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A FIRST-PRINCIPLES STUDY OF STRUCTURE, ELASTIC AND ELECTRONIC PROPERTIES OF $GeTiO_3$ AS ENVIRONMENTALLY INNOCUOUS FERROELECTRIC PEROVSKITES

The structural parameters, elastic properties, spontaneous polarization, electronic band structure, and density of states (DOS) of $GeTiO_3$ in tetragonal phase have been studied computationally using pseudopotential plane-wave (PP-PW) method based on the density functional theory (DFT). The generalized gradient approximation (GGA) was used to estimate the exchange-correlation energies. The equilibrium lattice parameter, unit cell volume, bulk modulus and its derivative are obtained and compared with the available theoretical data. The elastic characteristics such as elastic constants, Poisson's ratio, elastic modulus, and anisotropy factor are obtained in the pressure range 0–50 GPa. Our computed results of elastic constant satisfy Born's stability criterion. In view of Pugh's prediction standard, the material is taken as ductile. Once the elastic constant is calculated, the Debye temperature of $GeTiO_3$ compound is also evaluated from the average sound velocity. The density of states, band structures, and charge-density distribution are discussed and compared with previous computational results. The calculation within Berry's phase approach indicate a high spontaneous polarization of tetragonal $GeTiO_3$ (1.125 C/m^2). Thus, the substance is identified as a promising environmentally friendly ferroelectric material.

Keywords: density functional theory, elastic properties, electronic structure, spontaneous polarization, $GeTiO_3$ compound.

1. Introduction

Ternary oxides constitute the most fascinating class of materials exhibiting a variety of structures and properties. The name perovskite [1, 2] is used to refer to any member of a very large family of compounds that has the formula ABO_3. For them, the B ion is surrounded by an octahedron of O ions. There are numerous combination of A and B cations which give ternary perovskite-type oxides such as $A^{1+}B^{5+}O_3$, $A^{2+}B^{4+}O_3$, $A^{3+}B^{3+}O_3$ types and oxygen- and cation-deficient phases. The ferroelectric perovskite ABO_3 has been used for infrared sensors, electromechanical transducers, and optical modulators due to its large dielectric constant and noticeable pyroelectric, piezoelectric, and electro-optic effects [3–7]. Most of the perovskite compounds were studied using first-principles calculations [8, 9]. $GeTiO_3$ is one of the promising Pb-free ferroelectric material. It was known that Pb-containing materials are hazard to the environment. As a result, current studies have extensively geared toward identifying new lead-free ferroelectric materials. As it is shown in [1], among the perovskite crystals studied to date, $GeTiO_3$ has likely the highest spontaneous polarization. Theoretical reports show that $GeTiO_3$ exists in cubic ($Pm3m$ space), polar tetragonal ($P4mm$ space), and polar-rhombohedral (R3m space). Analyzing the relative energy of the optimized structure of cubic, polar tetragonal, and polar rhombohedral phases clearly reveals that the polar rhombohedral phase has the lowest energy and is considered as stable, as indicated in [10]. However, its relative energy difference with the lowest energy of polar tetragonal phase is too small. M.F.M. Taib *et al.* evaluated the properties of cubic ($Pm3m$ space group) $GeTiO_3$ using the first- principles method through GGA-PBEsol

[10]. The dynamical properties of a new perovskite $GeTiO_3$ materials have been investigated using first-principles calculations based on the density functional theory within the gradient generalized approximation (GGA) by M.K. Yaakob *et al.* [11]. As reported by M.F.M. Taib *et al.* [12], in order to decrease the harmful of Pb^{2+} element, the effect of active lone pair Ge^{2+} in $GeTiO_3$ compound eventually expected to be more environmental friendly material. Moreover, A.I. Lebedev [13] explained that strong ferroelectric properties can be obtained for the tetragonal ($P4mm$) phase of $GeTiO_3$. Furthermore, the computations of phonon spectra show that cubic $GeTiO_3$ is the most favorable (stable) in terms of energy in the rhombohedral phase ($R3m$). Cohen and P. Ganesh [14] also reported on the novel compounds $Pb_{0.5}Ge_{0.5}TiO_3$ and $Sn_{0.5}Ge_{0.5}TiO_3$ with strong ferroelectric properties.

As far as we know, there is no experimental report on different phases of $GeTiO_3$. Concerning theoretical investigations, there are a limited number of first-principles studies of elastic properties, spontaneous polarization, Debye temperature, and electronic charge density of $GeTiO_3$ in the tetragonal phase. As a result, it is very crucial to study the electronic and structural properties of the tetragonal phase of $GeTiO_3$. In this study, our aim is to investigate the structural, electronic, and elastic properties and the spontaneous polarization of the tetragonal phase of $GeTiO_3$ using the density functional theory (DFT). The results obtained of calculations will be compared with previous theoretical results. The paper is organized as follows: in Section 2, we will give the computational details. Section 3 is devoted to the results and discussion, including structural parameters, elastic and electronic properties and previous available theoretical data. We summarize our main finding in Section 7.

2. Computational Details

The physical properties of ferroelectric perovskites have been a subject of intense theoretical works for last five decades. However, during the last decades there is a paradigm shift to the first-principles density functional theory due to the advancement of computational tools. The first-principles method based on the density functional theory is implemented using the Quantum-ESPRESSO (QE) open-source code [15]. QE is an integrated suite of computer codes for electronic structure calculations and the modeling of materials based on the density-functional theory, plane-wave basis set, and pseudopotentials to represent electron-ion interactions. The generalized gradient approximation (GGA) of Perdue–Burke–Ernzerhof (PBE) is used for the exchange correlation functional [16]. The norm-conserving pseudopotential is used to describe the interaction between the ion core and the valence electron. Self-consistent norm-conserving pseudopotentials are generated using the Hamann–Schluter–Chiang scheme [17]. The states of Ge $4s^2$ $4p^2$, Ti $3d^2$ $4s^2$, and O $2s^2$ $2p^4$ were explicitly treated as valence states. The electronic wave functions were expanded in a plane wave basis set with an energy cutoff of 1088.45 eV, and the k-point sampling of the Brillouin zone was constructed using the Monk–Horst pack mesh scheme [18] with the use of $6 \times 6 \times 6$ grids in primitive cells of $GeTiO_3$ compound. Moreover, the spontaneous polarization is calculated according to the modern theory of polarization, namely, Berry's phase approach [19]. The spontaneous polarization (P) arises from both ionic polarization (P_{ion}) and electronic polarization (P_{el}).

3. Results and Discussions

3.1. Structural properties

To determine the equilibrium lattice parameters of the system, the cutoff energy and Monk Horst–Pack mesh are fixed at 1088.45 eV and $6{\times}6{\times}6$ k-point, respectively. The tetragonal (P4mm, 99 space group) phase of $GeTiO_3$ crystal has two lattice parameters, a and c. The ratio of $c/a = 1.102$ was fixed in the calculations, and all changes were made in terms of the lattice parameter a; which is obtained by minimizing the energy of the system. The values for lattice parameters of the compound were optimized as shown in Fig. 1. The equilibrium lattice parameters were found to be $a = b = 3.771$ Å, $c = 4.155$ Å and summarized in Table 1. The results obtained from the calculation are comparable with the available theoretical finding [21]. Moreover, the bulk modulus is another fundamental physical property in the solids, and it can be used as a measure of the average bond strengths of atoms of crystals. In order to determine the ground state properties, a series of total energy calculations as a function of the volume was fitted to an equation of state according to Murnaghan $E(V)$ curve [20]. The total energy as a function of the volume and a variation of the pressure with respect to the volume are shown in Fig. 2, *a* and *b*, respectively. The calculated values of the bulk modulus, equilibrium unit cell volume, and the dimensionless bulk modulus derivative of $\mathrm{GeTiO_3}$ are given in Table 1.

4. Elastic Properties

Elastic constants of the crystals provide a critical information to study the mechanical properties of materials. The elastic constant tensors are determined from the stresses induced by small deformations of the equilibrium primitive cell as [22];

$$C_{ikl} = \left(\frac{\partial \sigma_{ij}}{\partial \varepsilon_{jkl}}\right)_x = \left(\frac{1}{V}\frac{\partial^2 E}{\partial \varepsilon_{ij}\varepsilon_{kl}}\right)_x, \tag{1}$$

E denotes the Helmholtz free energy, σ_{ij} and ε_{kl} are the applied stress and Eulerian strain tensors, and x is the coordinates. For the case of tetragonal system, there are six independent elastic constants that should satisfy the well-know Born stability criteria [23]

$$C_{11} - C_{12} > 0, \quad C_{11} + C_{33} - 2C_{13} > 0, \quad C_{11} > 0,$$

$$C_{33} > 0, \quad C_{44} > 0, \quad C_{66} > 0,$$

$$2C_{11} + C_{33} + 2C_{12} + 4C_{13} > 0,$$

and

$$\frac{1}{3}(C_{12} + 2C_{13}) < B < \frac{1}{3}(C_{11} + 2C_{33}). \tag{2}$$

We can see that all the elastic constants listed in Table 2 satisfy the mechanical stability conditions. One can find that the six elastic constants for the tetragonal phase of $\mathrm{GeTiO_3}$ increase with the pressure. The elastic constants C_{11} and C_{33} change rapidly with the pressure, C_{12} and C_{13} change moderately under the pressure, while C_{44} and C_{66} increase slightly with the pressure, as shown in Fig. 3. From the calculated elastic constants, the mechanical parameters such as the Young modulus E, Poisson's ratio n, and shear modulus G are determined by using the Voigt–Reuss–Hill (VRH) average approximation [24–26]. The bulk and shear moduli in the VRH approximation are given by

Table 1. **Calculated unit cell volume, equilibrium constants, and bulk modulus of $\mathrm{GeTiO_3}$ in the ferroelectric phase**

Source	Lattice constants (Å)	V (Å^3)	B (GPa)	B'
Our work	$a = 3.771$ and $c = 4.155$	65.35	165	4.63
Theory [21]	$a = 3.710$ and $c = 4.619$	63.57		

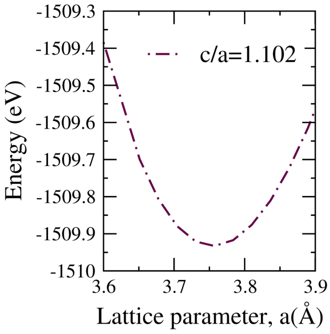
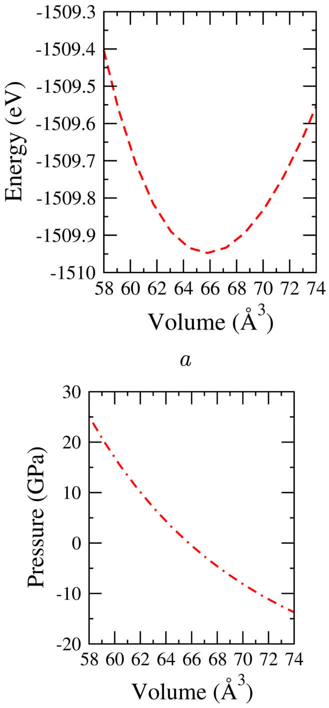


Fig. 1. Total energy of the tetragonal (P4mm) phase of $\mathrm{GeTiO_3}$ as a function of the lattice parameter



a

b

Fig. 2. Dependence of the total energy per unit cell volume (*a*) and a variation of the pressure with respect to the volume (*b*)

$$G = \frac{1}{2}(G_v + G_\mathrm{R}), \quad B = \frac{1}{2}(B_v + B_\mathrm{R}), \tag{3}$$

where B_R and G_R are the Reuss bulk and shear moduli, and B_v and G_v correspond to the Voigt bulk and

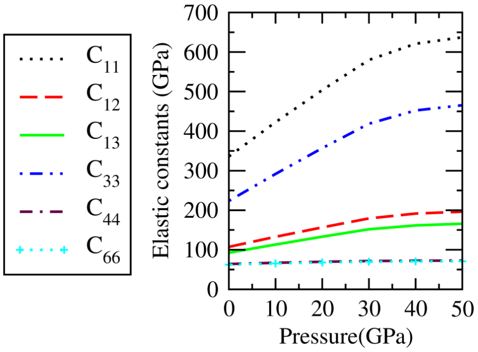


Fig. 3. Calculated elastic constants of $GeTiO_3$ in the tetragonal phase under different pressures

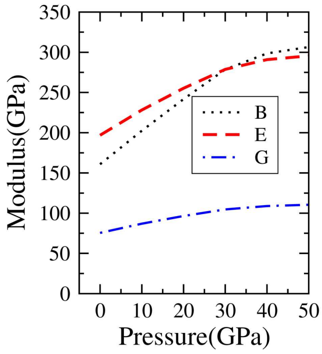
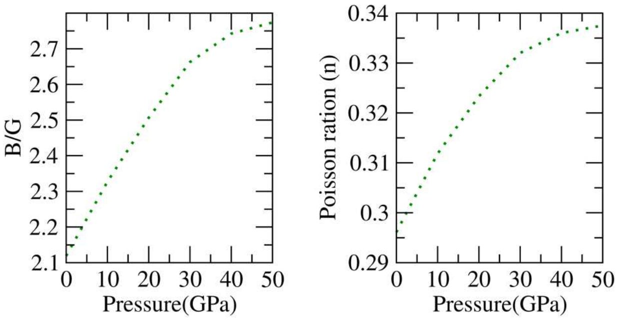


Fig. 4. Elastic modulus of $GeTiO_3$ compound under different pressures



a *b*

Fig. 5. Computed (*a*) B/G and (*b*) Poisson's ratio (n) of $GeTiO_3$ under different pressures

shear moduli,

$$B_v = \frac{1}{9}[(C_{11}+C_{22}+C_{33})+2(C_{12}+C_{23}+C_{31})],$$

$$G_v = \frac{1}{15}[(C_{11}+C_{22}+C_{33})-(C_{12}+C_{23}+C_{31})+$$

$$+3(C_{44}+C_{55}+C_{66})], \tag{4}$$

$$B_{\mathrm{R}} = [(S_{11}+S_{22}+S_{33})+2(S_{12}+S_{23}+S_{31})]^{-1},$$

$$G_{\mathrm{R}} = 15[4(S_{11}+S_{22}+S_{33})-(S_{12}+S_{13}+S_{23})+$$

$$+3(S_{44}+S_{55}+_{66})]^{-1}. \tag{5}$$

The Young modulus (E) and Poisson's ratio (n) are given by

$$E = \frac{9BG}{3B+G}, \quad n = \frac{3B-2G}{2(3B+G)}. \tag{6}$$

As shown in Fig. 4, the computed values of the elastic moduli such as B, G, and E increase monotonously with the pressure, and the trend is linear for B, but nonlinear for G and E. These results mean that the volume change resistance increases linearly, while the shape change resistance E and stiffness G increase non-linearly with the pressure. Generally, a large elastic modulus means a high hardness of materials. Figure 5 shows the pressure dependence of the B/G and Poisson's (n) ratio of the $GeTiO_3$. Poisson's ratio is used to explain the stability of the material by providing the characteristics of the bonding forces.

According to H. Fua *et al.* [27], the calculated Poisson's ratio increases monotonically until the pressure becomes equal to 30 GPa. The value is always between the upper 0.5 and the lower 0.25 limit in the studied pressure range. With respect to S.F. Pugh [28], 1.75 is the critical value that separates the brittleness and ductility behavior of materials. When the ratio of $B/G > 1.75$, the material is associated with ductility, and, as $B/G < 1.75$, it is taken as brittle. As shown in Fig. 5, *a*, the B/G ratio increases monotonically with the pressure, which is always more than 1.75 in the studied pressure range. These indicate that $GeTiO_3$ becomes more ductile

Table 2. **Computed elastic constants in the tetragonal phase within the 0 to 50 GPa pressure range**

P	C_{11}	C_{12}	C_{13}	C_{33}	C_{44}	C_{66}
0	336.13	107.31	92.29	223.47	64.05	62.38
10	422.40	132.65	113.14	291.62	67.33	65.55
20	503.76	156.64	133.01	356.96	69.81	68.01
30	579.87	179.24	151.64	418.61	71.68	69.88
40	621.03	191.45	161.65	452.07	72.53	70.72
50	637.17	196.26	165.76	465.25	72.88	71.03

with an increment of the pressure. Moreover, the anisotropy factor A is a measure of the degree of elastic anisotropy possessed by the crystal. The universal anisotropy index (A^U) is given by [29]

$$A^U = \frac{5G_v}{G_\mathrm{R}} + \frac{B_v}{B_\mathrm{R}} - 6. \tag{7}$$

For an isotropic materials, the value of A^U must be zero. A deviation greater than zero represents the degree of anisotropy. In Table 3, it is shown that as the pressure increases, the computed value of A^U also increases. The result indicates that the comparatively small elastic anisotropic characteristic is observed in the tetragonal phase of $\mathrm{GeTiO_3}$. To understand the anisotropic behavior of mechanical moduli, we obtained the 3D surface representations of the direction-dependent a) Young modulus, b) sheared modulus, and c) Poisson's ratio of $\mathrm{GeTiO_3}$ using ELATE [30] at the zero pressure, as shown in Fig. 6, *a–c*. The maximum and minimum values of Young modulus, shear modulus, and Poisson's ratio are shown in Table 4.

4.1. Debye temperature θ_D

Once elastic parameters such as the bulk modulus B, shear modulus G, and Young modulus E are obtained, it is of importance to calculate the Debye temperature which is a suitable parameter to describe phenomena of solid-state physics which are associated with lattice vibrations, elastic constants, the specific heat, and melting point temperature [31]. The calculation of the Debye temperature at low temperatures is then given in terms of the elastic constants, as expressed in [32];

$$\theta_\mathrm{D} = \frac{h}{k}\left[\frac{3n}{\pi}\left(\frac{N_\mathrm{A}\rho}{M}\right)\right]^{1/3} v_m, \tag{8}$$

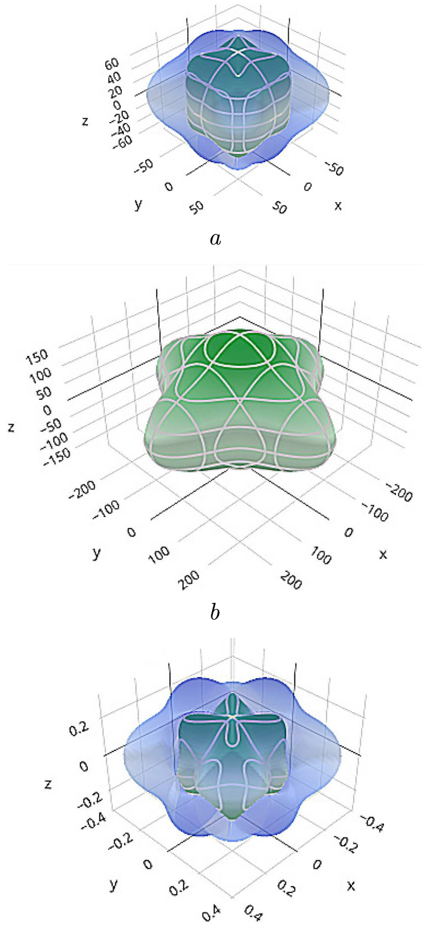
where h is Planck's constant; k is Boltzmann constant; N_A is Avogadro's number; ρ is the density; M is the molecular weight, and n is the number of atoms in a formula unit. The average sound velocity v_m is expressed in terms of the longitudinal sound velocity v_l and transverse sound velocity v_t which can be obtained from the elastic constant parameters such as

Table 3. **Computed elastic moduli of $\mathrm{GeTiO_3}$ in the tetragonal phase**

P	B	G	E	B/G	n	A
0	160.92	75.43	196.84	2.11	0.29	0.37
10	202.37	86.96	228.18	2.32	0.31	0.64
20	241.70	96.43	255.23	2.50	0.32	0.92
30	278.59	104.63	278.74	2.66	0.33	1.21
40	298.52	108.85	290.85	2.74	0.33	1.38
50	306.44	110.47	295.53	2.77	0.33	1.44

Table 4. **Maximum and minimum ranges of the Young modulus (E), shear modulus (G), and Poisson's ratio (n)**

	E		G		n	
	E_max	E_min	G_max	G_min	n_max	n_min
$\mathrm{GeTiO_3}$	282.90	165.73	114.4	62.38	0.49	0.17



a

b

c

Fig. 6. Spatial dependence of (*a*) shear modulus (*b*), Young modulus, and (*c*) Poisson's ratio of $\mathrm{GeTiO_3}$ at the zero pressure

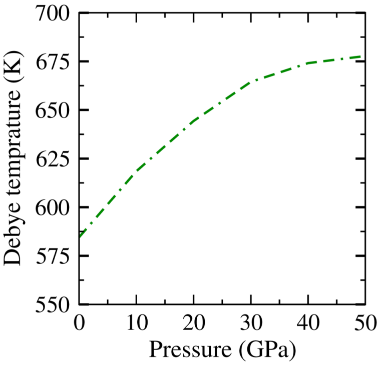


Fig. 7. Dependence of the Debye temperature of $GeTiO_3$ on the pressure

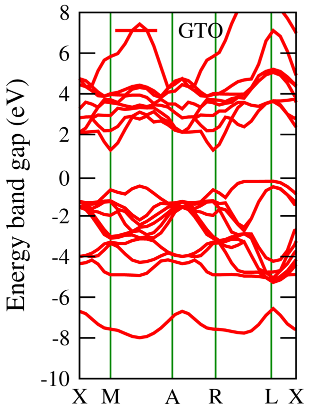


Fig. 8. Electronic band structure

Table 5. **Calculated longitudinal, transverse, and average sound velocities (v_l, v_t, and v_m in m/s) and the Debye temperatures (θ_D in K) of $GeTiO_3$ at the zero pressure**

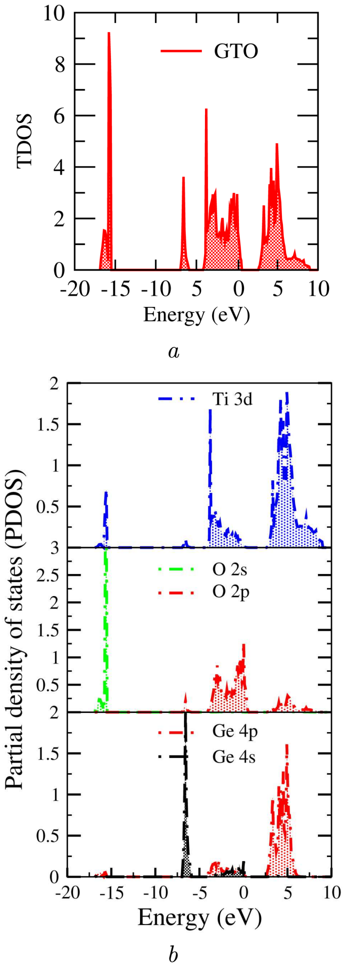
ρ, g/cm^3	v_l	v_t	v_m	θ_D
4.7016	5902.010	4095.742	4527.72	582.072

the shear modulus (G) and the bulk modulus (B) [33]

$$v_m = \left[\frac{1}{3}\left(\frac{2}{v_t^3} + \frac{1}{v_l^3}\right)\right]^{-1/3}, \tag{9}$$

$$v_l = \left(\frac{B + \frac{3}{4}G}{\rho}\right)^{1/2}, \tag{10}$$

$$v_t = \left(\frac{G}{\rho}\right)^{1/2}. \tag{11}$$



a

b

Fig. 9. Total density of states (*a*) and the oartial density of states (*b*)

The calculated longitudinal sound velocity, transverse sound velocity, and Debye temperature are given in Table 5. The Debye temperature is directly related to the average sound velocity. Thus, the large average sound velocity results in the large Debye temperature. Figure 7 shows the pressure dependence of the Debye temperature for tetragonal $GeTiO_3$. It is found that the Debye temperature θ_D increases monotonically with the pressure and exhibits a trend similar to the minimum thermal conductivity, following the Callaway–Debye theory [34].

5. Electronic Band Structures and Density of States (DOS)

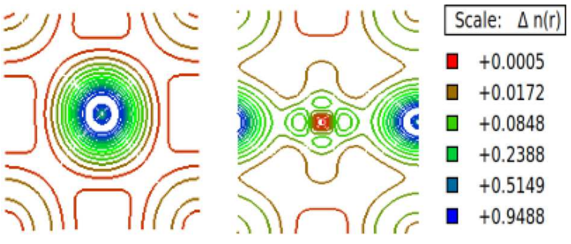
The electronic properties of compounds are obtained from their energy band structure and density of states. The calculated electronic band structures along the direction of high-symmetry Brillouin zone of tetragonal $GeTiO_3$ using the PBE-GGA approximation is shown in Fig. 8. The analysis of the electronic band gap shows that $GeTiO_3$ has an indirect band gap with a high value of 1.68 eV in the tetragonal phase. To the best of our knowledge, there is no experimental value available to compare it. However, the calculated band gap value is in good agreement with the previous theoretical findings [35]. The total and partial densities of states (DOS) for the ferroelectric phase of $GeTiO_3$ are shown in Fig. 9, *a* and *b*. The distributions of the total and partial densities of states are in the interval –20.0 to 10.0 eV. Analyzing the DOS of the tetragonal phase of $GeTiO_3$ shows that the highest valence band is mainly dominated by electron O-2p and Ge-4s states lying in the energy range from –8.0 to 0 eV with a less contribution of Ti-3d states. The existence of a hybridization between Ge-4s and O-2p is evident. Furthermore, the lowest conduction bands (CBs) is mainly originated from the Ti-3d and Ge-4p orbitals with small contributions of O-2p states.

The electron density contours denote the charge distribution in an atom, which establishes, in turn, the nature of the bond among different atoms. The electronic charge density map serves as a complementary tool for achieving a proper understanding of the electronic structure of the system being studied. The ionic and covalent characters of a material can be related to the charge transfer and sharing between the cation and anion. The charge density behaviors of $GeTiO_3$ in 100 and 110 planes have been depicted in Fig. 10. The Ge atoms are at the four corners, the Ti atom is at the center of the plane, while the O atoms are on the top and below the position of the Ti atom. The charge density plot indicates that there is a strong ionic character along the Ti–O bond, while the Ge–O bond has strong covalent character.

6. Spontaneous Polarization

Ferroelectric (FE) materials have a spontaneous electric polarization that can be reversed by the application of an external electric field. The theoretical understanding of FE materials is described by the so-called modern theory of polarization. The total polarization is simply the sum of the electronic and ionic contributions,

$$P_t = P_i + P_e. \tag{12}$$



a *b*

Fig. 10. Electronic charge density in 100 and 110 planes of $GeTiO_3$

The ionic contribution is obtained by summing the product of the position u_k of each ion in the unit cell with the nominal charge Z_k of its rigid core.

$$P_i = \frac{|e|}{\Omega}\sum Z_k u_k, \tag{13}$$

whereas the electronic contribution is determined by evaluating the phase of the product of overlaps between the cell-periodic Bloch functions along a densely sampled string of neighboring points in the k space

$$P_{\mathrm{el}} = -\frac{2|e|i}{(2\pi)^3}\int\limits_A d\mathbf{k}\sum_{n=1}^{M}\int\limits_0^G \left\langle u_{nk}\left|\frac{\partial}{\partial k}\right|u_{nk}\right\rangle dk, \tag{14}$$

where the sum n runs over all M occupied bands, G is a reciprocal lattice vector, and the state u_{nk} is the lattice-periodic part of the Bloch wave function. The resulting spontaneous polarization of $GeTiO_3$ in the tetragonal phase is 1.125 C/m^2, which is consistent with other calculations [13].

7. Conclusions

In summary, the structural parameter, bulk modulus, elastic properties, electronic band structure, and density of states (DOS) of $GeTiO_3$ in the tetragonal phase have been investigated by the use of the density functional theory (DFT) with the generalized gradient approximation (GGA) as implemented in the quantum espresso package. The calculated lattice parameter and bulk modulus are $a = b = 3.771$ Å, $c = 4.155$ Å at 165.0 GPa. The obtained equilibrium lattice constants and bulk modulus are found to be in good agreement with the available theoretical data. The calculated electronic band structure of $GeTiO_3$ has an indirect gap with a band gap of 1.68 eV. Combined with the density of states and the electronic charge density, the characteristics of band structures have been analyzed. The pressure dependence of the elastic properties of $GeTiO_3$ have been calculated by the use of the GGA approach. The obtained elastic constants are in good agreement with theoretical values. Furthermore, parameters such as Poisson's ratio, anisotropy factor, Young modulus, and shear modulus are obtained from the values of elastic constants. The longitudinal sound velocity, transverse sound velocity, and Debye temperature for $GeTiO_3$ have been investigated. The spontaneous polarization in the tetragonal phase of $GeTiO_3$ is calculated using Berry's phase formulation. The obtained value (1.12 C/m^2) shows the high polarization compared to most common ferroelectric materials.

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ДОСЛІДЖЕННЯ З ПЕРШИХ ПРИНЦИПІВ СТРУКТУРИ, ПРУЖНИХ І ЕЛЕКТРОННИХ ВЛАСТИВОСТЕЙ ПЕРОВСКИТІВ $GeTiO_3$ ЯК ФЕРОЕЛЕКТРИКІВ, БЕЗПЕЧНИХ ДЛЯ НАВКОЛИШНЬОГО СЕРЕДОВИЩА

Чисельно вивчено структурні параметри, пружні властивості, спонтанну поляризацію, електронну зонну структуру та густину станів $GeTiO_3$ в тетрагональній фазі з використанням наближення плоских хвиль для псевдопотенціалу в рамках теорії функціонала густини. Наближення узагальненого градієнта використано для оцінки обмінно-кореляційних енергій. Розраховано рівноважний параметр ґратки, об’єм елементарної комірки, об’ємний модуль і його похідну та зіставлено з наявними теоретичними даними. Константи пружності, модуль Пуассона, модуль пружності і коефіцієнт анізотропії знайдено для діапазону тисків 0–50 ГПа. Розраховані константи пружності задовольняють критерію стабільності Борна. За стандартом передбачення П’ю речовину можна вважати гнучкою. За величиною пружної константи і середньої швидкості звуку оцінено температуру Дебая. Проведено порівняння густини станів, зонної структури та розподілу зарядової густини з результатами попередніх чисельних результатів. Розрахунок на основі фазового підходу Беррі показав високу спонтанну поляризацію $GeTiO_3$ в тетрагональній фазі (1,125 Кл/м^2). Таким чином, дана сполука є перспективним фероелектричним матеріалом, безпечним для навколишнього середовища.

Ключові слова: теорія функціонала густини, пружні властивості, електронна структура, спонтанна поляризація, сполука $GeTiO_3$.