Ab initio Results for the Structural and Electronic Properties of Intrinsic Defects in PbTe.

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Keywords: Defects in PbTe, Formation energies, Density Functional Theory

Abstract

In this work, we have performed spin-polarized calculations for the structural and electronic properties of vacancies and anti-site defects in the rocksalt PbTe. Our obtained results have shown that both the Pb and Te antisites are the favorable defects in Pb and Te-rich conditions, respectively. Moreover, in the perfect stoichiometry condition, the antisites, as well as the Te vacancy, are equally probable to find. Considering the charge injection in the system, all the defects change from the 2+ charge state to the 2- one within 14 meV, at around 80 meV from the valence band edge within the bandgap. This feature makes it difficult to experimentally characterize these defects in PbTe.

Introduction

Thermoelectric devices (TD) have great promise in dealing with the challenges of the growing demand for alternative clean energy, and Te-based materials well-known candidates for them. Their most stable structure are the NaCl structure (PbTe and SnTe), and rhomboedric (GeTe) [1]. Delaire et al. [2], show that TO phonons play a significant role to the decreasing of the lattice contribution of the thermal conductivity of PbTe, once the figure of merit, ZT is given by

\[ ZT = \frac{\sigma S^2 T}{\kappa_L + \kappa_T}, \quad (1) \]

where \( \kappa_L \) and \( \kappa_T \) are the electronic and the lattice thermal conductivity, respectively, \( \sigma \) is the electronic conductivity and \( S \) is the Seebeck coefficient. Moreover, we have shown that the high values for the dielectric constant, together with anharmonic LA-TO coupling, reduces the lattice thermal conductivity and enhances the electronic conductivity in PbTe [3].

It was also shown in the literature that, by alloying this material with Se or with Sn, both their electronic conductivity and dielectric permittivity are also enhanced [4]. So, the remaining question is whether the intrinsic defects in this material play the same role (i.e., enhances ZT by reducing the thermal conductivity or by increasing the electronic conductivity). However, there is a few recent experimental data on this subject.

Point defects are well known to give rise to new electronic states close to the valence or conduction band edges, inside or not in the bandgap, which contribute to a change in the electronic density of states (DOS) near the Fermi energy [5]. Besides, they are results from small deviations from the stoichiometric composition during the PbTe growth in equilibrium at elevated temperatures [6]. So, depending on the nature of the defect induced states, they can contribute, or not, to an enhancement of ZT.

From the theoretical point of view, two interesting results were published which, despite the fact the authors have used the same computational method with slightly different details, they reach the same conclusions [7,8]: The most stable defects with the lowest formation energy for Pb-rich condition are Te vacancies (+2), and Pb vacancies (-2), whereas those for Te-rich growth conditions are Te anti-sites (+2), and Pb vacancies (-2). While Wang et al. did their calculations by including spin-orbit interactions (SOI) in a 216 atoms supercell [7], Bajaj et al. did them in a 250 atoms supercell but have neglected SOI effects [8]. However, none of them have included spin polarized effects in their calculations.

So, in order to include these missing effects, we show in this work, our preliminary results for the formation energies and electronic properties of vacancies and anti-site defects in the rocksalt PbTe, by using spin-polarized total energy calculations.

18th Brazilian Workshop on Semiconductor Physics (BWSP 2017)

DOI: 10.17648/bwsp-2017-70074
**Methods and Results**

Our calculations were done by using the density functional theory (DFT) within the local density approximation (LDA) and the PBE (Perdew, Burke, and Ernzerhof) parametrization for the generalized gradient approximation (GGA), gradient conjugated techniques together with the supercell models, as implemented in the Vienna *ab initio* simulation package (VASP) [9]. The valence electrons, as well as the ionic core interactions, were described by the PAW method [10].

In the calculations, we have included the scalar relativistic effects (mass-velocity and Darwin terms) and spin-orbit interactions (SOI) as well. The Monkhorst-Pack (4×4×4) mesh have been adopted for the Brillouin zone integrations [11]. All the calculations were performed in the spin-polarized mode with a 300 eV energy cutoff in the plane-wave expansions.

All the studied defects in PbTe were described by a (2×2×2) supercell, which is equivalent to 64 atoms. This supercell size was chosen due to the large dielectric constant in PbTe, 194.3 [3], that minimizes the error associated with charged defect-defect interaction [7]. With this supercell, the defect-defect distance is around 12.78 Å, which is close to the vacuum thickness used in surface total energy calculations [12]. The equilibrium structure for each case was obtained through ionic relaxations performed until the residual forces on the ions have values less than 10 meV/Å.

Before proceeding to the defect calculations, we first optimized the PbTe in the NaCl structure in order to have a good description of the equilibrium properties of the bulk. The calculated results were fit using the Vinet equation of state resulting in \( a_0 = 6.39 \text{ Å}, B_0 = 0.49 \text{ Mbar}, B_0' = 4.6 \). At the equilibrium position, we have obtained the bulk band structure which shows a narrow bandgap at the L point of the Brillouin zone of around 0.17 eV. Our results are, then, in good agreement with the available experimental data \( a_0 = 6.46 \text{ Å}, B_0 = 0.41 \text{ Mbar}, E_g = 0.19 \text{ eV at } T = 4 \text{ K}; E_g = 0.31 \text{ eV at } T = 300 \text{ K} \) [3, 13, 14].

The defect formation energy [15, 16] was obtained as

\[
E_D(q) = E_{\text{tot}}^e(q) - E_{\text{tot}}^b(q) - n_Pb \mu_{Pb} + n_{Te} \mu_{Te} + q \mu_e,
\]

where the two first terms on the right side of the supercell with and without the defect, respectively, \( n_{Pb} \) and \( n_{Te} \) are the number of Pb and Te atoms, \( \mu_{Pb} \) and \( \mu_{Te} \) are their respective chemical potentials, \( q \) is the defect charge state and \( \mu_e \) is the electron chemical potential, which is related to the Fermi energy of the system and vary from the top of valence band energy to the bottom of conduction band one. The constraints for the Pb and Te chemical potentials are directly related to their bulk formation energies,

\[
\mu_{PbTe} = \mu_{Pb}^{\text{bulk}} + \mu_{Te}^{\text{bulk}} - \Delta H_f
\]

that is given by

\[
\mu_{Te}^{\text{bulk}} - \Delta H_f \leq \mu_{Te} \leq \mu_{Te}^{\text{bulk}},
\]

where the left side term is the Pb-rich and the right side one is the Te-rich condition, respectively.

![Figure 1. Formation energies of the studied defects dependence with Te chemical potential variation evaluated for \( \mu_e = 0 \text{ eV} \) (i.e., Fermi level at the valence band maximum).](image1)

![Figure 2. Same as Fig. 1 but keeping \( \mu_e = E_g \text{ eV} \) (i.e., Fermi level at the conduction band minimum).](image2)
Table I. Charge and total spin configurations obtained for the defects in PbTe at their calculated most stable state in the Pb- and Te-rich conditions.

<table>
<thead>
<tr>
<th>Defect</th>
<th>Charge (electrons)</th>
<th>Spin (ℏ units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb vacancy</td>
<td>2+</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>0</td>
</tr>
<tr>
<td>Pb anti-site</td>
<td>2+</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>2</td>
</tr>
<tr>
<td>Te vacancy</td>
<td>2+</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>1</td>
</tr>
<tr>
<td>Te anti-site</td>
<td>2+</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>2-</td>
<td>0</td>
</tr>
</tbody>
</table>

From Fig. 1, our results show that Pb anti-site and Te vacancy are the most stable defects at Pb-rich condition when the Fermi level is at the top of the valence band. When we consider the Te-rich situation, the Te anti-site has the lowest formation energy. This situation does not change when the Fermi level is increased to the bottom of the conduction band. However, at the Te-rich condition, the Pb vacancy became more stable, as depicted in Fig. 2.

In Table I, we show the main features obtained in our calculations when the spin-polarized mode was included. We would like to remark that the evaluated total energy differences among each defect spin state is very small (~ 0.08 meV) and so, in this case, the inclusion of spin-polarized effects cannot be considered decisive in determining the defect most stable spin state. However, our results indicate that for systems with more electrons, like in the anti-site defects when compared with the vacancy ones, these effects are more pronounced and affect both the evaluated total and formation energies.

Then, from Table I, at the 2+ charge state, the Pb and Te vacancies are a triplet, while the Pb anti-site is a singlet and the Te anti-site is a quintet. When considering the 2- charge state, the Pb vacancy became a singlet, the Te vacancy, a triplet, the Pb anti-site, a quintet, and the Te anti-site, a singlet.

Discussion

When we compare our obtained results (which are depicted in both Figs. 1 and 2) with the published theoretical ones [7,8], we found a slightly disagreement: while the published results pointed out that, at Pb-rich condition, the most stable defects are Te vacancies, and Pb vacancies, whereas those for Te-rich growth conditions are Te anti-sites, and Pb vacancies, our results show that the anti-sites, Pb and Te ones at Pb- and Te-rich situation, respectively, are the most stable ones. However, there is a good agreement about the obtained defect charge states. We believe that this is the main difference detected when the spin-polarized calculations are taken into account in the calculations.

Concerning the electronic properties, it is well known that, in PbTe, the bandgap is direct and at the L point of the Brillouin zone [17]. Our results show that, while the bands are derived from hybridized Pb 6p and Te 5p states, the conduction bands are formed by the Pb 6p states. Due to SOI effects, one conduction band is lowered in energy at the Γ point, and our obtained spin-orbit splitting of Pb 6p states was 1.2 eV, in agreement with the published 1.8 eV [17].

When the Pb vacancy is created, the local charge is disturbed which alters the covalent bonding with the neighboring Te atoms. The valence band states are strongly perturbed such that an acceptor-like state appears near the top of valence band. Our spin-polarized results show that this state is doubly degenerated with two unpaired electrons when the defect is at 2+ charge state.

Now, filling the Pb vacancy by a Te atom (creating the Te anti-site), the two Te extra 5p electrons pull the 6p state at the conduction band to the middle of the bandgap, creating another degenerated deep acceptor state which loses these two electrons when the Fermi level is located at the valence band maximum, as observed in our results.

Considering the creation of the Te vacancy, the removal of one Te atom strongly perturbs both the valence and conduction bands due to the charge disturbance on the neighboring Pb 6p states. Thus, a new degenerated state appears within the bandgap with Pb p-character, occupied with two unpaired electrons. As observed for the Te anti-site, this state loses two electrons when the Fermi level is located at the valence band maximum, having an acceptor character in this case.

Similarly, when we filled the Te vacancy with a Pb atom (the Pb anti-site), the Te vacancy induced state is now filled with four electrons, instead of six Te valence electrons. Our results show that this state is located close to the valence band maximum and has an acceptor character and loses two electrons when the Fermi level is located at the valence band maximum. It is interesting to remark that, at 2+ charge state, the remaining two electrons are paired and the system is a singlet.

Putting the Fermi level position at to the bottom of the conduction band, we remark that the induced defect levels change from the acceptor character to the donor one. All these features are in agreement with other theoretical calculations [7,18].
PbTe is one of the known materials which have its phase diagram from liquid to solid evaluated theoretically by the CALPHAD method, with good agreement with the experimental data. From the evaluated solidus line, the solubility on the Pb-rich side is lower than that on the Te-rich side of the perfect stoichiometric condition [8]. Based on this remark, we have then obtained the defect formation energies as a function of the chemical potential of the Pb atoms, keeping the Te chemical potential at the perfect stoichiometric situation, i.e., \( \mu_{\text{Te}} \approx -3.85 \text{ eV} \). The results are depicted in Fig. 3.

From Fig. 3, when the Fermi level is at the top of valence band, both anti-sites, as well as the Te vacancy are the most stable defects, all of them at the 2+ charge state. At around 80 meV (close to the middle of the bandgap), within a range of 14 meV, all the defects make a transition from 2+ charge state to 2- one. This is consistent to the experimental measurement of the temperature dependence of the resistance, which it drops considerably when the activation energy is 77 meV [19].

When the Fermi level is above the middle of the bandgap until the bottom of the conduction band, all the defects are equally probable to find. This remark together of the number of charge state transitions within a small range of energy make it difficult to experimentally characterize defects in PbTe. To emphasize these difficulties, in recent two peaks observed in the infrared photoreflectance experiments done by Zhang et al [20], while one of the resonant transitions was assigned to the Te vacancy, the other is still not clear to which defect it belongs.

A close analysis of Fig. 3 in the range 70 meV < \( \mu_{e} < 85 \text{ meV} \) (not shown here) show that the Pb vacancy has a negative U character: there is a (+/-) charge transition occurring at \( E_{v} + 71 \text{ meV} \), i.e., it is energetically more favorable to receive two electrons, instead of one. At \( E_{v} + 72 \text{ meV} \), the Pb vacancy is at the 2- charge state.

For the Te vacancy, it has charge transitions that starts at \( E_{v} + 77 \text{ meV} \) (2+/+), and finishes at \( E_{v} + 82 \text{ meV} \) (-/2-). The Pb anti-site has this range comprising from \( E_{v} + 77.5 \text{ meV} \) (2+/+) to \( E_{v} + 84 \text{ meV} \) (-/2-), and the Te anti-site, from \( E_{v} + 77 \text{ meV} \) (2+/+) to \( E_{v} + 80 \text{ meV} \) (-/2-), respectively. This scenario justifies the experimental difficulties to assign the observed data with a specific defect.

Concerning the changes in the structural properties of PbTe with the presence of defects, our results show that, for Te vacancy, the atoms around the defect site (first and second neighbors) experiences large rearrangement, when compared with the other defects.

For the Te vacancy, the Pb first neighbors relax 6% outward, while the Te second ones, around 1% inward. In the case of the Pb anti-site, the first neighbors move 2.9% inward and the second neighbors move 0.4% outward, while for the Te anti-site, these atoms relax 2.5% outward and 0.7% inward, respectively. Considering the Pb vacancy, these rearrangements are the smaller among the studied defects (1.25% inward for the Te first neighbors and 0.4% inward for the Pb second ones) due to strong bonds among the atoms around the defect site and thus, leading to higher formation energies, as observed in Figs. 1-3.

In summary, we presented our preliminary results for the formation energies, structural and electronic properties of defects in the rocksalt PbTe. Based on our results, we found that both the Pb and Te antisites are the favorable defects in Pb- and Te-rich conditions, respectively. Considering the stoichiometric situation, the Te vacancy is also equally stable, and when we inject charge in the system, all the defects change from the 2+ charge state to the 2- one within a range of 14 meV, at around \( E_{v} + 80 \text{ meV} \). In this situation, all studied defects are quite stable, making it difficult to experimentally characterize these defects in PbTe individually. This can be the main reason that there are few published experimental studies in the literature.

Acknowledgments

We acknowledge the financial support from the Brazilian agency FAPEMIG (both the grant CEX APQ 02695-14 and the PIBIC/FAPEMIG/UFSJ program).