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Determination of Structural, Electronic, and Elastic Properties of $SnTiO_3$ using Density Functional Theory

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Abstract

The harmful effect of lead Pb^{2+} base materials like $PbTiO_3$ on the environment and human health has raised ecological concerns, which has led to the investigation of lead Pb^{2+} free ferroelectric materials that are safe for the environment and human health and can be used in technological applications. In this research, the structural, electronic, and elastic properties of the cubic phase of $SnTiO_3$ were investigated using first principle calculation. The electronic structure calculation was done by using the generalized gradient approximation and Perdew-Burke Ernzerhof (GGA-PBE) functional as implemented in the pseudopotential plane wave approach within the framework of density functional theory (DFT) by using Quantum Espresso open sources computer code. The convergence test of total energy concerning energy cut-off wave function and k-point sampling was performed to ensure the accuracy of the calculations. Thermo_pw code was employed to compute the elastic constant using the Quantum Espresso software package and the result obtained was used to calculate mechanical parameters such as the elastic properties, anisotropy factor A, shear modulus G, bulk modulus B, Young's modulus E, and Poison's ratio n of the $SnTiO_3$. Furthermore, Debye temperature and longitudinal and transversal sound velocities were determined using the elastic constant. Therefore, the cubic phase of $SnTiO_3$ with a space group of (Pm3m) is a good ferroelectric material due to its Debye temperature and the covalent bonding nature of the atom within the solid crystal of the material.

Keywords: Temperature; Density Functional Theory (DFT); Electronic Properties; Ferroelectric Material.

I. INTRODUCTION

Perovskite is any material with a crystal structure following the chemical formulae of ABX_3 in which A and B are positively charged ions while X is a negatively charged ion. A and B are different in size, with the A-atom generally bigger than the B-atom [1]. These materials could have a significant impact on many industrial applications like energy production, information storage, optical waveguides, integrated optics applications, superconductors, and optoelectronic devices. The perovskite material classes have been recognized as semiconductors for photovoltaic and optoelectronic applications, such as photo-detection and light-emitting devices, and these crystal materials include $CaTiO_3$, $PbTiO_3$, $SnTiO_3$, $BaTiO_3$, and lead halide or any other materials that have perovskite structural formulae [2].

Lead titanate ($PbTiO_3$) a ferroelectric ceramic material is one of the most important members of the perovskite with large dielectric constant and piezoelectric, pyroelectric, and

ferroelectric properties, which finds application in memories, switching devices, infrared sensors, transducers, optical waveguides and other electronic components such as capacitors, ultrasonic transducers, thermistors, non-volatile memory, and other optoelectronic devices [3], [4], [5]. At room temperature, lead titanate is in a tetragonal phase (space group p4mm) and a ferroelectric material at a temperature above room temperature i.e. 763 K with a cubic phase (space group of pm3m) [6].

The harmful effects of lead-based materials like $PbTiO_3$ on the environment and human health have raised some ecological concerns. These led to the investigation of lead (Pb^{2+}) free ferroelectric materials by determining their electronic band structure, the partial density of state, and mechanical properties [7]. Lead is composed of about 60 per cent of the lead in the Pb^{2+} base materials. Research on finding a suitable eco-friendly replacement for lead (Pb^{2+}) free ferroelectric material has been ongoing because of its harmful nature [1]. Tin (Sn^{2+}), which is a member of group 14 in the periodic table, adjacent to lead (Pb^{2+}) with both elements possessing lone pairs of electrons appears a better option [8], and the perovskite material to replace it with is $SnTiO_3$ which is a material that exhibits ferroelectric properties in its cubic phase at a temperature above 763 K with a space group of pm3m and transition to paraelectric in its tetragonal phase with a space group of P4mm at ambient temperature [9].

Most of the theoretical studies on $SnTiO_3$ lately, has its focus on its physical properties and high polarization effect in the ferroelectric phase. In this study, the structural, electronic elastic properties, poison's ratio, anisotropic index, and Debye temperature of the cubic phase of $SnTiO_3$ were determined to serve as a competent replacement for $PbTiO_3$ in technological applications.

II. THEORETICAL BACKGROUND

A. Mechanical Property

This refers to the ability of a material to resist applied forces or load without breaking or permanently deforming. The mechanical parameters such as bulk modulus (B), shear modulus (G), Young's modulus (E), poison's ratio (n), and the anisotropic index (A) of the cubic $TiSnO_3$ can be derived from the calculated elastic constants C_{11}, C_{12}, C_{44} [2].

$$B = \frac{C_{11}+2C_{12}}{3} \quad (1)$$

$$G = \frac{1}{2}(G_V + G_R) \quad (2)$$

Where,

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

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

$$E = \frac{9GB}{G+3B} \quad (5)$$

$$n = \frac{3B-2G}{2(3B+G)} \quad (6)$$

The anisotropic index is given by (7)

$$A = 2\,C_{44}/(C_{11} - C_{12}) \quad (7)\ [3]$$

The ductility/brittleness nature of the studied material can be explained by using Pugh's criterion, when the B/G ratio is 1.75 which is the critical value, these values separate the ductility and brittleness behaviour of the material. So, when the ratio of B/G is lower than the critical value the material is brittle and if not, the material is ductile. Poisson's ratio is also a factor that gives more information about the mechanical stability of the material, and it describes the bonding forces of the material, and has lower and upper limits which are 0.25 and 0.5 respectively. If the value of the poison's ratio of material is within the lower and upper limit, it indicates that the inter-atomic force of material is central [1]. Debye temperature is an important parameter of solid crystal material that measures how strongly atoms vibrate within a solid material. The Debye temperature is calculated from the elastic constant data using (8), and which is found to be 589.41 K.

$$T_D = \frac{h}{k}\left[\frac{3n}{\pi}\left(\frac{N_A\rho}{M}\right)\right]^{\frac{1}{3}} V_m \quad (8)$$

Where h is the plank's constant, k is the Boltzmann's constant N_A is the avogadro's number, $and\ V_m$ is the average sound velocity. V_m is expressed in terms of the longitudinal sound velocity V_l and the transverse sound velocity V_t which can be obtained from the mechanical parameters such as sheared modulus (G), and bulk modulus (B).

$$V_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-\frac{1}{3}} \quad (9)$$

$$\text{Where, } V_l = \left[\frac{B+\left(\frac{3}{4}G\right)}{\rho}\right]^{\frac{1}{2}} \quad (10)$$

$$V_t = \left(\frac{G}{\rho}\right)^{\frac{1}{2}} \quad (10)$$

III. COMPUTATIONAL METHOD

Electronic and structural computations of the cubic $SnTiO_3$ were performed using density functional theory (DFT) implemented in Quantum Espresso open-source computer codes [12]. The electronic calculation was done within the function of generalised gradient approximation and Perdew-Burke Ernzerhof (GGA-PBE) exchange correlation. The electronic wave function was described by the plane wave self-consistent calculation which is a first principle energy code that uses both norm-conserving pseudopotential (PP) and ultra-soft pseudopotential (US-PP) implemented in the Quantum Espresso package. The structure of the cubic tin titanate ($SnTiO_3$) was viewed using Xcrysden software [13]. The k-point sampling convergence test was done to ensure the accuracy of the computation and the convergence point was archived and found to be $18 \times 18 \times 18$. The elastic constants were calculated by using thermo_pw computer code [14]. The result obtained (elastic constants) was used to calculate the mechanical parameters like the bulk modulus, shear modulus, Young's modulus, Poisson's ratio and anisotropic index. The

Debye temperature and longitudinal and transverse sound velocities were also computed.

IV. RESULTS AND DISCUSSION

A. Structural Optimization

Fig. 1 shows the crystal structure of cubic $SnTiO_3$. The structural parameter of the cubic $SnTiO_3$ was fully optimized, and the 35 Ry energy cut-off wave function and $18 \times 18 \times 18$ k-point grid sizes obtained from the convergence test were used. In this calculation, the value of the lattice parameter was varied for each set of calculations in the input file until the crystal structure was fully optimized. The lattice parameter of the cubic $SnTiO_3$ before the optimization was 3.951 Å and after full optimization of the structure, a lattice parameter of 3.634 Å was achieved, which was used throughout the computation, comparable to that obtained in [15].

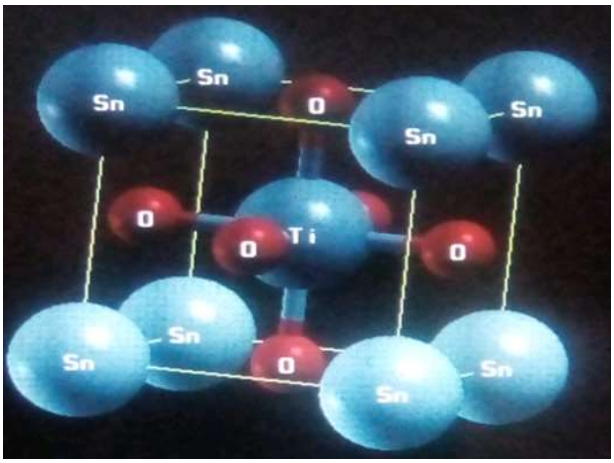

Fig. 1. Cubic structure of $SnTiO_3$.

B. Total Energy Concerning k-point Sampling

The convergence test of total minimum energy for k-point sampling was carried out, in which we varied the k-point and computing with an increment of $1 \times 1 \times 1$ up to 20 times, but all the other parameters in the input file remained fixed. We plotted a graph of total energy in Ry against K-point the convergence was achieved at 18×18×18 which was used throughout the computation. Fig. 2 shows the k-point convergence test of the studied material.

C. Total Energy Concerning Energy Cut-off Wave Function (ECUTWFC):

The convergence test of the energy cut-off wave function was carried out in which we varied the energy cut-off wave function with an increment of 5 at the range of 5 Ry to 45 Ry with all the parameters in the input file remaining fixed after the k-point convergence test was conducted. The convergence of the energy cut-off wave function is achieved after plotting a graph of total energy against the energy cut-off wave function which is 35 Ry, and an energy cut-off density of 140 Ry was used throughout the computation. Fig. 3 shows the energy cut-off convergence test of the studied material.

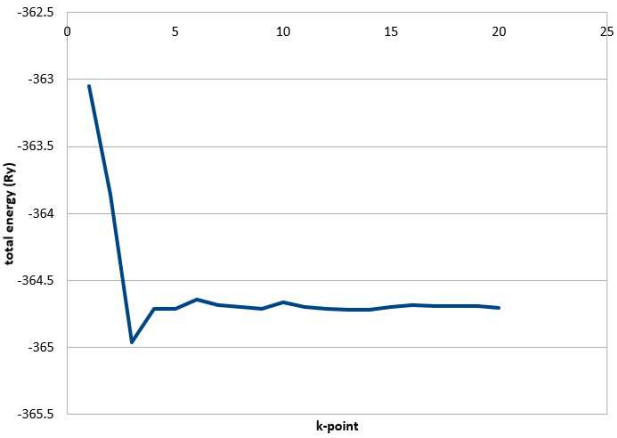

Fig. 2. k-point sampling convergence of cubic $SnTiO_3$.

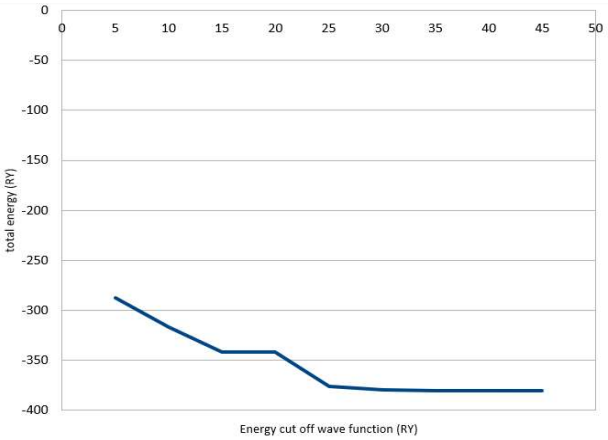

Fig. 3. Convergence points for energy cut-off wave function of cubic $SnTiO_3$.

D. Electronic properties:

Electronic band structure is a fundamental concept in solid-state physics and material science which represents the range of energy levels that an electron can occupy within a solid crystal material. It is important to understand the electrical, optical and magnetic properties of the materials. The electronic band structure of the cubic $SnTiO_3$ with a space group of (Pm3m) was plotted using the gnu plot software package and the material has an indirect band gap along the high symmetric axis of the Brillion zone as shown in Fig. 4. The material was found to have an indirect band gap of 1.67 eV which agrees with the value of 1.6 eV obtained in a similar research conducted in [16].

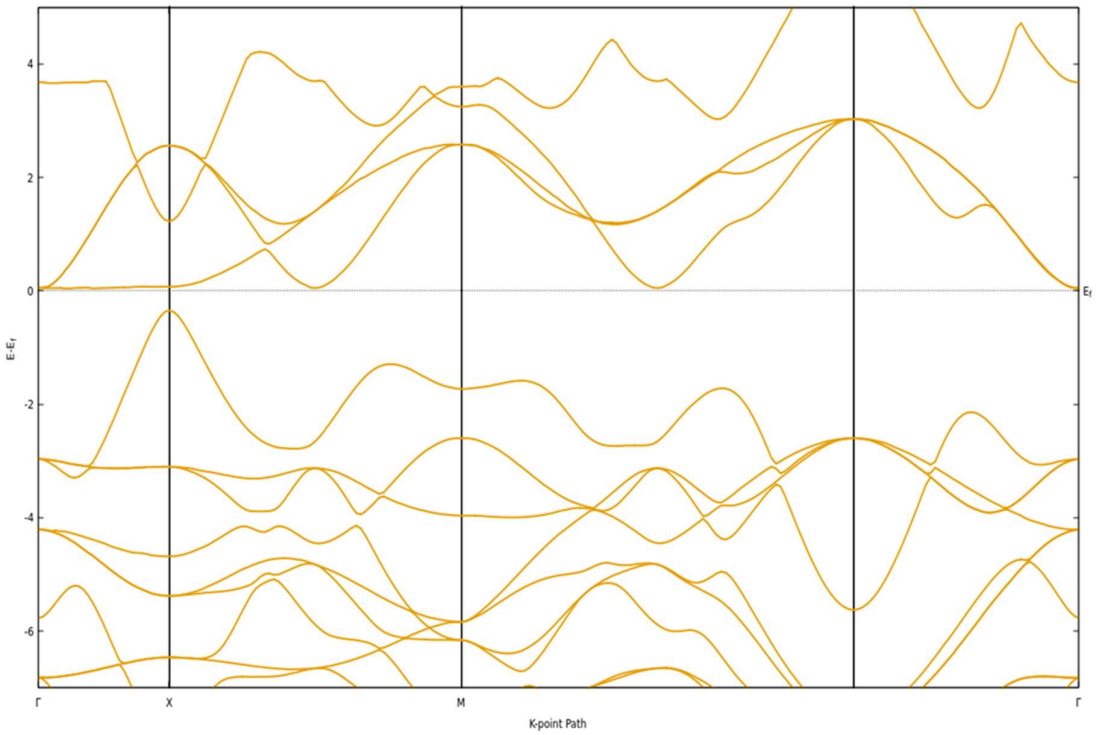

Fig. 4. Electronic band structure of the cubic $SnTiO_3$.

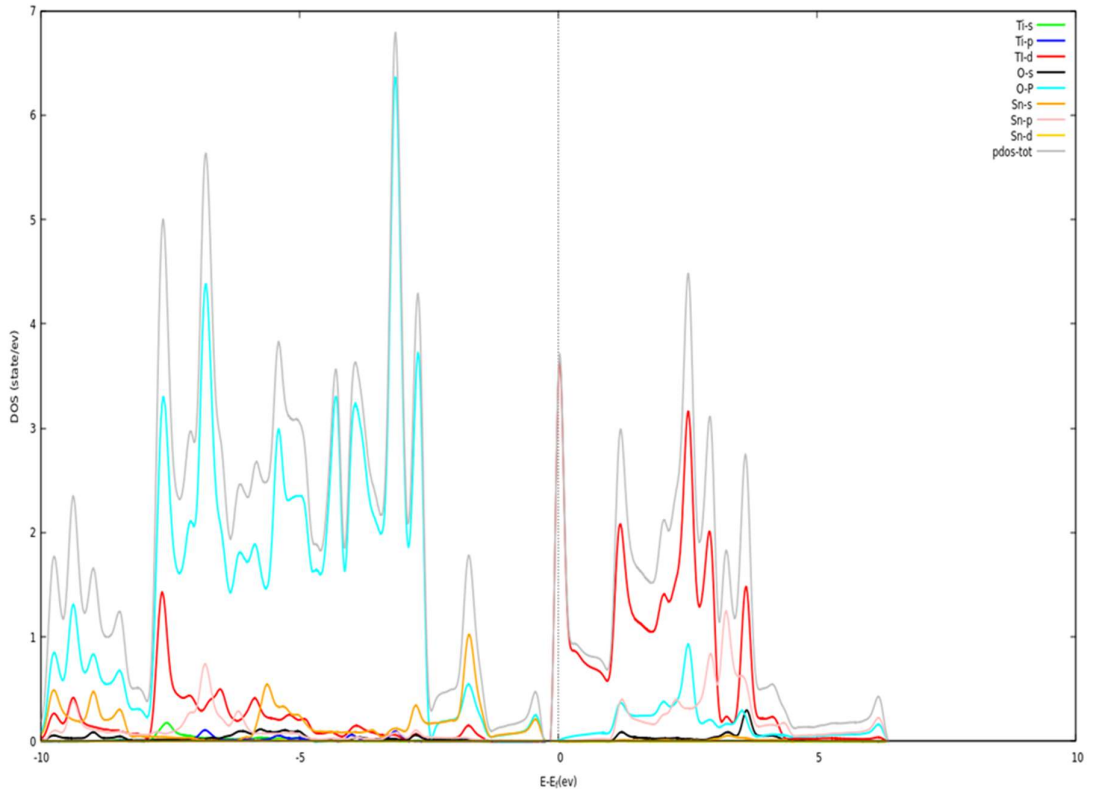

Fig. 5. Partial density of state of cubic $SnTiO_3$.

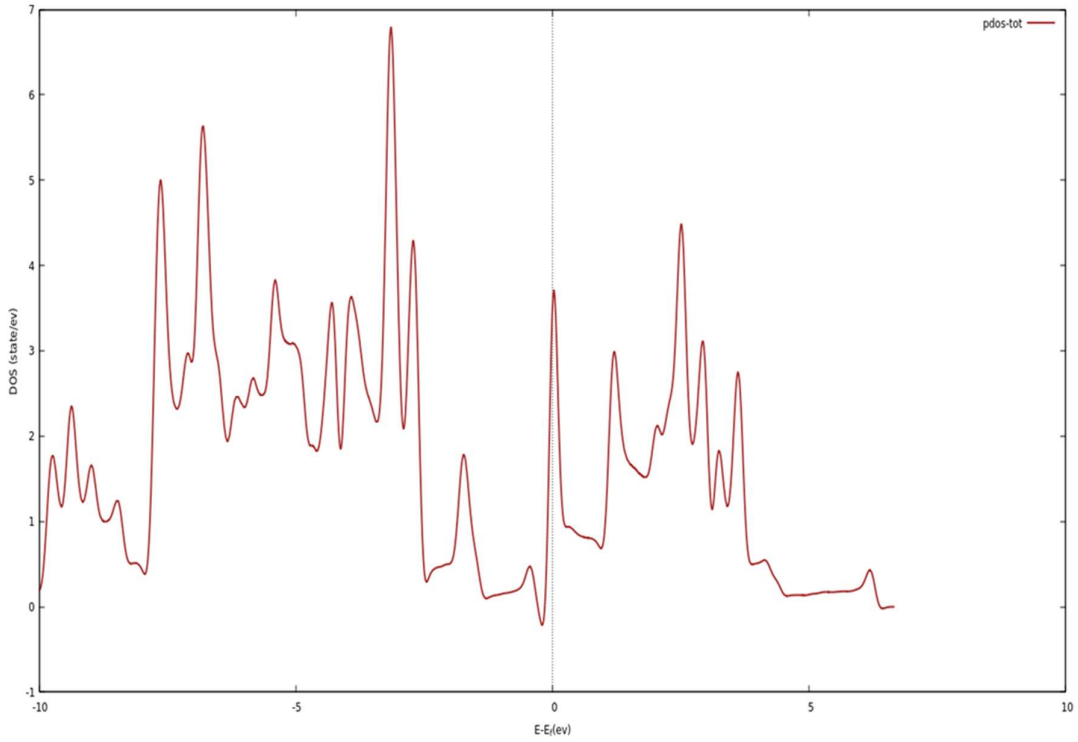

Fig. 6. Total partial density of state of the cubic $SnTiO_3$.

E. Partial Density of State (PDOS)

The partial density of the state of the material was plotted using the gnu plot software package. The PDOS gives information about the contribution of each atom or specific atomic orbital component to the overall state density. The PDOS graph of the cubic $SnTiO_3$ crystal is shown in Fig. 5 and Fig. 6 shows the total partial density of state of $SnTiO_3$, while the dotted line in the graph represents the fermi energy level lying between the uppermost part of the valence band and the lower part of the conduction band. The s-orbital (Ti), s-orbital (O), and p-orbital (Ti) which are indicated with green, black, and blue colours respectively give a small contribution in the valence band region and that of d-orbital (Ti), d-orbital (Sn) p-orbital (Sn) and p-orbital (O) which are indicated with red, yellow, pink and cyan colour respectively give a high contribution in the valence band region. These high contributions of atomic orbital describe the electrical conductivity and nature of covalent bonding between the atoms within the studied material. This covalent bond nature confirms the excellent behaviour of ferroelectric properties of the perovskite material [9]. The contribution of atomic orbital in the conduction band is the s-orbital (O), and the d-orbital (Sn), whose contributions are insignificant as indicated by black and yellow colours respectively. The d-orbital (Ti), p-orbital (Sn), and p-orbital (O) which are indicated with red, pink, and cyan colours respectively give a high contribution in the conduction band. Fig. 5 shows the total partial density of the state of the cubic $SnTiO_3$.

F. Elastic Properties

Elastic constants are important parameters of solids that describe the elastic properties of the crystal material. The elastic properties give more information about the mechanical stability, bonding character between the adjacent planes, brittleness ductility, stiffness, and anisotropic character [11]. The mechanical stability of the cubic material can be explained by the relations $C_{11}>C_{12}>0$, $C_{44}>0$, $C_{11}>0$, $C_{11}+2C_{12}>0$, and cubic stability condition $C_{12}<B<C_{11}$ [10]. These relations helps us to know whether the examined material is mechanically stable or not. Tables I and II show the calculated values of elastic constants and all other values of mechanical parameters of the cubic $SnTiO_3$ crystal material.

The Debye temperature predicts whether the material is ferroelectric or not, and the minimum Debye temperature for a ferroelectric material is 320 K [17]. Using the calculated elastic constants, the material under study ($SnTiO_3$) was found to have a Debye temperature of 589.41 K.

Table I. Values of the calculated elastic constants of the cubic $SnTiO_3$.

Elastic constant	Our work (Gpa)	Previous work [18] (Gpa)
C_{11}	306.53	314.65
C_{12}	90.53	119.41
C_{44}	93.83	94.06

Table II. Calculated values of mechanical properties of the cubic $SnTiO_3$.

Mechanical properties	Our work	Previous work [19]
Bulk modulus, (B)	162.53 (Gpa)	138.764 (Gpa)
Sheared modulus, (G)	99.26 (Gpa)	82.265 (Gpa)
Young's modulus (E)	247.42 (Gpa)	206.072 (Gpa)
Anisotropy index (A)	0.868	1.63
Poisson's ratio, (n)	0.250	0.252
Pugh's ratio (B/G)	1.64	1.68

V. Conclusion

In this study, the structural, electronic, and elastic properties of the cubic $SnTiO_3$ perovskite were determined within the framework of density functional theory by using Quantum Espresso computer code. The crystal structure of the cubic $SnTiO_3$ was fully optimized and a lattice parameter of 3.634 Å was achieved. The electronic band structure was calculated and found to have an indirect band gap of 1.67 eV. The partial density of state of the material was calculated and found to have a covalent bond between its atoms. This covalent nature of the bond confirms the excellent behaviour of the ferroelectric properties of the material. The mechanical properties such as the bulk modulus, Young's modulus, shear modulus, Poisson's ratio, Pugh's ratio, and anisotropic index were also calculated, and the results obtained confirm the brittle nature of the material, with a central inter-atomic force. Finally, the Debye temperature of the material was calculated to be 589.41 K, which shows the material is ferroelectric. Thus, the studied material is a good candidate for technological applications in devices such as information storage devices and piezoelectric sensors.

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