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## Author's Accepted Manuscript

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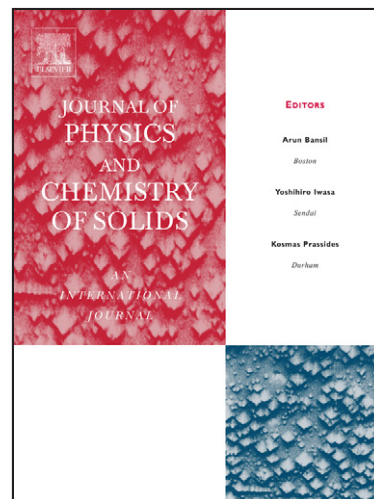
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**Electronic Structure of a Thermoelectric Material: CsBi<sub>4</sub>Te<sub>6</sub>**

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### Abstract

We have calculated the electronic structure of CsBi<sub>4</sub>Te<sub>6</sub> by means of first-principles self-consistent total-energy calculations within the local-density approximation using the full-potential linear-muffin-tin-orbital method. From our calculated electronic structure we have calculated the frequency dependent dielectric function. Our calculations shows that CsBi<sub>4</sub>Te<sub>6</sub> a semiconductor with a band gap of 0.3 eV. The calculated dielectric function is very anisotropic. Our calculated density of state support the recent experiment of Chung et al. [Science **287**, 1024 (2000)] that CsBi<sub>4</sub>Te<sub>6</sub> is a high performance thermoelectric material for low temperature applications.

There is a continued quest to find better thermoelectric materials in the material science community. Thermoelectric materials have a wide range of application and recent interest is in thermoelectric refrigeration. These materials are also used for conversion of heat into electrical power and cryogenic microsurgery. A good thermoelectric material should have basically three important properties; high electrical conductivity, high thermoelectric power and low thermal conductivity. In principal all of the mentioned three properties depend on the electronic structure of the material. Since the last three decades, the thermoelectric industry is using traditional semiconducting chalcogenide compounds for thermoelectric materials. Recently the work has become focused on ternary bismuth chalcogenides doped with alkali metals. The addition of alkali metals reduces the thermal conductivity of these materials.

Very recently Chung et al.[1] have reported on the synthesis of a new high performance thermoelectric material,  $\text{CsBi}_4\text{Te}_6$ , for low temperature applications. These authors have measured the thermoelectric power, conductivity and carrier concentration and hole mobility as a function of temperature. They have also demonstrated that when this material is doped it shows a very high thermoelectric figure of merit below room temperature. The thermoelectric properties of this material matches traditional materials at cryogenic temperatures. This very recent finding has motivated us to look into the electronic structure of this material. Up to now there is no calculation available regarding the electronic structure for this compound. The main aim of this manuscript is to study the electronic structure and the optical properties of this material to get a better insight into the fundamental aspects of this important material.

In order to study the electronic structure of  $\text{CsBi}_4\text{Te}_6$  we have used the full-potential linear muffin-tin-orbital (FPLMTO) method[2]. The calculations were based on the local-density approximation and we used the Hedin-Lundqvist[3] parametrization for the exchange and correlation potential. Basis functions, electron densities, and potentials were calculated without any geometrical approximation[2]. These quantities were expanded in combinations of spherical harmonic functions (with a cut-off  $\ell_{max} = 6$ ) inside non-overlapping spheres surrounding the atomic sites (muffin-tin spheres) and in a Fourier series in the interstitial region. The muffin-tin sphere occupied approximately 35% of the unit cell. The radial basis functions within the muffin-tin spheres are linear combinations of radial wave functions and their energy derivatives, computed at energies appropriate to their site and principal as

well as orbital atomic quantum numbers, whereas outside the muffin-tin spheres the basis functions are combinations of Neuman or Hankel functions[4, 5]. In the calculations reported here, we have used a pseudo-core for Cs composed of 5s, 5p and valence band 6s, 6p and 5d basis functions, and a pseudo-core for Bi made up from 5d and valence band 6s, 6p and 6d basis functions and for Te, finally a pseudo-core of 4d and valence band 5s, 5p and 5d basis functions. In addition the corresponding two sets of energy parameters, one appropriate for the semi-core 5s, 5p, 5d and 4d states, and the other appropriate for the valence states. The resulting basis formed a single, fully hybridizing basis set. This approach has previously proven to give a well converged basis[2]. For sampling the irreducible wedge of the Brillouin-zone we used the special k-point method[6]. In order to speed up the convergence we have associated each calculated eigenvalue with a Gaussian broadening of width 20 mRy.

### Calculation of the dielectric function

The ( $q = 0$ ) dielectric function was calculated in the momentum representation, which requires matrix elements of the momentum,  $\mathbf{p}$ , between occupied and unoccupied eigenstates. To be specific the imaginary part of the dielectric function,  $\epsilon_2(\omega) \equiv \text{Im}\epsilon(\mathbf{q} = 0, \omega)$ , was calculated from[7]

$$\epsilon_2^{ij}(\omega) = \frac{4\pi^2 e^2}{\Omega m^2 \omega^2} \sum_{\mathbf{k}n\sigma} \langle \mathbf{k}n\sigma | p_i | \mathbf{k}n'\sigma \rangle \langle \mathbf{k}n'\sigma | p_j | \mathbf{k}n\sigma \rangle f_{\mathbf{k}n} (1 - f_{\mathbf{k}n'}) \delta(e_{\mathbf{k}n'} - e_{\mathbf{k}n} - \hbar\omega) \quad (1)$$

In Eq. (1),  $e$  is the electron charge,  $m$  its mass,  $\Omega$  is the crystal volume and  $f_{\mathbf{k}n}$  is the Fermi distribution. Moreover,  $|\mathbf{k}n\sigma\rangle$  is the crystal wave function corresponding to the  $n^{\text{th}}$  eigenvalue with crystal momentum  $\mathbf{k}$  and spin  $\sigma$ . With our spherical wave basis functions, the matrix elements of the momentum operator can be conveniently calculated in spherical coordinates and for this reason the momentum is written as  $\mathbf{p} = \sum_{\mu} \mathbf{e}_{\mu}^* p_{\mu}$ , [8] where  $\mu$  is -1, 0, or 1, and  $p_{-1} = \frac{1}{\sqrt{2}}(p_x - ip_y)$ ,  $p_0 = p_z$ , and  $p_1 = \frac{-1}{\sqrt{2}}(p_x + ip_y)$ . [9]

The evaluation of the matrix elements in eq.(1) is done over the muffin-tin and the interstitial region separately. The integration over the muffin-tin spheres is done in a way similar to what Khan[10] and Gasche[7] did in their calculations using the atomic sphere approximation (ASA). A full detailed description of the calculation of the matrix elements will be presented somewhere else.[11]

The summation over the Brillouin zone in eq. (1) is calculated using linear interpolation on a mesh of uniformly distributed points, i.e., the tetrahedron method. Matrix elements,

eigenvalues, and eigenvectors are calculated in the irreducible part of the Brillouin-zone. The correct symmetry for the dielectric constant was obtained by averaging the calculated dielectric function. Finally, the real part of the dielectric function,  $\epsilon_1(\omega)$ , is obtained from  $\epsilon_2(\omega)$  using the Kramers-Kronig

$$\epsilon_1(\omega) \equiv \text{Re}(\epsilon(\mathbf{q} = 0, \omega)) = 1 + \frac{1}{\pi} \int_0^{\infty} d\omega' \epsilon_2(\omega') \left( \frac{1}{\omega' - \omega} + \frac{1}{\omega' + \omega} \right) . \quad (2)$$

For a monoclinic structure, we need to calculate three components of the total dielectric function,[10] corresponding to light polarized along a-axis, b-axis or c-axis.

In Fig.1 we show the crystal structure of CsBi<sub>4</sub>Te<sub>6</sub>. It has a monoclinic symmetry and contains 88 atoms in the unit cell. The x-axis of CsBi<sub>4</sub>Te<sub>6</sub> is very long. It is 12 times larger than the b axis and 4 times larger than c axis. Experimental lattice constants[1] a,b,c and angle( $\beta$ ) are 51.92 Å, 4.40 Å, 14.51 Å and 101.48°, respectively. This structure is very anisotropic and is composed of Bi<sub>4</sub>Te<sub>6</sub> slabs alternating with layers of Cs ions.

In Fig.2, we show the calculated density of states (DOS) for CsBi<sub>4</sub>Te<sub>6</sub>. The lowest lying states between 8 and 13 eV originate from the Bi and Te *s* states and pseudo core 5*p* states of Cs. A sharp peak around 8.0 eV is mainly 5*p* states of Cs suggesting the importance of these pseudo-core states and these states are not very far from the Fermi level. Usually people neglect these states. The peak at 11.0 eV is mainly Te *s* states and states between 11-13 eV are Bi *s* states. The states between 8-13 eV below the Fermi level is separated from a group of states between 0-5 eV below the Fermi level by a gap of around 3.0 eV. The states just below are mainly dominated by Te *p* and Bi *p* states with some mixture of Bi and Te's *s* and *d* states. The valence band is separated from the conduction band by 0.3 eV suggesting that this material is a small gap semiconductor. At present there are no measurement about the band gap in this material. Chung et al.[1] have estimated the band gap from the maximum value of the thermopower and the procedure gave a band gap in between 0.05 to 0.11 eV. Our calculated value of the band gap is higher than this value. LDA is known to underestimate the band gap and in some cases it can be underestimated by 50% This means that the real value of the calculated band gap is larger than present value. So values for the real bandgap measurements for example optical measurement are needed to get a precise information about the band gap. As regards the conduction band, the states between 0-5 eV above the Fermi level consist mainly of Te *p* and Bi *p* states with a mixture of Te *s* and *d* states. Above 5.0 eV, the Cs *d* states gave important contributions. Theoretical

investigations on Na-doped Si clathrate[12] show that high efficiency thermoelectric materials should have high electronic density of states near the highest occupied levels and free electron like density profile for the empty levels. In this regard, the  $\text{CsBi}_4\text{Te}_6$ , as shown in Fig.2, has a very high density of states at the top of the valence band and conduction band is more or less is free electron like. So our calculated density of states suggests that  $\text{CsBi}_4\text{Te}_6$  is a very high performance thermoelectric material. It has in fact been shown by Chung et al.[1] that  $\text{CsBi}_4\text{Te}_6$  is a high thermoelectric material. Our calculations also show that by adding a Cs atom, i.e. one electron per two units of  $\text{Bi}_2\text{Te}_3$  does not produce an intercalation compound, rather than that it reorganize the  $\text{Bi}_2\text{Te}_3$  network.

In Fig.3, we show our calculated dielectric function ( $\epsilon_2$ ) along three different directions, i.e. parallel to the a, b and c axis. Our calculated dielectric function is very anisotropic. Since the x-axis is very long in comparison to the y and z axis, also the dielectric functions look very different along x-axis. The interband transition in the dielectric function along the x-axis shows a sharp increase near the band edge. This peak is more and less dominating around 1.0 eV. For the dielectric function parallel to the y and z-axis, there is no sharp increase near the band edge and the dielectric function has a broader peak when compared with the peak along x-axis. The main broad peak in the dielectric function along the y and z-axis is located around 2.0 eV. The peak in the dielectric function along the z-axis is much broader than the peak along the y and z-axis. We have also tried to find the origin of these two different peaks in the calculated dielectric function. Since the different peaks are due to interband transitions it is useful for our discussion to first analyze the electronic structure of  $\text{CsBi}_4\text{Te}_6$  which was already discussed above. The origin of the peaks (Fig. 3) is due to interband transitions from valence- to conduction-band states. According to the selection rule only the transitions changing the angular momentum quantum number  $l$  by 1 ( $\Delta l = \pm 1$ ) are allowed. Further, this transition is only allowed within in same type of species. Having looked at the density of states (Fig.2) one can suggest that the first peak in  $\epsilon_2$  parallel to x-axis, around 1 eV, is due to the transition from Te-p to Te-s states. The peak in  $\epsilon_2$  parallel to the y and z-axis, around 2.0 eV, corresponds to the Bi-s  $\rightarrow$  Bi-p transition.

In summary we have shown that modern electronic structure theory is sufficiently developed to provide an accurate description of  $\text{CsBi}_4\text{Te}_6$ . The calculated value of the band gap is 0.3 eV which is larger than what Chung et al.[1] have obtained using a crude approximation. Our calculated density of states support the experimental finding that this material

is a high performance thermoelectrical material. Our optical calculations show that the dielectric function is very highly anisotropic. We hope our calculations will stimulate more experimental work on the optical properties of this material to clarify the optical anisotropy and the issue about the band gap.

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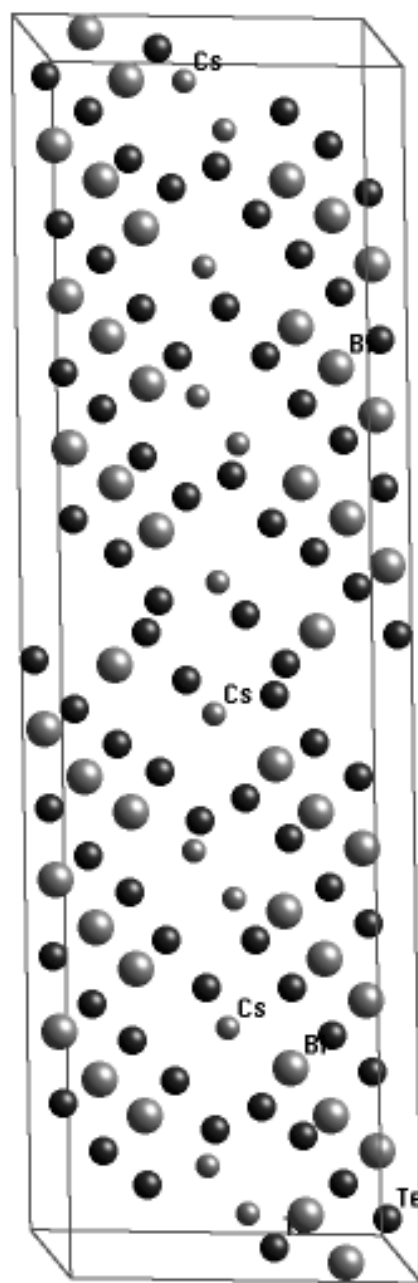


FIG. 1: Crystal structure of CsBi<sub>4</sub>Te<sub>6</sub>.

FIG. 2: Calculated density of states (DOS) for CsBi<sub>4</sub>Te<sub>6</sub>. The full line shows the total DOS. The Fermi level is set at zero energy and marked by a vertical dotted line.

FIG. 3: Calculated dielectric function ( $\epsilon_2$ ) for CsBi<sub>4</sub>Te<sub>6</sub> as a function of energy (eV). The full line shows the  $\epsilon_2$  parallel to x-axis while the dotted and dashed lines show the  $\epsilon_2$  parallel to y and z-axis, respectively.

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$x, z$

