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Phys. Status Solidi B **250**, No. 4, 669–676 (2013) / **DOI** 10.1002/pssb.201200672

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Feature Article

High-pressure studies of topological insulators Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3

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Received 7 September 2012, revised 7 November 2012, accepted 8 November 2012
Published online 5 April 2013

Keywords Bi_2Se_3, Bi_2Te_3, high pressure, Sb_2Te_3, topological insulators

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Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 are narrow bandgap semiconductors with tetradymite crystal structure (R-3m) which have been extensively studied along with their alloys due to their promising operation as thermoelectric materials in the temperature range between 300 and 500 K. Studies on these layered semiconductors have increased tremendously in the last years since they have been recently predicted and demonstrated to behave as 3D topological insulators. In particular, a number of high-pressure studies have been done in the recent years in these materials. In this work we summarize the main results of the high-pressure studies performed in this family of semiconductors to date. In particular, we review recent results that address the main characteristics of the pressure-induced electronic topological transition and structural phase transitions observed in this family of compounds. Future high-pressure studies to be performed on these 3D topological insulators are also commented.

1 Introduction Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 are narrow bandgap semiconductors with layered tetradymite crystal structure (space group R-3m) whose alloys have been extensively studied due to their promising operation as thermoelectric materials in the temperature range between 300 and 500 K. In fact, Bi_2Te_3 is one of the best thermoelectric materials operating at ambient conditions [1–4].

The layered tetradymite crystal structure of Bi_2Te_3 is formed by monoatomic sublayers of Te and Bi in hexagonal arrangement (see Fig. 1a). These sublayers are piled up along the *c*-axis forming a quintuple layer (Te–Bi–Te–Bi–Te) in a sandwich style. Finally, quintuple layers pile up along the *c* axis to form the complete structure. Inside the quintuple layer bonds are of ionic-covalent type, while Te–Te bonds between adjacent quintuple layers are mainly of van der Waals type with some contribution of long range Coulomb forces [5].

First high-pressure studies in these materials were performed more than 40 years ago. Most of them were electrical measurements performed with the aim to investigate the effect of pressure on the electrical conductivity and try to evaluate from them the pressure dependence of the bandgap, the pressure-temperature phase diagram, or the appearance of superconductivity [5–16]. Further high-pressure studies in these materials were performed in order to study and improve their thermoelectric properties [17–22]. In this context, a special emphasis in the search for better thermoelectric materials was done in the last 15 years using this family of semiconductors [23–35].

However, a large number of high-pressure studies in these materials have been performed in the recent years after the prediction and discovery that these semiconductors behave as 3D topological insulators [36–38].

3D topological insulators constitute a new class of materials which behave as insulators in the bulk but conduct electrical current in the surface [36, 39, 40]. They are band insulators characterized by the presence of a strong spin-orbit (SO) coupling which results in a valence and conduction band inversion at the Γ point. SO coupling leads to the opening of a narrow bandgap and causes certain topological invariants in the bulk to differ from their values in vacuum. The sudden change of invariants at the bulk-surface interface results in metallic, time-reversal invariant surface states whose properties are useful for applications in spintronics and quantum computation [39, 40].

As pointed out by Yu, high pressure techniques can have a big impact on the study of the recently discovered topological insulators [41]. In the following, we review most of the high-pressure studies on the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family to date.

2 High-pressure experiments

2.1 Earlier experiments The first high-pressure studies in the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family were performed more than 40 years ago. Most of them were electrical measurements performed in order to investigate the effect of pressure on the electrical conductivity to discover new phases, specially superconducting phases [5–16]. Several pressure-induced phase transitions were reported for Bi_2Te_3 and Bi_2Se_3. In particular, a semiconductor-metal phase transition was suggested above 8 and 10 GPa for Bi_2Te_3 and Bi_2Se_3, respectively. Several high-pressure structures were suggested but neither X-ray diffraction (XRD) nor neutron diffraction data were provided to prove them.

In 1981, Sakai et al., reported electrical resistance and XRD measurements in Sb_2Te_3 up to 15 GPa [42]. These authors noted a sharp change in the resistivity around 8 GPa, confirming previous works, and suggested that it was due to a semiconductor-metal structural phase transition. However, they could not identify the structure of the high-pressure metallic phase due to the low quality of the XRD pattern. Sakai et al. noted that while the pressure dependence of a/a_0 was monotonous the pressure dependence of c/c_0 changed considerably above 4 GPa, thus suggesting an increase of the repulsion of the lone pair of electrons of Te atoms above 4 GPa. The weak character of the bonding between the quintuple layers and the increase of the Te–Te repulsion was confirmed also by neutron scattering and Raman scattering measurements under uniaxial and hydrostatic pressure in Bi_2Te_3 [5]. In this context, it must be noted that a similar change of the lattice parameters of the R-3m phase was previously observed above 6.7 GPa in Bi_2Te_3, which was

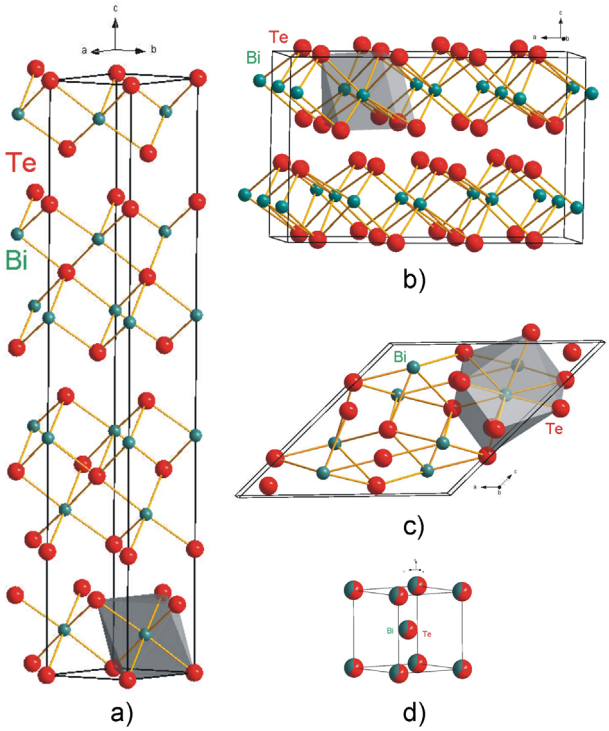

Figure 1 Structures of Bi_2Te_3 at ambient temperature and different pressures: (a) the low-pressure R-3m (α-phase); (b) C2/m (β-phase) above 8 GPa; (c) C2/c (γ-phase) above 14 GPa; (d) Im-3m bcc (δ-phase) above 14.5 GPa.

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attributed to an isostructural phase transition with a different *c*/*a* ratio [13].

An isostructural phase transition at relatively low pressures (about 4 GPa) was suggested by initial high-pressure measurements of Shubnikov-de Haas oscillations in thermoelectric measurements in the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family [19]. This transition was interpreted as a pressure-induced electronic topological transition (ETT) or Lifshitz transition; i.e., a change in the topology of the Fermi energy surface, which can be induced by the change of any parameter that is able to tune the electronic structure, such as compression or alloying [43]. It is important to note that the observation of the ETT in the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family at high pressures is not necessarily related to the fact that they are 3D topological insulators.

An ETT occurs when a band extremum, which is associated to a Van Hove singularity in the electronic density of states (EDOS), crosses the Fermi energy leading to a strong redistribution of the EDOS near the Fermi energy. The redistribution of the EDOS leads to a second-order isostructural phase transition, with no volume discontinuity and no change in Wyckoff positions, but which results in a change in the elastic constants and consequently in a change of the compressibility [44]. An ETT leads to anomalies in mechanical, electrical, and thermodynamic properties, as already commented, but it is also predicted to affect vibrational properties [45, 46].

The occurrence of the ETT in p-type Bi_2Te_3 at pressures between 2 and 5 GPa was confirmed by recent thermoelectric measurements [23, 31, 35], where the pressure at which the ETT occurs was found to depend on the hole concentration. Since the Fermi energy level depends on the carrier concentration the above result is clearly consistent and could explain why different authors observed the anomalies associated to the ETT at pressures differing by 2–3 GPa. Curiously, the presence of the pressure-induced ETT has not been observed in thermoelectric measurements in n-type Bi_2Te_3 and Sb_2Te_3 samples [34]. Consequently, these results suggest that the ETT mainly involves changes in the valence band maxima in these compounds.

In 2001, Polvani et al. conducted thermoelectric measurements in $Sb_{1.5}Bi_{0.5}Te_3$ and found an increase of the thermopower with increasing pressure up to 2 GPa and a decrease above this pressure. This behavior was suggested to be similar to those already observed in metallic alloys as a consequence of the ETT [25]. They commented that no structural change was observed in XRD patterns of $Sb_{1.5}Bi_{0.5}Te_3$ up to 6 GPa but did not show the pressure dependence of XRD patterns for discussion. These authors also measured the Raman-active modes till 3 GPa but reported no clear changes due to the ETT [25].

Thermopower results of Polvani et al. on $Sb_{1.5}Bi_{0.5}Te_3$ led to further experimental and theoretical (by means of *ab initio* calculations) efforts in order to understand the electronic band structure and thermoelectric properties of this family of compounds under pressure [26–35]. In particular, Jacobsen et al. [47] conducted high-pressure XRD measurements in Bi_2Te_3, $BiSbTe_3$, and Sb_2Te_3 up to 20 GPa in 2007. These authors evidenced the ETT around 3 GPa in both Bi_2Te_3 and Sb_2Te_3 (not in $BiSbTe_3$) by a change in the pressure dependence of the c/c_0 lattice parameter. Additionally, they reported the phase transition in the three materials between 7 and 10 GPa and proposed an orthorhombic I222 structure for the post-tetradymite phase despite many XRD peaks could not be attributed to the new structure. The high-pressure I222 phase was different to those previously suggested (without support of XRD measurements) like, among others, the orthorhombic Pbnm phase of Bi_2S_3, Sb_2S_3, and Sb_2Se_3 or the tetragonal $P4_2/nmc$ (anti-Zn_3P_2) phase [15].

In 2008, Ovsyannikov et al. performed high-pressure XRD measurements in $In_{0.1}Bi_{1.9}Te_3$ up to 8 GPa [31]. These authors confirmed the presence of the ETT near 4 GPa by a change in the pressure dependence of the *a* and *c* lattice parameters and showed that the structure of $In_{0.1}Bi_{1.9}Te_3$ between 4 and 8 GPa was also the R-3m phase stable at ambient pressure but with a different *c*/*a* ratio.

2.2 More recent experiments In 2009, Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 were predicted and discovered as 3D topological insulators [36–38]. The same year, Nakayama et al. performed XRD measurements up to 16 GPa in Bi_2Te_3 to confirm previous resistivity data that showed superconducting behavior around 10 GPa [48, 49]. They observed a change in the *c*/*a* ratio around 2 GPa, thus confirming the presence of the ETT in Bi_2Te_3 with no change in space group, and confirmed two pressure-induced phase transitions: above 8 GPa to an unknown structure (phase II or β-Bi_2Te_3) and above 14 GPa to another unknown structure (phase III or γ-Bi_2Te_3). It is noteworthy that the high-pressure phases were not resolved despite the fact that angle-dispersive powder XRD measurements were performed in a synchrotron source with helium as pressure-transmitting medium [49].

High-pressure XRD measurements at ambient temperature in Bi_2Te_3 were extended to 30 GPa by Einaga et al., who showed that Bi_2Te_3 undergoes another phase transition to a disordered body-centered cubic (bcc) Im-3m structure (phase IV or δ-Bi_2Te_3) above 14.5 GPa. In this phase, Bi and Te form an alloy occupying the same Wyckoff sites which coexists with the unknown phase III till 23 GPa and remains as a single phase between 23 and 30 GPa [50]. All phase transitions were found to be reversible and the R-3m phase was recovered on decreasing pressure. However, Buga et al. [51] have recently obtained two metastable phases of Sb_2Te_3 and $Bi_{0.4}Sb_{1.6}Te_3$ at ambient conditions after a high-pressure high-temperature treatment. One of the metastable phases had monoclinic C2/m structure, like α-As_2Te_3, while the other had the orthorhombic Pbnm structure, like Sb_2Se_3. Furthermore, it has been shown that annealing at 400 °C for 3 h leads to the original R-3m structure. This result for the C2/m structure is consistent with the pressure-induced phase transition of α-As_2Te_3 to β-As_2Te_3 with R-3m structure if one considers that the effects of pressure and temperature are almost inverse.

The pressure-induced ETT in Bi_2Te_3 nanocrystals was studied by means of XRD measurements up to 9 GPa by Polian et al. [52] who found a minimum of the *c*/*a* ratio around 2 GPa without change of the R-3m phase. These authors analyzed the pressure dependence of the volume and *a* and *c* lattice parameters by linearizing the Birch–Murnaghan equation of state vs. the Eulerian strain and evidenced a change of the bulk modulus for the volume and for the *c* lattice parameter around the ETT while no change was noted for the *a* lattice parameter. Consequently, these authors suggested that the ETT affected only the bond distances in the plane of the layers but not to the bond distances in the direction perpendicular to the layers. In a similar recent study for Bi_2Se_3, we realized that the analysis of the Birch–Murnaghan equation of state in terms of volume (or lattice parameters) vs. the Eulerian strain is subjected to very large errors both for pressure and for volume and lattice parameters even for very good data obtained using monochromatic X-rays from synchrotron sources. Therefore, it looks like that the use of Eulerian strain is not accurate enough to discuss the occurrence of the pressure-induced ETT. Instead, we noted that the change of the *c*/*a* ratio is characteristic of the ETT and can be traced with reasonable accuracy [53]. The same behavior of the *c*/*a* ratio indeed has been observed in recent XRD measurements of Sb_2Te_3 nanocrystals under pressure where the ETT has been clearly related to the presence of van der Waals forces in this family of compounds [54].

The puzzling results about the high-pressure phases of Bi_2Te_3 at room temperature were recently resolved by Zhu et al. by means of XRD measurements till 52 GPa. Results were analyzed on the basis of *ab initio* calculations following a particle swarm optimization algorithm for crystal structure prediction [55]. These authors confirmed that Bi_2Te_3 undergo a phase transition above 8 GPa from the layered R-3m (α-Bi_2Te_3) phase, where Bi is sixfold-coordinated, to a layered monoclinic C2/m (β-Bi_2Te_3) phase, where Bi is sevenfold-coordinated. Additionally, the C2/m phase transformed near 14 GPa to a monoclinic C2/c (γ-Bi_2Te_3) phase, where Bi is eightfold-coordinated, and above 14.4 GPa to a disordered bcc Im-3m phase, where Bi coordination is between 9 and 10. This last result was in good agreement with previous results of Einaga et al. [50]. Figure 1 shows the high-pressure phases of Bi_2Te_3 at room temperature till 52 GPa. All these phase transitions in Bi_2Te_3 have been recently confirmed by Zhang et al. [56].

After the clarifying work of Zhu et al. on high-pressure phases of Bi_2Te_3, XRD measurements were reported by Zhao et al. in Sb_2Te_3 at room temperature up to 40 GPa [57]. These authors confirmed that in Sb_2Te_3 the R-3m phase undergoes a phase transition to the monoclinic C2/m phase above 9 GPa. However, they proposed that, unlike Bi_2Te_3, the C2/m phase undergoes a phase transition to another C2/m phase above 15 GPa, where Sb and Te atoms are already disordered. Curiously, the C2/m phase of Sb_2Te_3 was observed to undergo a phase transition above 20 GPa to the disordered bcc Im-3m phase; i.e., the same disordered phase as in Bi_2Te_3. These results posed a question regarding whether the high-pressure phases of the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family are the same or not. The question has been almost resolved thanks to two recent works. The phase transition from C2/m to C2/c was recently confirmed in Sb_2Te_3 nanocrystals by XRD measurements up to 20 GPa [54]. Furthermore, the phase transitions to the C2/m, then to the C2/c, and finally to the Im-3m structures have been found in bulk Sb_2Te_3 by XRD up to 52.7 GPa [58]. Therefore, it seems that all three compounds may have the same high-pressure phases. However, XRD measurements in Bi_2Se_3 have been only performed till 20 GPa and show only the R-3m to C2/m phase transition [53, 59]. New high-pressure XRD measurements in Bi_2Se_3 at least till 30 GPa are needed to finally solve the question.

Additional information to discuss the nature of the ETT of the R-3m phase and to resolve the high-pressure phases of this family of materials at room temperature comes from recent high-pressure Raman scattering measurements. Early high-pressure Raman scattering measurements were performed up to a few GPa but that did not allow to discuss neither the ETT nor the high-pressure phases [5, 25]; however, these phenomena have been recently studied by means of high-pressure Raman measurements in Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 [53, 54, 60–62]. These studies show that the ETT is evidenced in the three compounds by a change of the pressure coefficients of both Raman mode frequencies and linewidths (see Fig. 2). Furthermore, on the basis of the eigenvectors of both types of modes (A_g modes correspond to atoms vibrating along the *c*-axis and E_g modes correspond to atoms vibrating in the plane perpendicular to the *c*-axis) it was concluded that the ETT affects both the pressure dependence of the *a* and *c* lattice parameters. Therefore, Raman scattering measurements have proved to be more sensitive than XRD measurements to detect the local changes produced by the ETT.

A curious feature is the large linewidth of most Raman modes at ambient pressure, specially the highest-frequency A_g^2 mode. The reason for the large linewidth is currently not known. It has been speculated that a strong electron-phonon coupling, like that causing phonon damping of LO modes in zincblende and wurtzite-like semiconductors, could be responsible for the large linewidth of the A_g^2 mode. It has also been suggested that a strong phonon-phonon coupling, leading to the decay of first-order phonons into sum or difference of other phonons, could be responsible for the large linewidth of the lowest-frequency modes.

As regards the discussion of the nature of the high-pressure phases of Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3, high-pressure Raman scattering measurements give support to the high-pressure phases found by Zhu et al. Raman-active modes of the C2/m phase can be clearly followed [53, 54, 60–62]. However, the analysis of the C2/c phase is more difficult due to the decrease of the intensity and the broadening of the Raman modes. In any case, the Raman spectrum of phase III shows more than nine modes. This is compatible with the 15 Raman-active modes of the C2/c phase but not with that of

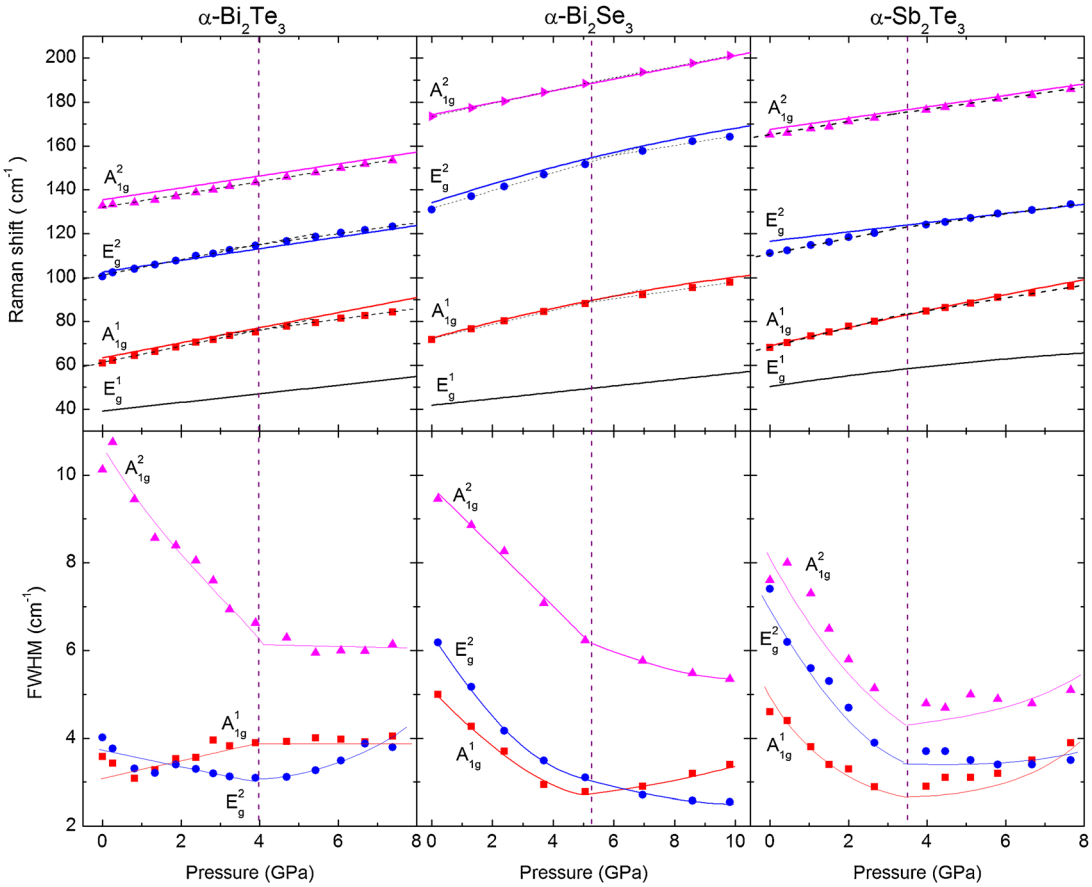

Figure 2 Pressure dependence of the Raman frequencies and linewidths (FWHM) in the α-phase of Bi_2Te_3, Bi_2Se_3, and Sb_2Te_3. The vertical dashed line is an estimation of the pressure at which the ETT occurs in each material.

the disordered C2/m phase proposed by Zhao et al. which should exhibit only three Raman-active modes ($2A_g + B_g$). Finally, the nature of the disordered bcc Im-3m phase cannot be resolved by Raman spectroscopy because this phase is predicted to be Raman inactive by symmetry considerations. In this context, the disappearance of the Raman signal above 20, 25, and 26 GPa for Bi_2Te_3, Sb_2Te_3, and Bi_2Se_3, respectively [53, 60, 61], is a clear indication that at least this high-pressure phase seems to be Raman-inactive like the Im-3m phase. In summary, the results of Raman scattering measurements point to common high-pressure phases for the three compounds of this family.

High-pressure optical measurements are important for the understanding of the pressure dependence of the electronic structure of these narrow bandgap materials and how it affects their electrical and thermoelectrical properties. In this sense, initial estimations of the decrease of the bandgap in Bi_2Te_3 were obtained from electrical measurements [6]. The decrease of the indirect bandgap in Bi_2Te_3 has been recently confirmed by transmittance and reflectivity measurements in the mid-infrared region up to 6 GPa [60]. Above this pressure a free carrier absorption tail appears in the far-infrared region and overlaps with the bandgap absorption preventing its measurement. On the other hand, recent measurements in the mid-infrared region have shown that the optical gap of Bi_2Se_3 increases with increasing pressure [63]. This result is in good agreement with *ab initio* calculations which show that the direct allowed transition at the Γ point in Bi_2Se_3 increases up to 9 GPa, i.e., after the ETT, but still preserves the band inversion at the origin of its 3D topological insulator character. Preservation of topological non-triviality of the electronic structure has also been shown for Bi_2Te_3 in recent *ab initio* calculations [64]. In contrast, there are no mid-infrared measurements of the optical gap in Sb_2Te_3. A decrease of the indirect bandgap in Sb_2Te_3, as in Bi_2Te_3, has been recently predicted by *ab initio* calculations [65]. Unfortunately, this material is usually grown with a very high concentration of free carriers, thus the intense free carrier absorption tail overlaps with the bandgap absorption thus making optical transmission measurements impracticable.

An interesting aspect of this family of semiconductors that is receiving increasing attention is the observation of pressure-induced superconductivity. Between 2010 and 2012, several papers have reported pressure-induced superconductivity in Bi_2Te_3 [56, 64, 66–68]. Electrical measurements of Einaga et al. noted the ETT around 2 GPa in Bi_2Te_3 and observed superconductivity above 9 GPa with a different

behavior of superconductivity above 11 GPa [66]. They attributed superconductivity above 9 GPa to phase II of Bi_2Te_3 and the different behavior above 11 GPa perhaps due to the mixture with phase III. On the other hand, J.L. Zhang et al. reported superconductivity in p-type Bi_2Te_3 ($p \sim 10^{18}$ cm^{-3}) between 3 and 6 GPa [64, 67]. As already commented, their *ab initio* band structure calculations indicate that the R-3m structure at pressures above the ETT maintains the topologically non-trivial electronic structure present at ambient pressure. Consequently, they suggested that Bi_2Te_3 could be a 3D topological insulator and also a pressure-induced topological superconductor. C. Zhang et al. reported pressure-induced superconductivity in Bi_2Te_3 in the high-pressure phases up to 22 GPa [68] and found that the superconductivity of the R-3m phase has bulk properties and it is not related to dislocations caused by pressure. They also noted an increase of the superconducting transition temperature from 3 till 10 K between 8 and 14 GPa (where phase II occurs). All these results have been recently confirmed by S.J. Zhang et al. [56], who have shown the topological nature of superconductivity in the R-3m phase but not in the high pressure phases.

Finally, we have to mention that for the implementation of technological devices with 3D topological insulators one of the most important goals is the control of the 2D electrical conduction in the surface of these materials. For this purpose, Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 should exhibit a good bulk insulating character. However, since this family of 3D topological insulators have a rather small bandgap between 0.15 and 0.3 eV, most of the as-grown samples have rather high bulk conductivity due to a high concentration of free 3D carriers caused by defects and/or impurities. The bulk contribution masks the conductivity of 2D carriers even in the lowest carrier density samples [69, 70].

Recent transport measurements performed in Bi_2Se_3 by Segura et al. [63] up to 5 GPa have shown that compression can help in reducing the 3D charge density and enhancing the relative contribution of 2D carriers to conductivity. Their results indicate that the Hall electron concentration and mobility depend on sample thickness, thus evidencing the coexistence of 3D electron transport in the bulk and 2D electron transport in the surface of the sample. A decrease of the 3D electron concentration on increasing pressure was found, with the electron concentration of all samples at 5 GPa being two orders of magnitude below the initial electron concentration at ambient pressure. It is proposed that 3D electrons are trapped by a shallow-to-deep transformation of native donors, as a consequence of a band reordering in the conduction band. This model is supported by the decrease of the direct bandgap at the Γ–U direction of the Brillouin zone predicted by electronic structure calculations. However, the analysis of the transport properties at 5 GPa, where 2D electron transport dominates over 3D electron transport, suggest that 2D electrons have much higher Hall areal concentration and much small mobility than those expected for the Dirac cone 2D states in 3D topological insulators. Consequently, these authors considered that non-intrinsic 2D electrons, for example caused by surface oxidation, must be also present in the samples. These extra 2D electrons do not have topological nature and would also mask the topologically protected 2D states. A similar effect of increase of the resistivity on increasing pressure in Bi_2Se_3 till 8 GPa has been reported by Hamlin et al. suggesting that pressure can help in suppressing bulk conductivity in order to unmask the conductivity of surface states [59]. These authors also reported unusual magnetoresistance measurements in the R-3m phase of Bi_2Se_3 not presently understood. More Hall-effect and magnetoresistance measurements at high pressures and low temperatures are needed to determine the transport parameters of the different types of carriers contributing to charge transport in these semiconductors. These measurements will help to devise strategies for the control of 2D charge carriers aiming at the implementation of 3D topological insulators in practical applications.

3 Conclusions High-pressure studies of 3D topological insulators of the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family are a hot topic in the last 4 years despite the first studies were undertaken more than 40 years ago.

High-pressure measurements of XRD, Raman, resistivity, and thermopower have revealed the presence of a pressure-induced electronic topological transition in these compounds at low pressures that seems to be driven by the change of the van der Waals forces in this family of layered materials. The ETT leads to considerable changes and anomalies in the mechanical, vibrational, electrical, and thermodynamic properties. In fact, the results of high-pressure measurements indicate that the ETT can be considered as a second-order isostructural phase transition.

Recent high-pressure XRD measurements with the help of the most advanced *ab initio* calculations have allowed us to resolve the puzzling XRD patterns of Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 at pressures above 7 GPa. These studies have revealed that these compounds seem to undergo the same pressure-induced phase transitions (R-3m → C2/m → C2/c → Im-3m) as already confirmed by recent high-pressure Raman scattering measurements. Only high-pressure XRD measurements of Bi_2Se_3 above 20 GPa are still lacking to check the nature of the C2/c and Im-3m phases suggested by Raman scattering measurements till 30 GPa. The knowledge of the structure of these materials at different pressures is crucial to understand the physical properties of these compounds. Curiously, many of the phases observed at different pressures in Bi_2Te_3 have been observed also in Bi and in Bi_4Te_3 with similar trends of superconducting behavior [71]. These results suggest a universal behavior for all compounds of the $(Bi_2)_m(Bi_2Te_3)_n$ family that it is worth to be explored.

Recent high-pressure optical measurements in the mid-infrared have allowed estimate the pressure dependence of the optical gap in Bi_2Se_3 and Bi_2Te_3; however, more insulating Sb_2Te_3 samples must be grown to perform these measurements in this material. The pressure dependence of the optical gap measured in these compounds is in very good

agreement with the evolution of the electronic band structure under pressure shown by *ab initio* calculations.

High-pressure thermopower measurements have revealed a different behavior in these semiconductors depending on the type of conductivity and carrier concentration. More comprehensive studies are needed to understand if the thermoelectric properties of these compounds can be improved by application of pressure. On the other hand, high-pressure electrical measurements at low temperatures have shown the occurrence of superconductivity in p-type Bi_2Te_3 not only in the low-pressure R-3m phase (above the pressure at which the ETT occurs) but also in the high-pressure phases. The topological nature of pressure-induced superconductivity in the low-pressure R-3m phase has been suggested by *ab initio* calculations. However, high-pressure electrical measurements in Bi_2Se_3 and Sb_2Te_3 at low temperatures would be desirable to prove the topological nature of the superconductivity in the whole family.

Finally, we have to mention that several high-pressure transport measurements have been conducted to prove the topologically protected surface states. Unfortunately, these compounds show a high 3D carrier concentration which masks the 2D carriers. High pressures have proved useful in trapping 3D carriers in Bi_2Se_3 in order to help unmask 2D carriers; however, further high-pressure experiments at low temperatures, with more insulating samples, and with samples free from surface defects are needed to evidence the effects of 2D carriers.

In summary, high-pressure measurements in topological insulators of the Bi_2Se_3, Bi_2Te_3, and Sb_2Te_3 family have allowed us to begin to understand many interesting properties of these compounds. However, many high-pressure studies are still needed to get a full picture of the behavior of these materials with the objective to turn 3D topological insulators into materials for amazing technological applications.

Acknowledgements This study was supported by the Spanish government and EU-FEDER under Grants: MAT2008-06873-C02-02, TEC2011-28076-C02-02, MAT2010-21270-C04-01/03/04, and by MALTA Consolider Ingenio 2010 project (CSD2007-00045). Due acknowledgement is also given to Generalitat Valenciana through projects Prometeo GV2011/035 and ISIC/2012/008. We are also indebted to the Vicerrectorado de Investigación y Desarrollo of the Universitat Politècnica de València (UPV2011-0914 PAID-05-11 and UPV2011-0966 PAID-06-11). E.P-G., A.M., and P.R-H. acknowledge computing time provided by Red Española de Supercomputación (RES) and MALTA-Cluster.

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