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PROPERTIES OF THALLIUM (TL) COMPOUNDS: AB-INITIO CALCULATIONS

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Abstract

The tight binding linear muffin-tin-orbital (TB-LMTO) method within the local density approximation (LDA has been used to calculate structural and electronic properties of thallium pnictides TlX (X=Sb, Bi) at high pressure. As a function of volume, the total energy is evaluated. Apart from this, the lattice parameter (a0), bulk modulus (B0), band structure (BS) and density of states (DOS) are calculated. From energy band diagram we observed metallic behaviour in TlSb and TlBi compounds. The values of equilibrium lattice constants and bulk modulus are agreed well with the available data.

Introduction

Nowadays, there is an urgent need for the alternatives of the energy utilization because of the depletion of the energy resources on our planet. Thermoelectric materials, which can realize the energy conversion between heat and electricity, might be potential candidates. Thermoelectric phenomena were discovered in the 19th century. However, practical applications for thermoelectric devices became feasible only after mid-20th century because of advancements in the semiconductor technologies. After two decades, there was no breakthrough discovery in the thermoelectrics. But this field is experiencing a re-discovery for several reasons: First, current environmental concern requires new alternative materials to be able to do green energy conversion. Second, modern advanced techniques make it possible to synthesize many new compounds with complex structures and characterize their properties. Last but not least, reliable theoretical calculations by powerful computers are now available for predicting and understanding structural, electronic and thermal properties of materials, which makes the selection of the new materials much easier. The thermoelectric properties of some thallium compounds have been reported [1-7]. Recently, thallium chalcogenides such as Tl9BiTe6 [8] and Tl2SnTe5 [9] have been found to have excellent thermoelectric properties with extremely low thermal conductivities at room temperature. Thermoelectric properties of several quaternary thallium tellurides [10] have also been reported. The structural parameters, electronic behavior and thermodynamic properties of thallium phosphide (TlP) in its zincblende phase have been studied by Ciftci et. al. [11] using the plane-wave pseudopotential approach in the framework of density-functional theory within the LDA and GGA approximations implemented in VASP code. Under hydrostatic pressure the low pressure phase is destabilized and structural phase transition occurs. For thallium phosphide compound, the phase transition from zincblende (B_3) phase to NaCl (B_1) phase appears at a range pressure 4.47 GPa to 7.626 GPa [11-14]. In the present study we have reported, the high pressure structural and electronic properties of thallium pnictides TlX (Tl=Sb, and Bi) using *ab initio* Tight Binding-LMTO with LDA.

Method of Calculation

The total energy, structural stability, electronic band structure (BS) and density of states (DOS) for thallium compounds are calculated in nonmagnetic (NM) states using TB-LMTO method with atomic sphere approximation (ASA) [15, 16]. Von-Barth and Hedin [17] parameterization scheme had been used for exchange correlation potential. TlSb and TlBi compounds crystallize in the CsCl-type structure (space group, 221). The CsCl structure has a body centre cubic structure with one formula unit per unit cell[3]. Lattice: Body centered cubic (BCC) and Basis: Tl at (0, 0, 0) and Sb/Bi at (0.5, 0.5, 0.5). The Wigner-Seitz sphere was chosen in such a way that the boundary potential was minimum and charge flow between the atoms was in accordance with the electro-negativity criteria. The E and K convergence were also checked. The tetrahedron method [18] of Brillouin zone integration had been used to calculate the total density of states. We have used 8x8x8 K grid (512 K points) in the Brilliuon zone. To find the equilibrium lattice constant, the total energies are computed by changing the volume from $1.05V_0$ to $0.60V_0$ using Birch of state [19].

Results and Discussion

The total energy is calculated which gives energy vs. volume curve. The energy vs. volume curve for TlSb and TlBi are shown in Fig. 1. The calculated value of equilibrium lattice constant for TlSb and TlBi are 3.75 Å and 3.81 Å respectively in the NaCl Structure, and compared with theoretical [20] value in table 1.

TABLE 1. Calculated equilibrium lattice parameter a0 (Å), bulk modulus B0 (GPa), first order derivative B'0(Å) and total energy Etot (Ry.)

Solids	Lattice Constant(Å)	Bulk modulus (GPa)	First order derivative B'$_0$(Å)	Total energy E_{tot} (Ry.)
TlSb Present	3.75	81.12	19.16	-53427
Other	3.48[a]	---	---	---
TlBi	3.81	55.27	12.15	-83513
Present	3.98[a]	---	---	---
Other				

We have also calculated bulk modulii as 81.12 and 55.27 GPa and pressure derivatives as 19.16 and 12.14 for TlSb and TlBi under ambient conditions, respectively.

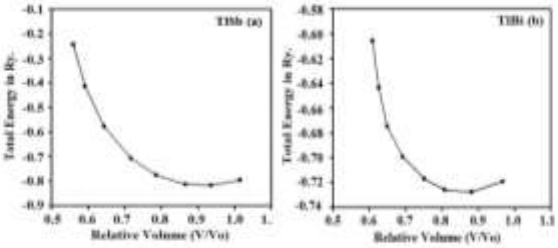

Figure 1. Variation of total energy for TlSb and TlBi.

The lattice parameters and bulk modulus in both B_1 structures are also tabulated in table1and compared with the available experimental and theoretical results [20]. We have carried out electronic band structure calculations for the thallium pnictides namely; TlX (X = Sb and Bi) in their CsCl phases. As discussed, the TlX compounds are metallic in nature. We have therefore, calculated the band structure (BS) along the high symmetry directions and density of states (DOS) at high pressure. For the sake of discussion on electronic properties of Tl-pnictides, we have presented BS and DOS diagrams for TlX in Fig 2 illustrate a combined picture of BS and DOS in CsCl-phase. As pressure is increased the lower energy bands are shifted to the higher energy side and more compressed bands are seen, which can be understood in terms of hybridization of Tl '*d*'-like states.

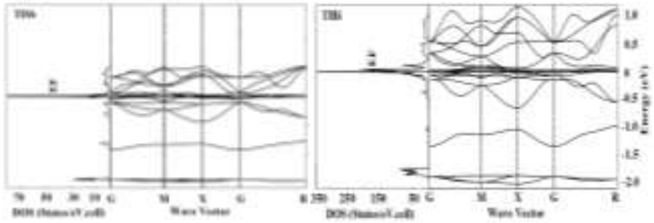

FIGURE 2. Band structure and density of states for TlX compounds.

In Fig. 2, the lowest lying bands in the valence band around -2.0 eV are due to 'p'-like states of Tl, and the next lowest energy bands are due to 's'-like states of Sb, which lie around -1.75 eV. The bands in the valence band just below the Fermi level (EF), in the range of -0.75 to 0.0 eV, arise due to Sb 'p'-like states. Also, in Fig. 2, for TlBi, Tl 'd '-like states can also be seen above the Fermi level (cluster of solid lines), which hybridize with Tl 'p'-like states.

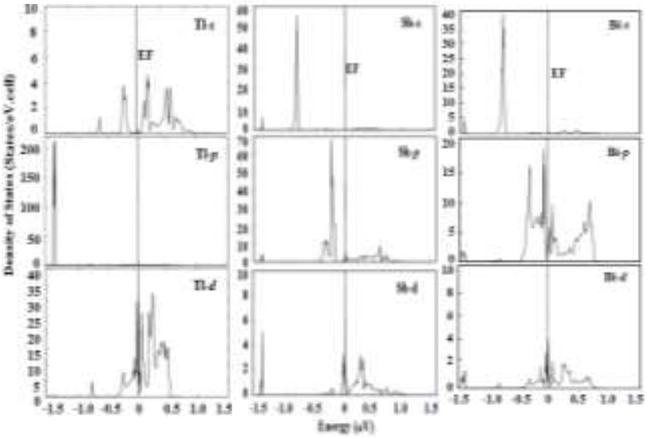

Figure 2. Partial Density of States For Tlx Compounds.

A small crossover of Tl '*d*'-like states at 'X' point can also be seen. The crossover of Tl '*d*'-like states in 'G–X' direction can be also seen. In general Fig. 2 describes a metallic picture of TlSb and TlBi compounds under high pressure. To understand a comprehensive picture of the elemental contributions to band structure we have plotted density of states in Figure 3. These figures reveal that lowest band around -1.5 eV due to Tl-*s*, band which hybridizes with Sb/Bi-s bands in these compounds. The Tl-*d* bands are quite broad and spread over the energy interval -1.0 eV to -0.5 eV.

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