Pressure induced semimetallic B2 phase of alkaline earth tellurides

Lavanya Kunduru\textsuperscript{1*}, Suresh Sripada\textsuperscript{2}, S. C. Rakesh Roshan\textsuperscript{3}, N. Yedukondalu\textsuperscript{3*}, M. Sainath\textsuperscript{3}

\textsuperscript{1}Department of Physics, JNTU, Hyderabad, 500085, Telangana, India
\textsuperscript{2}Department of Physics, JNTUHCEJ, 505501 Karimnagar, Telangana, India
\textsuperscript{3}Department of Physics, RGUKT, Basar, 504101, Telangana, India

Email: lavanyakunduru@rgukt.ac.in, nykondalu@gmail.com

Abstract. We report pressure induced structural, topological quantum phase transitions and Fermi surface topology in MTe (M = Ca, Sr, Ba) compounds under high pressure using first principles calculations based on density functional theory. MTe compounds undergo a first order structural phase transition from NaCl-type (B1) to CsCl-type (B2) phase at 24.2, 14.7, 4.9 GPa respectively and are consistent with the experimental observations. Electronic structure of MTe compounds were calculated using new parameterization of Tran Blaha-modified Becke Johnson (TB-mBJ) potential and the obtained band gaps are improved over LDA/GGA functionals. The three compounds under investigation are indirect band gap semiconductors at ambient conditions. Under high pressure, B2 phase of (Ca/Sr)Te and BaTe are found to be node-line and Dirac semimetal, respectively without inclusion of spin-orbit coupling.

Key words: High pressure, Band inversion, Node-line and Dirac semimetal, Fermi surface

1. Introduction

MTe (M = Ca, Sr and Ba) compounds are simple binary systems which belong to the class of II-VI semiconductors and these form an important family of closed-shell ionic systems and crystallize in B1 structure at ambient conditions. The MTe compounds are indirect and narrow band gap semiconductors at ambient conditions and these materials are expected to show semi metallic/metallic nature under high pressure. Therefore, extensive studies are reported on exploring the structural phase transitions and metallization under high pressure \cite{1–4}. Zimmer et al \cite{5} performed high pressure X-ray diffraction measurements to determine the structural phase transformations in CaTe and SrTe under high pressure. They found that CaTe \cite{5}, SrTe \cite{5} and BaTe \cite{6} transform from the B1 to the B2 structure at 35, 12 and 4.8 GPa, respectively. Although several studies were available in the literature on MTe compounds which focussed on structural and electronic properties at ambient pressure, a recent study on B2 phase of CaTe \cite{7} revealed that it is a topological node-line material at high pressure without inclusion of spin orbit coupling (SOC) and becomes strong topological insulator with inclusion of SOC. However, topological phase transitions at high pressure in SrTe and BaTe are unexplored. Further, to explore topological phase transitions in heavy metal alkaline earth tellurides namely SrTe and BaTe, we have systematically investigated the pressure induced structural phase transitions, electronic properties and Fermi surface topology of B2 phase of MTe compounds, which exhibits nodal-line and Dirac semi metallic nature under hydrostatic pressure without inclusion of SOC as observed in CaTe \cite{7} with different band topology.
2. Computational Details

All the first principles calculations were carried out using plane wave pseudo potential approach as implemented quantum espresso package [8]. Norm conserving pseudo potentials are used to treat the electron-ion interactions whereas electron-electron interactions are treated within generalized gradient approximation with Perdew-Burke-Ernzerh parameterization. The plane wave cutoff energy was set to 100 Ry and a k-mesh of 16x16x16 within Monkhorst-Pack grid scheme to compute structural properties at ambient as well as at high pressure.

The electronic structure calculations were performed using new parameterization of TB-mBJ potential as implemented in WIEN2k package [9]. To achieve energy eigen value convergence, wave functions in the interstitial region were expanded in plane waves with cutoff \( K_{\text{max}} = 7/RMT \), where RMT is the smallest atomic sphere radius and \( K_{\text{max}} \) denotes the magnitude of largest k vector in plane wave expansion, while the charge density was Fourier expanded up to \( G_{\text{max}} = 12 \). The muffin-tin radii were assumed to be 2.4 Bohrs for Ca, S ; 2.5 Bohrs for Sr, Se and 2.6 Bohrs for Ba, Te.

3. Results and Discussion

3.1 Structural Properties

As a first step, we performed geometry optimization of the MTe compounds at ambient as well as at high pressure up to 50 GPa for both B1 and B2 phases. As it can be seen from the figure 1(a), the calculated enthalpy difference w.r.t B1 phase as a function of pressure shows the CaTe, SrTe and BaTe compounds undergo a structural phase transition from B1 to B2 at 24.2, 14.7 and 4.9 GPa, and are consistent with the experimental transition pressures 35 GPa, 12 GPa and 4.8 GPa [6], respectively. The transition pressures decrease from CaTe>SrTe>BaTe which is due to increase in size of metal cation.

![Figure 1](image1.png)

Figure 1: (a) Calculated enthalpy difference w.r.t B1 phase and (b) relative volume as a function of pressure for CaTe, SrTe and BaTe compounds. The experimental data is taken from ref. [10].

We find a large deviation in transition pressure for CaTe because there exists an intermediate phase between B1 and B2 phases and the crystal symmetry of which is still under debate. The calculated volumes as a function of pressure are in good agreement with the experimental data [10]. The obtained volumes show a sharp discontinuity with a volume collapse of 7 % for CaTe, 8.4 % for SrTe and 12.2 % for BaTe compounds at the transition pressure which indicates a first order structural phase transition in these compounds as depicted in figure 1(b).

3.2 Electronic and topological properties

It is well-known fact that the standard LDA/GGA functionals severely underestimate the band gap for semiconductors and insulators. To overcome this band gap problem, we had utilized new
parameterization of TB-mBJ potential (TB-mBJ:2), there is a significant improvement in the band gaps using TB-mBJ:2 potential but this potential is still underestimate the band gaps when compared to the experimental ones [11 and references therein]. From the calculated electronic band structure, the maximum of valence band occurs at $\Gamma$ and minimum of the conduction band occurs at X which leads to indirect nature of the band gap for MTe compounds.

As illustrated in figure 2, we also calculated the band gap as function of pressure to explore the metallization in the narrow band gap semiconductors. Interestingly, the band gap decreases with pressure and they become semi metals above 33 GPa for CaTe, 25GPa for SrTe [12] and 40 GPa for BaTe (see figure 2). As it can be seen from figure 3(a), The top of the valence band is mainly derived from 5p-states of Te and the minimum of conduction band states occurred from the d-states of metal atom. The calculated pressure dependent electronic band structures without inclusion of SOC show band inversion along M (in CaTe), M and $\Gamma$ (in SrTe) and $\Gamma$ (in BaTe) high symmetry directions as illustrated in figure 3.

As shown in figure 3(a-d) the electronic band structure without SOC shows band inversion which forms a node-line because of the coexistence of time-reversal and inversion symmetry as discussed in the ref.[13]. The band inversion at M and $\Gamma$ high symmetry points arises between 5p, states of Te and 3d/4d (eg)- states of Ca/Sr. While band inversion occurred along $\Gamma$-X directions in BaTe which forms a Dirac cone. Overall, the high pressure B2 phase of (Ca/Sr)Te and BaTe are found to be node-line and Dirac semimetals, respectively without inclusion of SOC as illustrated in figure 3. To get further insight on semi-metallization, we also calculated Fermi surface of these three compounds at 50 GPa. The band topology is represented by the Fermi surface at M and $\Gamma$ high symmetry points in the momentum space is presented in figure 4. Iso structural Fermi surface topology is predicted for CaTe and SrTe compounds at M and $\Gamma$ directions of the Brillouin Zone.

We could see a diamond shaped Fermi surface topology behavior at center of the Brillouin Zone for CaTe and SrTe while it is distorted sphere for BaTe. The Fermi surface topology change under high pressure might be a precursor for superconductivity in this class of materials.

Figure. 2: Calculated electronic band gap as a function of pressure for B1 and B2 phases of MTe compounds using TB-mBJ:2 potential.
Figure 3: Calculated electronic band structures of (a,b) CaTe, (c,d) SrTe and (e,f) BaTe at 40 (left) and 50 (right) GPa of pressure for B2 phase using TB-mBJ:2 potential.
Figure 4: Calculated Fermi surface for B2 phase of (a) CaTe, (b) SrTe and (c) BaTe compounds at 50 GPa.

4. Summary

We have carried out first principles calculations to investigate the high pressure behavior of MTe (M = Ca, Sr and Ba) compounds. We found that MTe compounds undergo a structural phase transition from B1 to B2 phase at 24.2, 14.7, 4.9 GPa, respectively. The calculated electronic band structures show an indirect band gap nature of both B1 (along Γ-X) and B2 (along M-Γ) phases. The high pressure B2 phase of (Ca/Sr)Te and BaTe are found to be node-line and Dirac semimetals, respectively without SOC. This work might be helpful in understanding the pressure driven topological quantum states of matter in binary compounds.

References

[1] H. Okada, K. Koyama, M. Hedo, Y. Uwatoko, K.Watanabe, 2008 Physica B 403 1612.
[2] V. Mishra, S. Chaturvedi, 2007 Physica B 393278.
[3] F. Kalarasse, B. Benmecer, 2008, J. Phys. Chem. Solid 691775.
[4] K. Biswas, D.V.S. Muthu, A.K. Sood, M.B. Kruger, B. Chen, 2007 C.N.R. Rao, J. Phys.: Condens.Matter 19 436214
[5] H.G. Zimmer, H. Winzen, K. Syassen, 1985 Phys. Rev. B 32 4066.
[6] Thomas A. Grzybowski and Arthur L. Ruoff, 1984 Phys. Rev. Lett. 53, 489
[7] Du, Y., Tang, F., Wang, D et al, 2017 npj Quant Mater 2, 3
[8] P. Giannozzi, S. Baroni, N. Bonini, M. Calandra, R. Car, C. Cavazzoni, D. Ceresoli, G. L.
Chiarotti, M. Cococcioni, I. Dabo, A. Dal Corso, S. Fabris, G. Fratesi, S. de Gironcoli, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri, L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Sclauzero, A. P. Seitsonen, A. Smogunov, P. Umari, R. M. Wentzcovitch, J. 2009, Phys. : Condens. Matter, 21, 395502.

[9] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz, 2001 WIEN2K, an Augmented Plane Wave Local Orbitals Program for Calculating Crystal Properties, Techn. Universitat: Wien, Austria.

[10] H. Luo, R.G. Greene, K. Ghandehari, T. Li, 1994, Phys. Rev. B 50, pp. 16232–16237

[11] N. Yedykondalu et al 2018, AIP Conference Proceedings 1942, 090030.

[12] Lavanya et al, 2018, AIP Conference Proceedings 1966, 020029

[13] H. Weng et al.,2015, Phys. Rev. B 92, 045108