

Electronic Structure of $\text{AgPb}_m\text{SbTe}_{m+2}$ Compounds – Implications on Thermoelectric Properties

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ABSTRACT

Novel quaternary compounds $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST-m) with different m values have been synthesized recently and some of these compounds show promising thermoelectric properties at high temperatures. The two end members of the series, PbTe ($m=\infty$) and AgSbTe_2 ($m=0$), are also known to be good thermoelectrics. In this paper, we discuss the results of *ab initio* electronic structure calculations for these two end members and for LAST-2 and LAST-14 to see how the electronic structure near the chemical potential μ evolves with m . Whereas PbTe and LAST-14 are narrow band gap semiconductors, the other two compounds show pseudo-gap structure. Even in the absence of a true gap, the rapidly varying density of states (DOS) near μ may be conducive to large Seebeck coefficient in LAST-2, LAST-14, and AgSbTe_2 .

INTRODUCTION

Thermoelectric properties of a material depend sensitively on the nature of electronic states near the chemical potential μ . It has been suggested that resonant structures in the single particle density of states (DOS) in the neighborhood of μ can indeed give rise to enhanced thermoelectric figure of merit [1]. *Ab initio* electronic structure calculations can provide important information about the energy dependence of DOS and the existence of such resonant structures[2].

Recently, quaternary compounds $\text{AgPb}_m\text{SbTe}_{m+2}$ (LAST-m) have emerged as materials for potential use in efficient thermoelectric power generation at high temperatures[3]. These compounds can also be written as $(\text{AgSbTe}_2)_x(\text{Pb}_2\text{Te}_2)_{1-x}$, where the two end compounds are known to exhibit large Seebeck coefficient [4, 5]. These systems possess rocksalt (NaCl) structure on the average where the Te atoms occupy the Cl sublattice sites and Ag, Sb, and Pb atoms occupy the Na sublattice sites in a random fashion. Detailed experimental information about the ordering of Ag, Sb, and Pb atoms for different m values at different temperatures is not currently available. However, there are some experimental indications that for large m values the system contains small domains of Ag-Sb-Pb-Te regions embedded in a PbTe matrix[3,6]. For $m=\infty$ (AgSbTe_2), earlier studies did not find any ordering of Ag and Sb ions[7]. However, recent careful X-ray diffraction studies do find some evidence of Ag-Sb order[8]. Monte Carlo (MC) simulations using an ionic model [Coulomb lattice gas (CLG) model] give a variety of nanostructures associated with the ordering of Ag and Sb ions, where ordered superlattice structures formed out of AgSbTe_2 layers separated by Pb_2Te_2 layers are observed for a large range of m values [9].

In order to investigate the relationship between different ordered nanostructures of these quaternary compounds observed in MC simulations[9] and their electronic structure, we have carried out detailed calculations for two compounds $\text{AgPb}_2\text{SbTe}_4$ (LAST-2) and $\text{AgPb}_{14}\text{SbTe}_{16}$ (LAST-14), and their parent compounds AgSbTe_2 and PbTe . These calculations are performed within the density functional theory (DFT) formalism, using the generalized gradient approximation (GGA)[10] and the projector augmented wave (PAW)[11] method as implemented in the *Vienna Ab Initio Simulation Package* (VASP)[12]. Each calculation begins with ionic optimization of a chosen structure, and the relaxed structure is then used to calculate single particle DOS and band structure. Spin-orbit interaction (SOI) is included.

In our *ab initio* calculations, initial structures of the compounds are the low temperature configurations obtained in MC simulations of the CLG model in which the Ag, Sb, Pb are assumed to be Ag^+ , Sb^{3+} , Pb^{2+} ; and Te is assumed to be Te^{2-} [9]. In this simulation, AgSbTe_2 is found to possess a tetragonal structure as shown in Fig. 1 (a), which can be reduced to the body-centered tetragonal (bct) structure [2 bct unit cells build up the tetragonal supercell]; LAST-2 and LAST-14 have layered structures formed out of AgSbTe_2 layers separated by Pb_2Te_2 layers. In the case of LAST-2, its supercell consists of 2 layers of AgSbTe_2 and 2 layers of Pb_2Te_2 . This alternately layered structure of LAST-2 can be obtained from the tetragonal supercell of AgSbTe_2 [Fig. 1(a)] by replacing 2 layers of AgSbTe_2 by 2 layers of Pb_2Te_2 which also can be reduced to the bct structure. In the case of LAST-14, its mono (bi)-layer structure consists of 1 (2) layer(s) of AgSbTe_2 sandwiched between 7 (14) layers of Pb_2Te_2 .

Earlier X-ray diffraction studies of AgSbTe_2 showed that this compound has (disordered) rocksalt (NaCl) structure at high temperature where the Ag and Sb atoms occupy the Na sublattice sites in a random fashion[7]. This may be the case in real samples of the LAST compounds since the ordering in the systems depends on the annealing and/or quenching schemes in which the system may not be able to reach the configuration obtained in MC simulations [9]. Recent work of Quarez *et al.* [8] shows that F-centered lattice ($\text{Fm}\bar{3}\text{m}$) is not adequate to describe the systems; $\text{Pm}\bar{3}\text{m}$ or $\text{P4}/\text{mmm}$ describe the system much better, but there is still no clear evidence of Ag and Sb ordering. Also a centrosymmetric $\text{R}\bar{3}\text{m}$ structure was found [8].

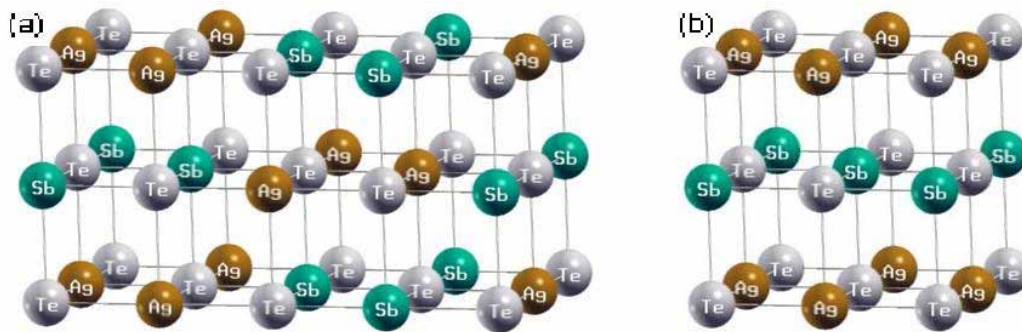


Figure 1: Different supercells of AgSbTe_2 : (a) tetragonal, which adopts the bct symmetry, and (b) cubic, which adopts the simple tetragonal (st) symmetry.

In order to see how the electronic structure of AgSbTe_2 and LAST-2 depend on the precise nature of Ag/Sb ordering, we have constructed a different ordered structure for AgSbTe_2 [see Fig. 1(b)] which is similar to the type-I antiferromagnetic structure[13] and can be reduced to the simple tetragonal (st) structure [2 st unit cells build up the cubic supercell], and a corresponding ordered structure for the LAST-2 by starting from this cubic structure of AgSbTe_2 [Fig. 1(b)] and replacing alternate layers AgSbTe_2 by layers of Pb_2Te_2 .

RESULTS AND DISCUSSION

We start our *ab initio* calculations with PbTe as a benchmark test. The results show that rocksalt PbTe has an optimal lattice constant of $6.5575 \text{ \AA}$ (a 1.8% increase from the experimental value [14]), and band gap of 0.0941 eV (experimental value is 0.19 eV [14]). Thus DFT-GGA overestimates the lattice constant and underestimates the band gap as we should expect.

Disordered rocksalt ternary compound AgSbTe_2 is known to be a semiconductor with lattice constant of $6.078 \pm 0.003 \text{ \AA}$ [7,15]. The precise role of Ag-Sb disorder on the electronic structure, particularly near the gap region, is not known. In our calculations, we find that different ordered structures after doing ionic optimization change their initial symmetry. For example, we find that the cubic structure [Fig. 1(b)] becomes a tetragonal with optimal lattice parameters: $a = 6.1537 \text{ \AA}$, and $c/a = 0.9836$. This structure (whose unit cell contains 8 atoms) can be further reduced to one with the st symmetry but with a smaller unit cell (containing 4 atoms) with $a = 4.3513 \text{ \AA}$, and $c/a = 1.3910$ which are consistent with current experimental values obtained in X-ray diffraction refinements [8]. The bct structure of AgSbTe_2 after ionic optimization gives $a = 6.1004$ and $c/a = 2.0267$ as optimal lattice parameters. In Fig. 2(a), we show the total DOS of both bct and st AgSbTe_2 structures. There is no gap at the Fermi level, but the Fermi level lies in a pseudo gap. The width of the pseudo gap depends sensitively on the arrangement of Ag and Sb atoms. Whether such a system in the presence of Ag-Sb disorder will give rise to a gap-like behavior in its optical response is an important question which we will address in the future. Due to rapid variation of the DOS near the Fermi energy one may expect this system to show large Seebeck coefficient as seen experimentally [5].

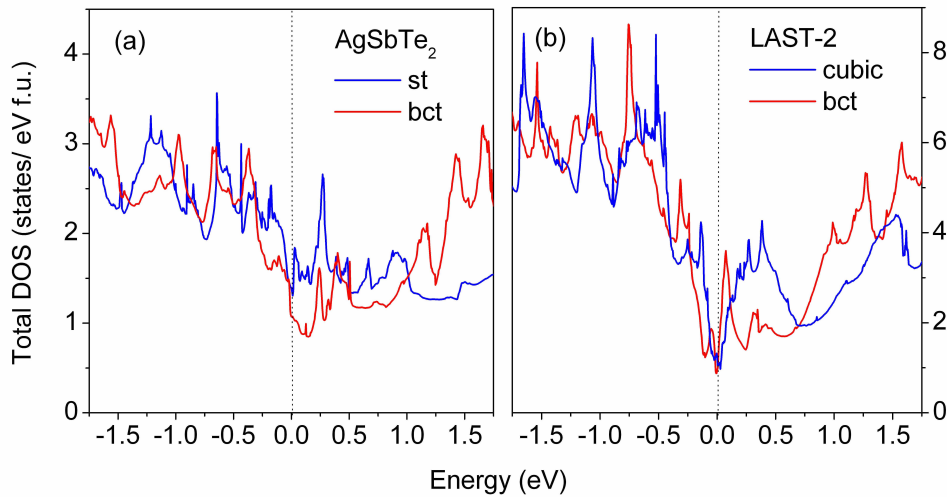


Figure 2: Total DOS of different structures of (a) AgSbTe_2 and (b) $\text{AgPb}_2\text{SbTe}_4$ [LAST-2].

For LAST-2, the total DOS of both cubic and bct LAST-2 reveal those of their parent compounds, AgSbTe₂ and PbTe, as shown in Fig. 2(b). There are well-formed pseudo-gaps and sharp peaks near the Fermi level.

Results of DOS and energy dispersion for the monolayer and bilayer structures of LAST-14 are shown in Fig. 3(a) and 3(b), respectively. In case of the monolayer structure, one can see quasi-1D and quasi-2D energy dispersion [in the layer, see Fig. 3(b)] that give rise to a peak (width ~ 0.05 eV) in the DOS near but above the valence band, and another peak below the conduction band. One can see the band gap of the dominant PbTe host matrix. This behavior persists for the bilayer structure. For the LAST-2 compound [see Fig. 2(b)], which consists of alternate layers of AgSbTe₂ and Pb₂Te₂, this peak structure persists but its shape is changed dramatically due to the 3-dimensional coupling perpendicular to the layers. In addition, the band gap region fills up and only a pseudo gap appears.

SUMMARY

In summary, our *ab initio* electronic structure calculations for AgSbTe₂, LAST-2 and LAST-14 shows that the LAST-14 shows semiconducting gap with resonant structures in the single particle DOS in the neighborhood of the chemical potential. AgSbTe₂ and LAST-2, on the other hand, show pseudo-gap behavior. The detailed structure of the DOS near the chemical potential depends on the Ag and Sb ordering. Thus Ag-Sb disorder which may be present in real systems will have profound effect on the states near the chemical potential and hence on the transport properties of these compounds. This needs further careful study. The sharp variations in the DOS near the chemical potential even in the absence of a real gap may be responsible for the large thermopowers seen in several LAST-m compounds and AgSbTe₂.

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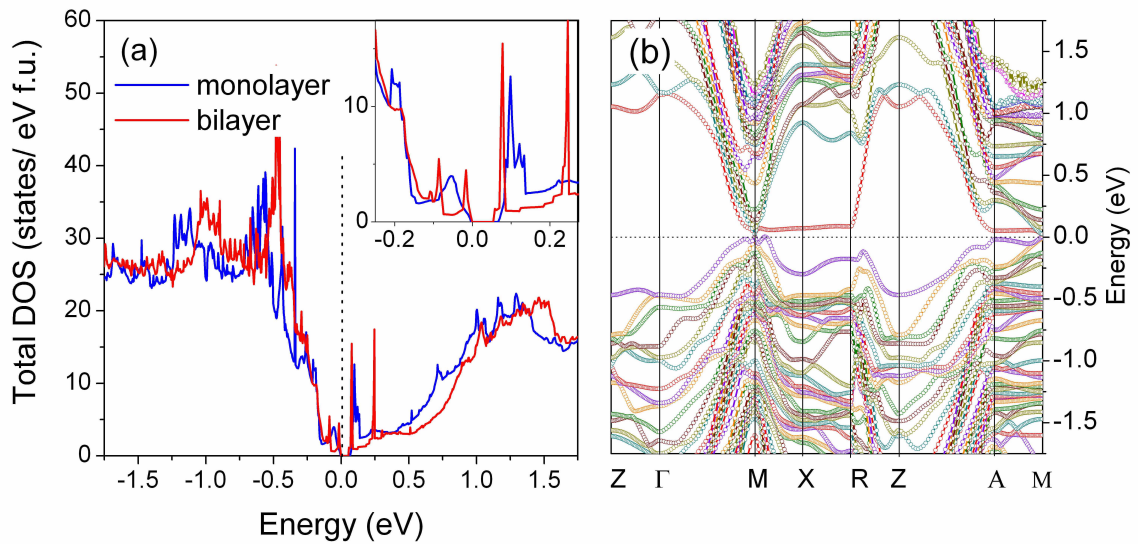


Figure 3: (a) Total DOS and (b) band structure of LAST-14.

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