14] Niu, H., Chen, X.Q., Liu, P., Xing, W., Cheng, X., Li, D. and Li, Y., 2012. Extra-electron induced covalent strengthening and generalization of intrinsic ductile-to-brittle criterion. *Scientific reports*, 2(1), p.718.
[15] Xing, H., Dong, A., Huang, J., Zhang, J. and Sun, B., 2018. Revisiting intrinsic brittleness and deformation behavior of B2 NiAl intermetallic compound: A first-principles study. *Journal of materials science & technology*, 34(4), pp.620-626.
[16] Hu, H., Wu, X., Wang, R., Jia, Z., Li, W. and Liu, Q., 2016. Structural stability, mechanical properties and stacking fault energies of $TiAl_3$ alloyed with Zn, Cu, Ag: First-principles study. *Journal of Alloys and Compounds*, 666, pp.185-196.
[17] Babalola, M.I., Iyorzor, B.E. and Okocha, O.G., 2019. Origin of half-metallicity in XCrBi (X= Hf, Ti, and Zr) half-Heusler alloys. *Materials Research Express*, 6(12), p.126301.
[18] Iyorzor, B.E. and Babalola, I.M., 2019. Structural, mechanical, electronic, and magnetic properties of LiO in cesium chloride, rocksalt and zinc-blende structures. *Journal of Applied Sciences and Environmental Management*, 23(1), pp.159-164.
[19] Phelan, D., Han, F., Lopez-Bezanilla, A., Krogstad, M.J., Gim, Y., Rong, Y., Zhang, J., Parshall, D., Zheng, H., Cooper, S.L. and Feygenson, M., 2018. Structural properties of barium stannate. *Journal of solid-state chemistry*, 262, pp.142-148.
[20] Orlovskaya, N. and Browning, N. eds., 2004. *Mixed ionic electronic conducting perovskites for advanced energy systems* (Vol. 173). Springer Science & Business Media.