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Tin-tellurium-phosphide: Investigation of composition dependent band structure and its experimental realization

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ABSTRACT

The experimental discernment of TCIs (topological crystalline insulators) and other Dirac materials in recent times, has opened a new platform for their applications in spin-electronics and quantum computing. A very promising material in thermoelectric and photovoltaic applications, namely SnTe, has been increasingly investigated by band engineering, however, there is not sufficient verification of any band-crossing characteristics or evolution of Weyl nodes yet. In this present study, we investigate a novel class of possible substitutional solid solutions of Sn, Te, and P of varying compositions by density functional theory, where specific crystal symmetry elements may allow the existence of robust topological states. With fine tuning of chemical composition, one can also locate the existence of Dirac-like nodes at certain points of the Brillouin zone from preliminary first-principle calculations. Apart from simulations, synthesis and structural examinations of Sn-Te-P, were also conducted. The structural analysis of a representative member of this system was also carried out with the help of the simulated XRD patterns, to indicate the existence of a new phase during synthesis in a condensed system combustion.

1. Introduction

1.1. Background of the topological theory

Topological insulators [1] are a special class of material, sometimes called 'a new quantum matter' that exhibits gapless surface or edge states and gapped bulk bands. A sub-class of this category is topological crystalline insulator [2] (TCI) that originates from a space group symmetry rather than time reversal symmetry as in Z_2 topological insulator. TCIs possess an even number of Dirac cones [3] in the surface state Brillouin zone for the crystal faces that are perpendicular to the mirror planes. Some of the standard examples include $Pb_{1-x}Sn_xSe$ which possess Dirac cones on the crystal faces normal to the mirror planes. In contrast, Bi_2Se_3 or Bi_2Te_3 contain topologically protected Dirac cones on any surface irrespective of mirror symmetry constraint. Another point to remember is that TCI phase [4] robustness continues even if time reversal symmetry no longer exists for that material. The surface or edge states of TIs are spin-polarized and massless. The birth of TCI phase can be certainly related to other types of symmetry that have the capability to protect surface state band-crossing. One such symmetry can be obtained in a properly chosen crystalline space group that carries this requirement. Hence, the broader classification of TIs can be done on the basis of symmetry, namely TIs protected by time reversal symmetry (these are further classified into strong and weak TIs) and TIs protected by space group symmetry.

In contrast, Weyl semimetals [5–7] is another category of material, where conduction and valence bands meet and a linear dispersion around a Weyl nodes pair is observed. The breaking of time-reversal symmetry or inversion symmetry causes the lifting of degeneracy, which in turn results in a gapless structure along with some band crossing points in semi-metals. Dirac semi-metals can be visualized as two superimposed Weyl semi-metals along with protection of degeneracy by crystal symmetry (and gap opening as well).

Initially, most of the research for TIs and other Dirac materials was focused on a theoretical framework, however, recently, many of those predicted materials were realized experimentally. Some of the examples are SnTe [8], PbTe, $Pb_{1-x}Sn_xSe$, Bi_2Te_3 and many other similar materials. SnTe [9] is a narrow gap semiconductor and possesses inverted bands at four L points [8] of the FCC Brillouin zone. It is known that an even number of band inversions leads to a

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weak TI phase with protected surface states with mirror symmetry. Any perturbation [10] to these symmetries such as the creation of strain in one direction can create the possibility of lowering of band inversion and hence migration to strong TI phase. Such transformation due to uniaxial strain in SnTe crystal has been reported. Another approach to create or design new Dirac materials or modification of the existing materials is by creating a super-lattice structure of two different materials. Theoretically, it has been shown that interplay of a thin layer of two materials creates the enormous possibility of phase transition from one TI state to another. A recent report suggests that transition from normal insulator to TI phase is always interrupted by a Weyl semimetal spin-less phase along with non-degenerate Dirac cones at or near to the Fermi level [11]. Note that most of the research for TIs and related new Dirac materials is focused on a selected crystalline solid with one heavy atomic mass element (for better spin-orbit coupling). However, enormous possibilities exist to design and synthesize the new topological materials, based on ab-initio calculations [12] and common growth techniques. An addition to all these designs, is incorporation of new elements in an existing material of non-trivial phase. The main role of new atoms can be their appropriate contribution to the valence band due to its p-orbital structure as well as altered spin-orbit coupling.

SnTe is emerging as an attractive option for applications such as thermoelectric devices, photovoltaics, photodetectors, and IR detectors. The band-gap of SnTe can be engineered by changing the particle size. SnTe, normally exhibits a band-gap of ~0.18 eV that can be changed up to ~0.80 eV. Although many different TI materials and Weyl semi-metals have been proposed and synthesized experimentally, the perceived toxicity of constituent elements can restrict their use and hence limit the applications. Hence, the author's goal for this paper is to develop new Dirac materials that exhibit the similar fascinating non-trivial topological properties without using environmentally unfriendly precursors. For SnTe, some modifications have been done by substituting the Sn atom with metallic impurities such as Mg ($Sn_{0.93}Mg_{0.04}Te$), Mn ($Sn_{0.93}Mn_{0.04}Te$), Cd ($Sn_{0.93}Cd_{0.04}Te$), and Hg ($Sn_{0.93}Hg_{0.04}Te$) [8]. In their band-structures, it was challenging to observe any band-crossing characteristics or evolution of Weyl nodes. However, a change in band-gap was observed due to doping; the highest was for the case of Cd impurity [8]. Hence, it will be interesting to try and investigate an 'all scale hierarchical architecture' [13].

A possibility of topological phase transition exists between two distinct TI phases but under the prerequisite of bulk-edge correspondence. Under this assumption, the band-gap must close at the phase transition point. This is mainly due to need to retain the quantized value of topological number unless the gap is closed [14]. Note that SnTe is a topological non-trivial material, and it is evident in its band-structure. A switching has been observed near the L points (symmetry related TRIM) of bands and, interestingly, the Valence band edge is derived from Sn and conduction band-edge is due to Te atoms [15]. In contrast to the case of PbTe, the valence band is primarily derived from the Te p-orbitals [15]. The difference in topological mass of SnTe and PbTe is a governing cause of different topology. The nontrivial mirror Chern number was ~ −2, whereas the Z_2 invariant was found to be trivial. The schematic 2D band dispersion diagram (near Fermi level) suggests the presence of a characteristic double Dirac cone-like structure. The presence of well-defined spin textures in the surface makes TI a useful category of material for nonlinear optical device fabrication. A spatial self-phase modulation (SSPM)- an ultrafast nonlinear effect has been observed for TIs [16]. One of the ways Weyl semimetals can be generated is by the 'breaking of the spatial inversion symmetry'. A valley dependent dimerization of Dirac surface states has been examined in order to produce the various classes of TIs including weak TIs, strong TIs, and topological crystalline insulators (TCI), by inducing a topological quantum phase transition [17].

1.2. Search for new Dirac materials

The discovery of crystalline topological insulators was a landmark in condensed matter physics and furnished good prospects in spin-electronics and quantum computing [18]. These crystalline topological insulators, however, differ from topological insulators since the band degeneracy in crystalline topological insulators renders a mirror plane symmetry which acts as a substitute for time-reversal symmetry in the case of conventional topological insulators [19]. These TCIs (Topological Crystalline Insulators) exhibit bulk-boundary correspondence which furnish the presence of gapless boundary modes [18]. These TCIs often show novel magneto-transport and thermoelectric properties due to these characteristic edge states protected from electrostatic confinement [20–22].

In this search for new and modified TCIs, SnTe was the first material discovered to possess topological properties [23]. The most common compound containing tin and tellurium is SnTe and it melts at 769° C. A eutectic combination of tin and tellurium contains ~85% of tellurium [24]. For this material, first principle calculations manifested band-inversions at four L points of the Brillouin zone along with further validation by ARPES on the (100) surface of this material to prove its topological properties [23]. However, SnTe crystals are found to be strong p-type narrow band semiconductors due to the existence of the high amount of vacant Sn vacancies, such that the TCI states are not occupied. However, in the solid solutions of IV-VI semiconductors of $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$, TCI surface states have been experimentally observed using spin-resolved photoelectron spectroscopy (SRPES) on the (001) surface [25]. In stark contrast to the SnTe crystals, the chemical potential of these solid solutions of $Pb_{1-x}Sn_xTe$ and $Pb_{1-x}Sn_xSe$ can be moderated to n-type or p-type by heat treatment during growth.

In recent years substitutional solid solutions of IV-VI semiconductors like $Pb_{(1-x)}Sn_xSe$, where $x = 0.23$ have exhibited great promise as a topological insulator. It was found on the basis of theoretical calculations and characterization that in this novel class of Dirac materials, crystalline symmetries can replace time-reversal symmetry to protect surface states. Preliminary results from first principle calculations show that this crystalline topological state is not strongly controlled by chemical composition or magnetic field ordering, which may usher a pathway for the manifestation of Dirac cones in a novel class of substitutional solid solutions [26]. Furthermore, the chemical potential for these compounds can also be tuned to n-type or p-type during the growth of these crystals making them ideal for the study of TCI states by ARPES.

In our present study, we investigate a novel class of possible substitutional solid solutions of Sn, Te and P, where certain determined crystalline symmetries allow the preservation of these metallic states on the surface. It is interesting to note that this system of Sn, Te, and P may form a substitutional solid solution due to their congruency in electronegativity and atomic size. During the investigation of topological states in such a semi-metal, the fact that the role of P in transition metal monopnictide (TMMPs) TaP, NbP and NbAs helps in violating the inversion symmetry acted as our inspiration to study these classes of compounds [27]. It is an also a well-established fact, that there is an existence of four Dirac nodes along the conjunction of the mirror plane and the surface plane [28]. We found this system of Sn,Te, and P to be an interesting system for its band structure, morphology and phase investigation. Moreover, we also studied from first-principle calculations whether these TCI states of these solid solutions are independent of the

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