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Topological Insulators: Electronic Band Structure and Spectroscopy

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Abstract. In this study, we present the results of our ab initio calculation of the elastic constants, density of states, charge density, and Born effective charge tensors for ferroelectric (rhombohedral) and paraelectric phases (cubic) of the narrow band ferroelectrics (GeTe, SnTe) pseudopotentials. The related quantities such as bulk modulus and shear modulus using obtained elastic constants have also been estimated in the present work. The total and partial densities of states corresponding to the band structure of Sn(Ge)Te(S,Se) were calculated. We also calculated the Born effective charge tensor of an atom (for instance, Ge, Sn, Te, etc.), which is defined as the induced polarization of the solid along the main direction by a unit displacement in the perpendicular direction of the sublattice of an atom at the vanishing electric field.

Keywords: ab initio calculation; elastic constant; charge density; Born effective charge tensors

1. Introduction

In recent years, the experimental and theoretical studies associated with these materials have greatly increased. The main results of these experimental and theoretical studies are that these materials show the characteristics of narrow gap semiconductors. An interesting feature of these materials is that the variation susceptibility mass with carrier concentrations in the two band region for GeTe is opposite to that observed for SnTe. That is, the mass for GeTe increases more rapidly while the mass for SnTe increases less rapidly with concentrations in the two band region [1]. The optical and electronic properties of GeTe get significantly modified depending on the change in the microscopic structure from the crystalline to the amorphous phase. Due to this characteristic, GeTe is an important basic material in phase-change alloys used in optical rewritable compact disks (CDs) and digital versatile disks (DVD) [2-5]. As a result of being narrow gap semiconductors, these materials are suitable as infrared detectors and light emitting devices [6].

In the past, some detailed works [1, 5, 6-9] have been carried out on the structural, electronic, optical, elastic, and dynamical properties of these compounds. Tsu et al. [1] described the electrical, optical, and band structure properties of GeTe and SnTe using thin films evaporated onto heated NaCl



substrates to lower carrier concentrations. Okoye et al. [6] calculated the optical and electronic properties of SnTe and GeTe using the generalized gradient and the local density approximation. Shaltaf et al. [5] investigated the electronic and phonon band structure, Born effective charge and optical dielectric tensors, and elastic properties of GeTe as a ferroelectric material in its low-temperature rhombohedral phase using the density functional perturbation theory. Husnu et al. [7] investigated the structural, electronic, and optical properties of narrow-band ferroelectric compounds (Ge, Sn) Te in the ferroelectric and paraelectric phase using the generalized gradient approximation. Nonaka et al. [8] analyzed the crystal structure of GeTe and Ge₂Sb₂Te₅ meta-stable phase using the powder x-ray diffraction method. Herman et al. [9] investigated the relativistic band structure of IV-VI compounds (GeTe, SnTe, PbTe, PbSe, and PbS) using the first-order perturbation theory.

As far as we know, no ab initio general potential calculations of the elastic constants, Born effective charge tensors for ferroelectric and paraelectric phases of SnTe, the charge density for paraelectric phases of these compounds, and the elastic constants, Born effective charge tensors for paraelectric phase of GeTe have been reported. Our main goal in this study is to provide some additional information using the density functional theory. Therefore, in this work, we investigated the elastic constants, density of states and Born effective charge tensors for ferroelectric and paraelectric phases of the narrow band ferroelectrics (GeTe, SnTe). The method of calculation is given in Section 2; the results are discussed in Section 3. Finally, the summary and conclusion are given in Section 4.

2. Method of calculation

In all of our calculations that were performed using the ab-initio total-energy and molecular-dynamics program VASP (Vienna ab-initio simulation program) [10-13] that was developed within the density functional theory (DFT) [14], the exchange-correlation energy function is treated within the GGA (generalized gradient approximation) by the density functional of Perdew et al. [15]. The potentials used for the GGA calculations take into account the 4s²4p² valence electrons of each Ge-, 5s²5p² valence electrons of each Sn-, and 5s²5p⁴ valence electrons of each Te-atoms. The GGA calculation within the core-state model potential of A (Ge, Sn) has only four valence electrons because the 3d¹⁰ and 4d¹⁰ have become part of the core. When including a plane-wave basis up to a kinetic-energy cutoff equal to 17 Ha, the properties investigated in this work are well converged. The Brillouin-zone integration was performed using special k points sampled within the Monkhorst-Pack scheme [16]. We found that a mesh of 12 x 12 x 12 k points was required to describe the elastic constants, density of states and Born effective charge tensors well. This k-point mesh guarantees a violation of charge neutrality less than 0.008e. Such a low value is a good indicator for an adequate convergence of the calculations. The unit cell of the crystal structure contains 3 GeTe and SnTe molecules (6 atoms) for ferroelectric phase and 1 GeTe and SnTe molecules (2 atoms) for paraelectric phase. When we started the calculations, we have optimized the structural properties first. The lattice parameters obtained as a result of this optimization are shown in Table 1 along with the experimental and theoretical results. The structural parameters obtained are in good agreement with the experimental and theoretical values [6, 17-18]. We used these structural properties in all of our subsequent calculations.

Table 1. The calculate equilibrium lattice parameters (a , and c) for GeTe and SnTe in Ferroelectric and Paraelectric phase

Material	Structure	Reference	a (Å)	c (Å)
GeTe	Rhombohedral (R3m)	Present	4.228	10.886
		Experimental ^a	4.156	10.663
	Cubic (Fm $\bar{3}$ m)	Present	6.024	
		Theory (GGA) ^b	6.011	
		Theory (LDA) ^b	5.858	
	Experimental ^c	5.996		
SnTe	Rhombohedral (R3m)	Present	4.502	11.489
	Cubic (Fm $\bar{3}$ m)	Present	6.309	
		Theory (GGA) ^b	6.404	
		Theory (LDA) ^b	6.231	
		Experimental ^c	6.327	

^aReference [6] ; ^bReference [17]; ^cReference [18]

Table 2. The calculated elastic constants (in GPa), isotropic bulk modulus (B , in GPa), shear modulus (G , in GPa), for GeTe and SnTe in Ferroelectric and Paraelectric phase

	SnTe(Fm$\bar{3}$m)	SnTe (R3m)	GeTe(Fm$\bar{3}$m)	GeTe (R3m)	
	Present	Present	Present	Theory^a	Expt^b
Elastic constant (GPa)				Clamped	relaxed
C_{11}	135.110	76.810	170.411	98.256	115.70
C_{12}	-0.514	16.562	10.057	112.00	
C_{13}		29.507		21.996	22.41
C_{33}		59.712		19.36	
C_{44}	15.130	30.124	28.974	32.096	36.76
C_{66}		42.711		27.20	
Bulk modulus (GPa)				69.003	86.51
B_V	44.694	40.498	63.508	59.51	
B_R		40.458		38.123	
B	44.694	40.478	63.508	49.891	
Shear modulus (GPa)					
G_V	36.203	32.293	49.455	48.655	
G_R	21.952	28.314	38.915	48.027	
G	29.078	30.304	44.185	48.341	44.80 49.96
				39.535	
				35.881	
				37.708	

^aReference [5] ; ^bReference [20]

3. Results and discussion

3.1. Elastic constants

We have derivated the elastic constants from the strain-stress relationship [19] for VASP calculations. The calculated elastic constants, bulk and shear moduli are given in Table 2 together with the

theoretical and experimental results [5, 20]. The obtained elastic constants for GeTe in ferroelectric phase are comparison with the theoretical values [5]. The C33 which is lower than the clamped value is higher than relaxed value. Apart from this, other elastic constants are in good agreement with the theoretical values. As can be seen from Table 2, the calculations carried out in both phases showed the presence of abrupt changes in the calculated parameters (elastic constants, bulk and Shear modulus). Unfortunately, there are no theoretical and experimental result for comparing with the present work for each phase of SnTe and paraelectric phase of GeTe. The calculated C11 and C33 elastic constant measure the a- and c- direction on resistance to linear compression, respectively. The C33 for either compounds in ferroelectric phase are lower than the C11. Therefore, the c- axis for either compounds are more compressible than the a- axis. We have defined the polycrystalline bulk (B) modulus and shear modulus (G) using the subscripts V (Voigt), R (Reuss) and H (Hill). The two approaches methods called the Voigt and the Reuss [21, 22] are used to calculate the polycrystalline modulus [23-25] using elastic constants. The bulk modulus is a measure of resistance to volume change by an applied pressure. The shear modulus is a measure of resistance to reversible deformations upon shear stress [26]. The bulk modulus given Table 2 is a good agreement with experimental and theoretical values. The calculated shear modulus for GeTe in both phases are higher than SnTe.

3.2. Electronic Properties

Band gap values obtained from the band structures of GeTe and SnTe in ferroelectric and paraelectric were calculated as 0.742 eV and 0.359 eV in the ferroelectric phase and 0.376 eV and 0.028 eV in the paraelectric phase, respectively, and the band gap character of these compounds for either of the phases was determined as direct [7]. Our results are in agreement with the results obtained in the previous calculation [5-6,27-29] (see Table 3). The change in the energy gap for the SnTe and GeTe can be understood qualitatively in terms of the difference between the relativistic effect in Ge and Sn (spin-orbital coupling) and the relativistic correction is extremely important in determining the positions of the energy bands. This change in energy gap may also be due to the presence of spontaneous polarization (change of the crystal field at the phase transition).

Table 3. Energy band gap for GeTe and SnTe in Ferroelectric and Paraelectric phase

Material	Structure	Reference	E_g (eV)
GeTe	Rhombohedral (R3m)	Present	0.742 direct
		Theory ^a	0.48 direct
		Theory ^b	0.48
		Theory ^c	0.3369
	Cubic (Fm3m)	Present	0.376 direct
		Theory (LDA-GGA) ^d	0.399-0.340
SnTe	Rhombohedral (R3m)	Present	0.359 direct
	Cubic (Fm3m)	Present	0.028 direct
		Theory (LDA-GGA) ^d	0.074-0.061
		Experimental ^d	0.2

^aReferance [5]; ^bReferance [27]; ^cReferance [28]; ^dReferance [6,29]

The total and partial densities of states for GeTe and SnTe in ferroelectric phase are illustrated in Figure 1. As you can see from these figures, the lowest valence bands occur between about -25 and -22 eV are dominated by d states. Similarly, the valence band that occur between approx. -12 and -5 eV are dominated by s states. The highest occupied valence bands results from the sp-hybridization of Ge and Te bands. The other states also contribute to the valence bands, but the values of densities of these

states are so small compared to the sp-hybridization. The lowest unoccupied conduction bands just above the Fermi energy level are dominated by p states.

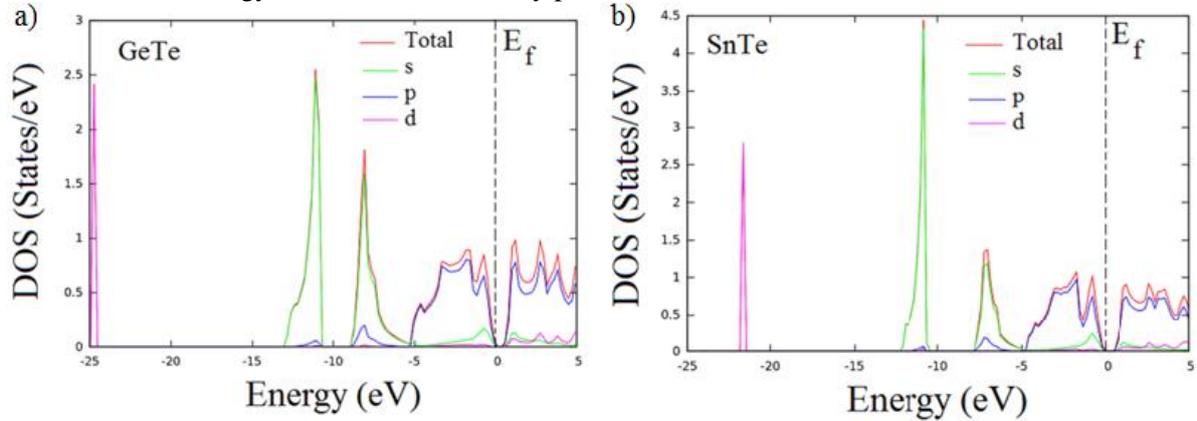


Figure 1. The total and projected density of states for a) GeTe and b) SnTe in ferroelectric phase

The two-dimensional charge density distribution is illustrated in Figure 3. Examination of the nature of chemical bonding defining the distribution of valence charges between atoms is necessary to explain the overall shape. The overall shape of charge distributions suggests the covalent bond of Ge-Te and Sn-Te. Ionicity is directly associated with the character of the chemical bond. In these figures, the shape of charge distribution shows a low electron accumulation between Ge and Sn atoms. This is a clear indication of the ionic bond. The large electron accumulation between Te atoms and their as spherical character indicates a strong directional covalent between these atoms. Therefore, the bonding of GeTe and SnTe as general can be classified as a combination of ionic, covalent, and metallic characters. In addition, evidence of metallic bonding is presented in electron density distribution map, as illustrated in the Figure 1 and Figure 2.

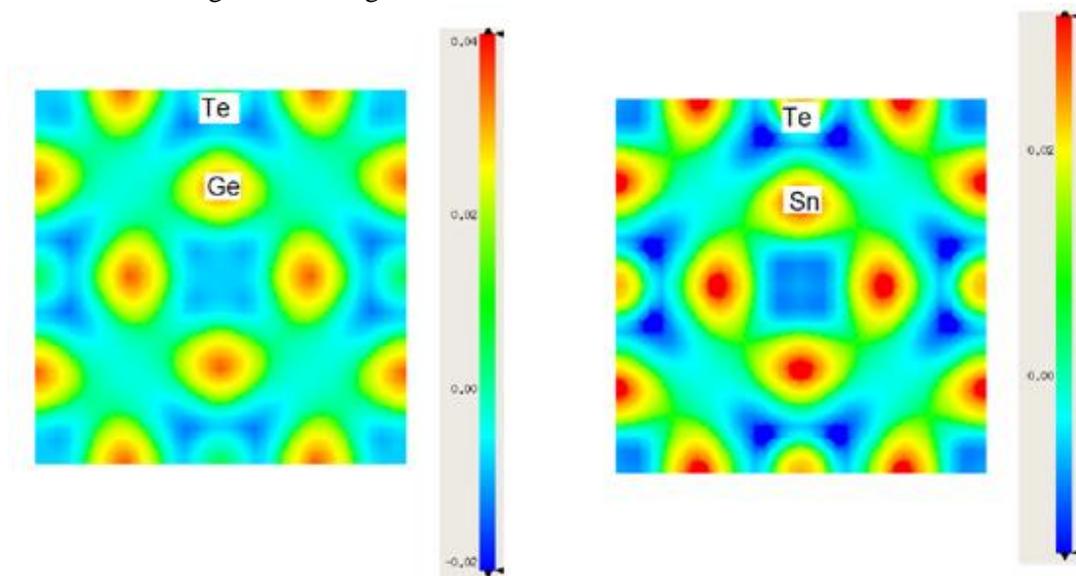


Figure 2. Charge density distribution of the valance charge of GeTe and SnTe in the 100 direction

3.3. Born effective charges

The Born effective charge (BEC) Z^* is a fundamental quantity for the study of lattice dynamics, controlling the long range Coulomb part of the force constants and defined the change in polarization as a result of the displacement of an atom in the crystal [30]. The polarization value at different directions of the crystal may be different. Therefore, BEC can take different values for that depending

on the polarization. BEC especially occurs in the ionic and covalent bonded structure (strong covalent bond between atoms). The BEC tensor of an atom k is defined as

$$Z_{k,\gamma\alpha}^* = V \left. \frac{\partial P_\gamma}{\partial k,\alpha} \right|_{E=0} \quad (1)$$

where P_γ represents the polarization and the derivative is evaluated under the condition of vanishing macroscopic electric field. V is the unit cell volume. BEC quantities are important to study ferroelectric materials, because phase transitions in these materials hold a place from the competition of long range Coulomb interactions and short range force [31]. Until now, anomalous charges in ferroelectric materials were explained qualitatively in the framework of a bond orbital model [32]. Our study helps to clarify the debate on the real nature of the chemical bonding in narrow band ferroelectrics and bring out the role of the Ge(Sn) atom. The BEC tensors of GeTe and SnTe in cubic and Rhombohedral phase are diagonal, with one (cubic: $Z_{11}^* = Z_{22}^* = Z_{33}^*$) and two (Rhombohedral: $Z_{11}^* = Z_{22}^* \neq Z_{33}^*$) independent components. SP hybridization between Ge and Te is well known and was already pointed out from our calculation [7,33]. In this context, it seemed realistic, following [34], to focus on sp-hybridization changes to explain intuitively large anomalous contributions [35]. Results for theoretical cubic and rhombohedral structures are reported in Table 1 and 5. The first line brings together the charge of nucleus and the core electrons included in the pseudopotential. The other contributions come from the valence electron levels. Sets of bands were identified by the name of the main atomic orbital which generated this energy level in the investigated compound. Their dominant character was confirmed by partial density plots [7].

We computed the BEC tensors for the ferroelectric phase, too. In the present paper we only comment on eigenvalues of these tensors (Tables 1 and 4) that already allow a pertinent comparison with the cubic phase. The Z^* eigenvalues of Ge (Sn) and Ge correspond to an eigenvector aligned along the ferroelectric axis. In the case of Te, eigenvector associated to the highest eigenvalue approximately point in the Ge(Sn) – Te direction: we identify this highest contribution as Te (\parallel) while the others are referred to as Te (\perp), by analogy with the cubic phase. The Z^* eigenvalues of Ge and Te in rhombohedral phase are in agreement with the results obtained in the previous calculation [5].

Table 4. The calculated Born Effective charge for Ge, Sn, and Te in in Ferroelectric and Paraelectric phase

	Nominal	Z^*	Cubic (Fm $\bar{3}$ m)	Rhombohedral (R3m)	
Ge	+4	Z_{11}^*	10.432	5.515	6.771 ^a
		Z_{33}^*	-	3.349	4.550 ^a
Te	-2	Z_{11}^*	-11.761	-5.406	-6.638 ^a
		Z_{33}^*	-	-3.373	-4.479 ^a
Sn	+4	Z_{11}^*	7.121	5.805	
		Z_{33}^*	-	5.251	
Te	-2	Z_{11}^*	-6.760	-5.716	
		Z_{33}^*	-	-5.281	

Reference [5]

4. Conclusion

In the present work, we conducted a detailed investigation of the elastic constants, density of states and Born effective charge tensors for ferroelectric and paraelectric phases of the narrow band ferroelectrics (GeTe and SnTe) crystals using the density functional methods. The second-order elastic constants have been calculated, and the related quantities such as bulk modulus and shear modulus have also been estimated. BECs of Ge, Sn, and Te atoms in rhombohedral and cubic phases are analyzed. The Born effective charge tensor is strongly anisotropic with a difference of 2.0 between parallel and perpendicular components. We examined the band structure as well as the change of Born effective charge tensors with atomic positions and all of our results have been discussed and compared with the available theoretical and experimental results.

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