I. INTRODUCTION

Understanding and dealing crystallographic structure has been center of new material research findings, exploring chemical and physical properties of materials with varies thermodynamics variables have been research interest for the last three decades. Howard et al has applied group-theoretical method to the space group and crystal structures of centrosymmetric, zone-boundary-tilted members of perovskite and elpasolite groups in relationships with bond lengths, bond angles, polyhedron volumes and distortions. Knight et al explained that KCaF$_3$ under go structural phase transitions at 560 k from a rhombohedral space group Cmcm to an orthorhombic Pbnm upon cooling. Lufaso and woodward showed KCaF$_3$ frequently crystallize as space-group Pbnm at ambient temperature. Comley noted that in SrTiO$_3$, rotating TiO$_6$ octahedron at corner of crystal system along any crystallographic directions result in irreducible representations. Obviously, under varies external variables crystal structure prefer to retain a simple irreducible symmetric crystal structure. Bismuth ferrite exhibit varies nature and order either in bulk form or thin film over ranges of phase transformation temperature.

Any BiFeO$_3$ distortion from the space group Pbnm pervskite structure will result in degeneracy between the d-states labeled $t_{2g}$(triplet) and $e_g$(doublet). Deviation has been due to FeO$_6$ octahedron tilt and altered infinitesimally. However, infinitesimal deviation had significant impact on magnetic, electronic and optical property of BiFeO$_3$. These degenerate energy levels ordered and filled by electrons based on Hund’s rules: electron’s spins must have highest multiplicity of both total spin & total angular momentum where start filling from lowest energy level (see Fig.2).

Crystal field theory model describes the magnetic behavior of crystallographic structure and significance of deviation angle which play critical role in an antisymmetric magnetic interaction, the so-called Dzyaloshinskii-Moriya(DM), which is due to spin-orbit interaction & often induce a weak antiferromagnetism in ferrites.

Therefore, in this work we explore role and effect of strained antisymmetric BiFeO$_3$ crystal structure which are derivative of Pbnm space group.

BiFeO$_3$ shows β and γ paraelectric orthorhombic phases between 1200K and 1100K temperatures with space group Pbnm structure. The Pbnm structure made from simple cubic pervskite structure of BiFeO$_3$ unit cell with A-site cation at the corners and the B-site at the corner coordinated by six oxygen located at the face centers forming an oxygen octahedron, rotating the oxygen octahedron about three cubic axis a, b, and c by the angles α, β, and γ, respectively, neighboring octahedron must be rotated as well, which minimize the symmetry. Then, structure of pseudo cubic formed with constituent unit cell of 12 oxygen anions, 4 B-site cations, and 4 A-site cations (see Fig.1).

In this work we considered psuedo cubic structure strained to reduced volume from original unstrained Pbnm structure as displayed on Table.I.

Strain force vector directions are $\vec{a}$, $\vec{b}$, $\vec{c}$, $\vec{a}'$ and $\vec{b}'$. Further Compressed to 15° between plane $\angle BC$ with $\alpha$-angle for amplified antisymmetric effect on Pbnm structure.

II. COMPUTATIONAL METHOD

Ab initio calculation were performed using the projector augmented wave(PAW) method as implemented in gpaw code. The electron wave-function is approximated using the implementation of a projector augmented wave method & the Schrödinger equation applied to total energy functions are solved self-consistently using the Kohn-Sham scheme. All electron waves are expanded over periodic potential plane with a method.
of P.E.Blöchl having a band, a k-points, and a reciprocal lattice grid indices. A plane wave cut-off energy used is 520 eV. The sum of plane wave kinetic energy limit \( \frac{1}{2} [G + E]^2 < E_{\text{cut-off}} \). The minimal energy \( E_{\text{cut-off}} \) where the plane wave is expanded in the reciprocal lattice vector grid \( G \) of first Brillouin zone. The k-points within Brillouin zone (BZ) is chosen according to Monkhorst-Pack scheme\(^{17}\), where a \( K \)-meshes of \( 8x8x8 \) is used.

The interactions of the valence electrons with the core electrons and nuclei is treated using compensation charge both long-range electrostatics and nodal shape of orbitals correctly addressed within a projector augmented wave (paw) data sets\(^{16,18}\).

The number of valence electrons considered for each element within the paw data sets is Bi(10d\(^{10}\) 6s\(^{2}\) 6p\(^{3}\)), Fe(3s\(^{2}\) 3d\(^{6}\) 4s\(^{2}\)), and O(2s\(^{2}\) 2p\(^{4}\)). Geometry relaxations are carried out using BFGS minimizer\(^{19}\), where optimizations of the atomic coordinates and the unit cell degrees of freedom is done within the concept of the Hellmann-Feynman forces and stresses\(^{20,21}\) calculated on the Born-Oppenheimer(BO) surface\(^{22}\). The convergence criteria for the forces were set at 0.05 eV/Å. The exchange-correlation energies are approximated within the generalized gradient approximation of PBE\(^{23}\) & a \( K \)-mesh of \( 3x3x3 \) is used in a geometry relaxation calculations. Hubbard model\(^{24}\) selected for better description of d-orbital of Fe : \( U_{c_{ff}}=7.5 \) eV with spin polarized calculation applied.

In calculation of the band gap, we have used Tauc plot method\(^{25}\) which extrapolate by fitting a straight line to the linear segment to intersect \( \hbar \omega \)-axis from the plot of \((\hbar \omega \alpha)^{2} \) against \( \hbar \omega \).

\[
(h \omega \alpha)^{1/2} = A(h \omega - E_g) \tag{1}
\]

where \( h \) is the Plank’s constant, \( \omega \) is frequency \( \alpha \) is absorption coefficient, \( E_g \) is band gap and A is proportionality constant.

For band structure calculation a special set of k-points mesh \( 8x8x8 \) is used and implemented exchange-correlation functionals within PBE approximation\(^{29}\).

Crystal field theory explains that degenerate d-orbitals of orthorhombic crystal structure split into \( t_{2g} \) triplet and \( e_g \) doublet states due to the crystal field splitting energy. The \( Fe^{+3} \) ion is surrounded by an octahedron oxygen with valance electrons of 5 d orbitals having spins aligned parallel producing 5 \( \mu_{\beta} \) per \( Fe^{+3} \) ion\(^{26}\). The d orbitals barely interact with nearby \( Fe^{+3} \) sites. However, exchange interaction made with six neighboring oxygen 2p orbitals. The general Hamiltonian becomes,

\[
H = J_{AF} \sum_{\langle ij \rangle} S_i \cdot S_j - J_H \sum_i s_i S_i - \sum_{\langle ij \rangle, \sigma, \sigma'} t_{ij}^{\sigma, \sigma'} c_i^\sigma c_j^{\sigma'} + D_{ij} (S_i^3 X_j^3) \tag{2}
\]

where \( \alpha, \beta \) stands for d-orbitals of anisotropic hopping matrix elements \( t_{ij}^{\alpha, \beta} \) with several possible outcomes of creation operator with introduction of canted ant-ferro magnetism, \( J_{AF} \) is antiferromagnetic super exchange coupling constant between spins\((S_i, S_j)\) of \( t_{2g} \) and \( e_g \) energy levels and \( J_H \) is Hund’s coupling constant on-site spins\((S_i, S_i)\) and the DM interaction\(^{27}\). Eq.(2) show that the source of multiferroic order are coupling constant and the DM interactions.

One can analyze and understand material’s optical response property once incident photon energy imparted to the electron, & material’s response is given as

\[
\varepsilon(\omega) = \varepsilon_1(\omega) + i \varepsilon_2(\omega) \tag{3}
\]

The imaginary part \( \varepsilon_2(\omega) \) of dielectric function is calculated using the following expression

\[
\varepsilon_2(\omega) = \left( \frac{4 \pi^2 e^2}{m^2 \omega^2} \right) \sum_{i,j} i|M| j^2 f_i (1-f_i) \delta(E_f - E_i - \omega) d^3 k \tag{4}
\]

Where, \( M \) is the dipole matrix, \( i \) and \( j \) are initial and final states respectively; \( f_i \) is the Fermi distribution function for the \( i^{th} \) state and \( \omega \) is the frequency of the incident photon.

Real part \( \varepsilon_1(\omega) \) of the dielectric function can be found from Kramers-Kronig equation\(^{28}\).

\[
\varepsilon_1(\omega) = 1 + \frac{2}{\pi} \sum_{\omega' \rightarrow \omega} \frac{\varepsilon_2(\omega') d\omega'}{\omega'^2 - \omega^2} \tag{5}
\]

Where, \( P \) stands for the principle value of the integral. From dielectric function, all the other optical proper-
III. RESULTS AND DISCUSSION

Pseudo cubic paraelectric orthorhombic structure with Pbmn space group with lattice parameters a=5.482 Å, b=5.73 Å and c=7.86 Å has been considered for variates antisymmetric structure calculation. unstrained Pbmn space group is similar to experimental parameters. Band structure calculated in Fig.(4) and Fig.(5) based on spin-orbit coupling implemented in electronic structure code GPAW. One can input crystallographic information file of any space group for special k-point band paths & export from online website which made available at http://www.materialscloud.org/tools/seekpath/.

All selected antisymmetric crystal structure had simultaneous broken spatial-inversion and time-reversal symmetry upon symmetry operation this in turn favors magnetic and electric order pairing. Therefore, degenerate bands at the boundary of the Brillouin zone splits up and narrows the gaps between conduction & valance bands near Γ point.

Degenerate bands shown where there is band crossing except those strained in $\bar{ac}$, $\bar{abc}$ and Pbmn structure. Two high energy degenerate levels($e_g$) and three low energy levels($t_{2g}$) not including two anti-bonding and bonding bands which were created due to hybridization of spin-orbit interaction either constructive or distractive way.

As depicted on Table I those structure strained in $\bar{ac}$, $\bar{abc}$ resulted in simultaneous magnetic and electric order pairing with larger optical band gap as shown in Fig.(6). However, only polarization exhibited in $\bar{ac}$, since strain vector direction or polarization is perpendicular to the spins, magnetization becomes zero due to Lebeugle et al. The relation, $\mathbf{P} \propto \mathbf{\epsilon}_{ij} X(\mathbf{\tilde{S}}_i \mathbf{\tilde{S}}_j)$, where $\mathbf{\tilde{S}}_i$, local spins and $\mathbf{\epsilon}_{ij}$ is the unit vector connecting the two sites.

Magnetic and electric order coupling shown in all antisymmetric structures except in paraelectric Pbmn & $\bar{ac}$ strained structures. However, in Fig.(4) $\bar{ac}$ strained behave like photonic crystal band structure in such away that the dispersion relation is linear unlike electronic band structure which is parabolic, and spin-orbit
interaction evolve with possible $S = 1$ states contrast to electron $S = 1/2$ state & ignored magnetization. Moreover, refractive index is relatively smallest as shown in Fig.(3) compared to others & decline with range of 13 to 8, 8 to 5, 5 to 3 & 3 to 1 as per incident photon energy. Hence, BiFeO$_3$ strained in specific direction could be considered as photonic crystal. Moreover, strain could promote remarkably fast photon energy transfer for photon’s energy close to smaller optical band gap and enhanced photovoltaic effect with greater photo sensitivity.

ACKNOWLEDGMENTS

We are grateful to Ministry of Science and Higher Education of Ethiopia for financial support and International Science Program, Uppsala University, Sweden are gratefully acknowledged for providing computational facilities. We are also thankful to the office of VPRTT of Addis Ababa university for supporting this research under a grant number AR/032/2021.

FIG. 3. Calculated dielectric function $\varepsilon(\omega)$ and $\tilde{n}(\omega)$ according to Eq.(7). Colors: real part $\varepsilon_1(\omega)$ is given in red color solid lines, imaginary part $\varepsilon_2(\omega)$ is given in black color solid lines, & $\tilde{n}(\omega)$ is given in blue color solid lines(For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
TABLE I. Strain force acted on symmetric Pbnm space group with possible strain vector direction resulting in varies morpho-
logical, magneto electric changes with respective band gap displayed for comparison.

| Space group | Vector Strain Direction | Unit-cell volume(Å³) | Cell parameters | Bandgap(eV) | Magnetic Moment(µµB) |
|-------------|-------------------------|----------------------|-----------------|------------|---------------------|
| Pbnm        | -                       | 247.04087            | \( a = 5.482234\)Å   \( b = 5.729905\)Å  \( c = 7.864368\)Å  
\( \alpha = 90^\circ \)  
\( \beta = 90^\circ \)  
\( \gamma = 90^\circ \)  | 2.71\(^{41}\) | 0.000 |
| P₁          | \( \vec{a}, \vec{b} \)  | 247.09827602         | \( a = 5.48223\)Å   \( b = 5.73078\)Å  \( c = 7.865\)Å  
\( \alpha = 44.0^\circ \)  
\( \beta = 89.2715^\circ \)  
\( \gamma = 90^\circ \)  | 0.915853 | 178 |
| P₁          | \( \vec{a}, \vec{b}, \vec{c} \) | 247.09827602         | \( a = 5.48223\)Å   \( b = 5.73078\)Å  \( c = 7.865\)Å  
\( \alpha = 75.0^\circ \)  
\( \beta = 89.2715^\circ \)  
\( \gamma = 89.0002^\circ \)  | 1.93949 | 44 |
| P₁          | \( \vec{a}, \vec{c} \)  | 247.09827602         | \( a = 5.48223\)Å   \( b = 5.73078\)Å  \( c = 7.865\)Å  
\( \alpha = 44.0^\circ \)  
\( \beta = 90^\circ \)  
\( \gamma = 89.0002^\circ \)  | 1.86041 | 0.000 |
| P₁          | \( \vec{b}, \vec{c} \)  | 247.09827602         | \( a = 5.48223\)Å   \( b = 5.73078\)Å  \( c = 7.865\)Å  
\( \alpha = 44.0^\circ \)  
\( \beta = 89.2715^\circ \)  
\( \gamma = 90^\circ \)  | 0.923963 | 90 |

IV. Reference

1Howard, C.J, Luca, V. & Knight, K.S.(2001): High temperature phase transitions in tungsten trioxide-the last word?. J. Phys., Condensed Matter, 13, 1-11, https://doi.org/10.1088/0953-8984/14/3/308.

2Howard, C.J., Kennedy, B.J. & Woodward, P.M.(2003). Ordered double perovskites- a group-theoretical analysis, Acta Crystallogr: 59, 463-471, https://doi.org/10.1107/0108768103010073.

3Knight, K.S(2009a). Parameterization of the crystal structure of centrosymmetric zone-boundary-tilted perovskites: An analysis in terms of symmetry-adapted basis-vectors of the cubic aristotype phase Can. Mineral. 47, 381-400, https://doi.org/10.3749/canmin.47.2.381.

4Knight, K.S, Darlington, C.N.W. & Wood, I.G.(2005b). The crystal structure of KCaF3 at 4.2 and 300 K: a revaluation using high-resolution powder neutron diffraction, Powder Diffraction 20, 7-13, https://doi.org/10.1154/1.1835959.

5Lufaso, M.W., Woodward, P.M.(2001).Prediction of crystal structures of perovskites using the software SPuDS. Acta Crystallogr 57, 725-738, http://doi.org/10.1107/010876810101828.

6Comley, R.A.(1964).Lattice dynamics and phase transitions of strontium titanate. Phys Rev. 134, A981-A997, https://doi.
FIG. 4. Scatter spin-orbit coupled band structure calculated using Eq.(2). The colors show the spin character: blue designated as spin down, red as spin up and dashed gray lines as bands without spin-orbit coupling respectively (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

FIG. 5. Time-reversal symmetry band structure scatter plot are either red or blue signaling that the bands are approximate eigenstates of the spin projection operator along the z-axis, spin up is displayed as red and spin down is displayed as blue (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).
FIG. 6. Tauc plots vs. photon energy $\hbar\omega$ for direct band gap $E_g$ transition together with a linear extrapolation of $(\alpha\hbar\omega)^2$ for antisymmetric strain vector direction $\vec{a}\vec{b}$, $\vec{a}\vec{b}\vec{c}$, $\vec{a}\vec{c}$, $\vec{b}\vec{c}$. 

7M. Tokunaga, M. Akaki, T. Ito, S. Miyahara, A. Miyake, H. Kuwahara & N. Furukawa (2015). Magnetic control of transverse electric polarization in BiFeO$_3$. Nat. Commun. 6:5878 doi:10.1038/ncomms8878.
8John D. Morgan, and Werner Kutzelnigg(1993). Hund’s Rules, the Alternating Rule, and Symmetry Holes. J. Phys. Chem. 97, 2425-2434. https://doi.org/10.1021/j100112a051.
9Cheong, SW., Mostovoy, M. Multiferroics(2007) a magnetic twist for ferroelectricity. Nature Mater 6, 13-20. https://doi.org/10.1038/nmat1804.
10Donna C. Arnold, Kevin S. Knight, Finlay D. Morrison, and Philip Lightfoot(2009) Ferroelectric-Paraelectric Transition in BiFeO$_3$: Crystal Structure of the Orthorhombic $\beta$ Phase. PRL 102, 027602 https://doi.org/10.1103/PhysRevLett.102.027602.
11Donna C. Arnold, Kevin S. Knight, Gustau Catalan, Simon A. T. Redfern, James F. Scott, Philip Lightfoot, and Finlay D. Morrison(2010).The $\beta$ to $\gamma$ Transition in BiFeO$_3$: A Powder Neutron Diffraction Study. Adv. Funct. Mater. 20, 2116-2123, https://doi.org/10.1002/adfm.201000118.
12M. Brahlek, A. K. Choquette, C. R. Smith, R. Engel-Herbert, and S. J. May(2017) Structural refinement of Pb$_n$-type perovskite films from analysis of half-order diffraction peaks. Journal of Applied Physics 121, 045303; https://doi.org/10.1063/1.4974362.
13J. Enkovaara, C. Rostgaard, J. Mortensen, J. Chen, M. Duham, L. Ferrighi, J. Gavnholt, C. Glinsvad, V. Haikola, H. Hansen, H. Kristoffersen, M. Kuisma, A. Larsen, L. Lehtovaara, M. Ljungberg, O. Lopez-Acevedo, P. Moses, J. Ojainen, T. Olsen, V. Petzold, N. Romero, J. Stausholm-Miller, M. Strange, G. Tirtsaris, M. Vanin, M. Walter, B. Hammer, H. Høkkinen, G. Madsen, R. Nieminen, J. Nørskov, M. Puska, T. Rantala, J. Schütz, K. Thygesen, K. Jacobsen, Electronic structure calculations with GPAW: a real-space implementation of the projector augmented-wave method, J. Phys. Condens. Matter 22 (2010) 253202. https://doi.org/10.1088/0953-8984/22/25/253202.
14J. Mortensen, L. Hansen, K. Jacobsen, Real-space grid implementation of the projector augmented wave method, Phys. Rev. B 71 (2005), 035109. https://doi.org/10.1103/PhysRevB.71.035109.
15W. Kohn, L. Sham, Self-consistent equations including exchange and correlation effects, Phys. Rev. 140 (1965) A1133-A1138, https://doi.org/10.1103/PhysRev.140.A1133.
16P. Blöchl, Projector augmented-wave method, Phys. Rev. B 50 (1994) 17951. https://doi.org/10.1103/PhysRevB.50.17951.
17H. Mostek, J. Pack, Special points for Brillouin-zone integrations, Phys. Rev. B 13 (1976) 5188. https://doi.org/10.1103/
First principles study of structural, electronic and optical properties of BiFeO$_3$

T. Shen, C. Hu, H. L. Dai, W. L. Yang, H. C. Liu, X. L. Wei (2015).

First principles study of structural, electronic and optical properties of BiFeO$_3$ in ferroelectric and paraelectric phases.

J. Phys. Chem. C 119, 18974-18980.