Structure impact on the thermal and electronic properties of bismuth telluride by ab-initio and molecular dynamics calculations

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Abstract. We use molecular dynamics and ab-initio methods to predict the thermal and electronic properties of new materials with high figures of merit. The simulated systems are bulk bismuth tellurides with antisite and vacancy defects. Optimizations of the materials under investigation are performed by the SIESTA code for subsequent calculations of force constants, electronic properties, and Seebeck coefficients. The prediction of the thermal conductivity is made by Non-Equilibrium Molecular Dynamics (NEMD) using the LAMMPS code. The thermal conductivity of bulk bismuth telluride with different stoichiometry and with a number of substitution defects is calculated. We have found that the thermal conductivity can be decreased by 60% by introducing vacancy defects. The calculated thermal conductivities for the different structures are compared with the available experimental and theoretical results.

1. Introduction

The interest for high-performance thermoelectric materials is considerably increased during the last decades owing to the development of new deposition methods, which allow one to modify the properties of the materials by tailoring their structure at the atomic level. The thermoelectric effectiveness of a given material is quantified by the figure of merit Z, which is proportional to the
second power of the Seebeck coefficient and to the electrical conductivity, while it is inversely proportional to the sum of the lattice and the electronic thermal conductivities. Recent research aiming to increase the adimensioned product $ZT$ has been mainly oriented towards the decreasing of the thermal conductivity, the nanostructuration being the key for achieving this decrease [1].

According to the Slack’s principle of “a phonon glass and an electron crystal” [2] new generations of thermoelectric materials should be electrical conductor as good as crystalline metals, and thermal conductor as bad as glasses. From a structural point of view, ideal thermoelectric materials should contain i) long-periodic (with heavy elements as the best) lattice structures, and ii) ordered / disordered pore [3] and other defect systems, like superlattices [4] and thin films [5] of different structures and compositions in order to have a very effective scattering of thermal phonons.

$\text{Bi}_2\text{Te}_3$ is considered the best thermoelectric material at room temperature, with ZT of the order of one. It belongs to the class of thermoelectric materials with a large Seebeck coefficient [6]. This property is mainly due to its large anisotropy, which is a consequence of the different strength between the Van der Waals bonds among the adjacent Te atoms and the covalent bonds between Bi and Te atoms [7]. Porous bismuth telluride, thin films, nanowires or nanotubes exhibit lower thermal conductivity. Introduction of antimony or other substituted atoms into the $\text{Bi}_2\text{Te}_3$, possibly with change of stoichiometry, intentional introduction of structural defects, or incorporation of dopants like Sb and Se into the matrix lattice, are some ways to decrease the thermal conductivity [8].

Among the simulation approaches, Molecular Dynamics, based either on Equilibrium or Non-Equilibrium methodologies (EMD and NEMD, respectively), is often the preferred method because it does not require the knowledge of the phonon relaxation time, in contrast to the Boltzmann Transport Equation and the Monte Carlo methods.

The present article is composed of two distinct parts: i) the study of the thermal conductivity of structures containing vacancy and antisite defects by NEMD; ii) the ab-initio DFT study of the cohesive energies and the density of states of the same defected structures. The goal is to calculate $ZT$ in function of the structure, the compositions and the temperature, both for individual and segmented bismuth telluride materials, by DFT and molecular dynamics methods. The final aim is to propose ideal p-n-p-n-type circuits for thermoelectric energy conversion and power generation at the appropriate effective temperature intervals.

2. Simulation methods

First-principle calculations were performed in the framework of the density-functional theory (DFT), with the electron exchange-correlation taken into account by the Perdew, Burke, and Ernzerhof (PBE) generalized-gradient approximation (GGA). Troullier-Martins pseudopotentials and the DZP basis set, as implemented in SIESTA code [9], were also used. The Brillouin-zone integrations were performed by mean of a Monkhorst-Pack 8x8x8 k-points grid. Relaxation of the structures was performed by a conjugate-gradient minimization scheme. Both cell size and atomic positions were optimized. We assumed that the equilibrium geometries had been found when the Hellmann-Feynman forces on the atoms were smaller than 0.04 eV/Å and the components of the stress tensor were less than 0.02 GPa. All the calculations were spin-polarized.

The prediction of the thermal conductivity of $\text{Bi}_2\text{Te}_3$ was made by the NEMD method (also known as direct method), which is similar to the hot-plate and cold-plate experimental setups, proposed by Kotake and Wakuri [10] and Amrit et al. [11], respectively. This method is often the preferred one for nanoscale studies, as shown in a plethora of papers. In this method, the heat flux is along the z direction. Tri-dimensional periodic boundary conditions are used. The planar slab heat source and heat sink are located at the $\frac{1}{4}$ th and $\frac{3}{4}$ th of the simulation cell, respectively. The resulting steady temperature profile is symmetric according to the positions of the two thermostats, which are perpendicular to the z-direction. After reaching the steady state, the temperature profile and the heat power of the two thermostats were collected over several millions of time steps, in order to achieve a good statistical accuracy. Then, the thermal conductivity was determined by using the Fourier’s law. In all simulations the average temperature of the system was kept constant (100K, 200K, 300K, 400K,
500 K), while the thermostats were set with a temperature difference of 10% in comparison to the average temperature of the system. The Debye temperature of Bi$_2$Te$_3$ is 155 K. Thus, in the chosen temperature range, the quantum effects can be considered negligible. In the case of bulk Bi$_2$Te$_3$, we used the method proposed by Shelling [12], which allows one to find the thermal conductivity of an infinite system. The calculations were done using 8x8x2, 8x8x4, and 8x8x8 cells (1720, 3840 and 7680 atoms respectively). The effective thermal conductivity of defected structures, was determined by using only the 8x8x4 cell, which contains 3840 atoms. The aim was to understand the impact of vacancy and anti-site defects on the thermal conductivity by comparing with the thermal conductivity of the bulk Bi$_2$Te$_3$.

For the MD simulations, we used the two-body interatomic Morse potential developed by Qiu and Ruan, which gives a quite good description of the thermal properties [13]. This potential contains two terms: a short-range interaction term and a Coulombic term describing the long-range electrostatic interactions.

The charges we used for the Coulombic terms are: -0.26 for Te-1, 0.38 for Bi, and -0.24 for Te-2. The masses were: 127.6 a.m.u for Te, and 209.0 a.m.u for Bi. The long-range Coulombic interactions were computed by performing the Ewald's summation.

Bulk Bi$_2$Te$_3$ belongs to the space group D$_5^{3d}$ (R-3m), with a rhombohedral lattice structure. The hexagonal cell parameters are a=b=4.386 Å and c=30.497 Å. The unit cell contains 15 atoms, which are distributed in 3 quintuples. Each quintuple has two types of Tellurium atoms, the first one (Te-1) at the edges of the quintuples and the second one (Te-2) at the middle of the quintuples (orange and violet colours, respectively, in figure 1.a). The interaction of Te-1 and Te-2 with the Bismuth atoms has ionic character, while the one between two tellurium atoms belonging to different quintuples (Te-1 with Te-1) is a combination of Van der Waals and covalent bonds, which makes these bonds less strong than the previous ones.

3. Results and Discussions

3.1. Thermal conductivity

The thermal conductivity for infinite system size of bulk Bi$_2$Te$_3$ is plotted as a function of the temperature in figure 1b (dotted lines serve as a guide for the eyes). In the same figure, EMD results by Qiu et al [13] and two experimental values of the thermal conductivity at 300K are reported for comparison.

![Fig.1. a) Bi$_2$Te$_3$ structure in the yz plane. The quintuple and the conventional hexagonal cell are displayed. Each quintuple is composed by 5 monolayers according to the sequence: Te-type1, Bi, Te-](image)
type 2, Bi, Te-type 1. Three quintuples form the conventional hexagonal cell. b) Thermal conductivity
for bulk Bi₂Te₃ calculated by NEMD (after the extrapolation to an infinite size) as a function of
temperature (black squares). The theoretical EMD results by Qiu et al [13] (red cycles) and two
experimental values at 300K by Goldsid [14] and Satterthwaite and Ure [15] are also reported for
comparison. The dotted lines serve as a guide for the eyes.

The NEMD results are in very close agreement with the experimental ones. The temperature
dependence of the bulk Bi₂Te₃ thermal conductivity is the one typical of crystalline solids. At higher
temperatures, phonon-phonon scattering, which is the predominant scattering process, shows a 1/T
dependence with temperature [11]. This reduction of the thermal conductivity with the temperature
within the Debye model is explained by the increased scattering rate of higher frequency phonons.
Higher temperatures correspond to a larger population of these phonons and this results in the increase
of the scattering rate.

The difference between the results obtained by the two molecular dynamics methods has also been
noticed in previous studies. The EMD method underestimates the thermal conductivity in comparison
to the NEMD one. There are two main reasons of that. The first one is related to the EMD
methodology and to the fact that only the linear part of the temperature profile is used to extract the
thermal conductivity (this might give a thermal conductivity 10% greater). The second reason is
related with the EMD methodology and the important structure size effects. As the EMD method is
more expensive computationally, only small size cells can be used, leading to the filtering of the long
wavelength phonons.

After the calculation of the bulk Bi₂Te₃ thermal conductivity, several stoichiometries of
monocrystalline BiₓTe₁₀₀₋ₓ have been studied. The purpose is to find the stoichiometries with anti-site
and vacancy defects (n-type) with the lowest thermal conductivity or with the highest ZT. The
structures including vacancy and antisite defects we have considered are reported in Table 1.

Tab.1. Bismuth telluride structures with n-type antisite and vacancy defects.

| Percentage | Antisite n-type | Vacancy n-type |
|------------|-----------------|----------------|
| 2%         | Bi₃₈Te₆₂        | Bi₃₈Te₆₀       |
| 4%         | Bi₃₆Te₆₄        | Bi₃₆Te₆₀       |
| 6%         | Bi₃₄Te₆₆        | Bi₃₄Te₆₀       |
| 8%         | Bi₃₂Te₆₈        | Bi₃₂Te₆₀       |
| 10%        | Bi₃₀Te₇₀        | Bi₃₀Te₆₀       |

Figure 2 shows that, both in the case of antisite and vacancy defects, the thermal conductivity
decreases with respect to the one of stoichiometric Bi₂Te₃. Vacancies are more effective in decreasing
the thermal conductivity than antisite defects. This was expected because antisite defects are just the
exchange of two types of atoms, while in the vacancy case the empty space destroys the continuity of
the lattice, giving an additional scattering mechanism for phonons.

In the next section, the electronic partial density of states of the stoichiometric Bi₂Te₃, as well as of the
structures including vacancies and antisite defects, are provided to get a deeper understanding of the
physical phenomena occurring with the creation of defects.
3.2. Electronic properties
The usual unit cell Bi$_x$Te$_y$ (111) composed of 15 atoms and the larger unit cell Bi$_{48}$Te$_{72}$ (221) composed of 60 atoms were successfully optimized by the procedure of false and true unit cell calculations. Different Monkhorst-Pack k-point grids were used: 2x2x1, 4x4x2, k=8x8x4, 16x16x4, and 32x32x4. Spin polarized calculations give a band gap of 0.2 eV and 0.16 eV for the usual (111) and the large (221) bismuth telluride cell, respectively. These results are in agreement with the experimental values of 0.16-0.22 eV [16]. The band gap of one quintuple thin film, calculated with the same method, is much larger and reaches the value of 1.2 eV. Electronic properties for thin films of bismuth telluride are studied for a set of quintuples (one, two and three) with a corresponding thickness of 1, 2 and 3 nm, respectively, and for several types of defects. Single antisite and vacancy defects correspond to approximately a concentration of 1.67 %. Results of cohesive energy calculations are presented in Figure 3a, where the ideal crystal case corresponds to the lowest value. Doubling the concentration (3.34%) of the antisite Bi and Te defects does not change the chemical formula of composition, but the cohesive energy becomes much higher in comparison to the single type defects (see figure for details). It should be especially noted that a large cell system was relaxed to create nano-grain materials, with lower stability in comparison to the usual material. This instability is related with the atomic reorganizations. Additional calculations of transport properties (Seebeck coefficients and electronic conductivity) were made by the BoltzTraP software [17]. The Seebeck coefficient of Bi$_x$Te$_y$ was found to be 160 μV/K, while, in presence of antisite defects, its value is much smaller: 90 μV/K. It was also found that the Bi$_x$Te$_y$ electrical conductivity is not affected very much by antisite defects and its value remains similar to that of the pure crystal. The projected densities of states for single Te atoms explain the nature of levels at Fermi energy: they are occupied by antisite atom and neighbour atoms, as it can be seen from the comparison between the Partial DOS and the Total electronic DOS for Te antisite structure calculations (Figure 3b).
4. Conclusions
Combined molecular dynamics and first-principle calculations showed important decrease of the thermal properties of defected structures, especially vacancy and antisite defects. Thermal conductivity decreases even 60% with 4% Bi vacancies while Seebeck coefficients were found to decrease slightly for structures with both defect types. These findings can be used further in order to synthesize optimal thermoelectric bismuth telluride materials.

Fig.3. a) Cohesive energy of bismuth telluride with antisite (as) and vacancy (vac) defects. The appropriate numbers of defects is indicated in the legend. b) Electronic density of states for different type of single-defected bismuth tellurides (Bi and Te antisite and vacancy defects) and individual substituted atom in the case of Te antisite bismuth telluride. Open points denote the Fermi energy levels.

5. References
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