ESRF	**Experiment title:** Structure and high pressure polymorphism in the topological insulator system of tetradymite Bi-Te-Se compounds	**Experiment number**: CH 3038
Beamline: ID27	**Date of experiment**: from: 08/06/2013 to: 11/06/2013	**Date of report**: 01/09/2013
Shifts: 9	**Local contact(s)**: Paraskevas Parisiadis	*Received at ESRF:*

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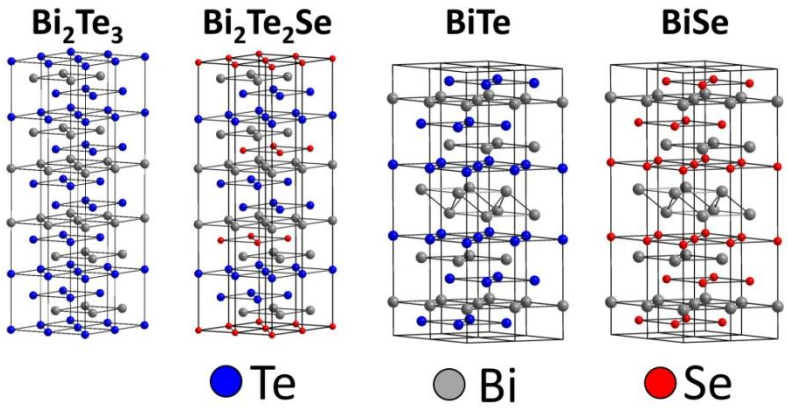
Report:

We have performed high pressure crystallograpic studies of three tetradymite compounds $Bi_2Te_{3-x}Se_x$ (x = 0, 1, and 2.5) and two additional structures, BiTe and BiSe. It is known that Bi_2Te_3 (x = 0) undergoes three phase transitions when the pressure is increased to 25 GPa. At the highest pressures Bi_2Te_3 is known to form a a cubic crystalline alloy, where Bi and Te is completely randomly distributed, but the structures of the intermediate HP phases were only recently claimed to be solved [1].

In the present beamtime we reinvestigated the pressure behavior of Bi_2Te_3 to confirm the reported structure solutions and to determine the compressibility of each phase. Furtermore, Bi_2Te_3 acts as a reference system for the primary system studied during the beamtime, namely Bi_2Te_2Se.

Bi_2Te_2Se is currently the best known topological insulator and there is a great interest in studying its properties under pressure [1-4]. In the fully ordered state the 3*a* atomic site is fully occupied by Se, but depending on the sample preparation, the site displays varying degrees of mixing of Se and Te. Thus, for this beamtime we prepared two samples of a Bi_2Te_2Se: 1) a fine powder of a highly ordered Bi_2Te_2Se single crystal and 2) a disordered version prepared by quenching molten Bi_2Te_2Se in a quartz tube into water, which produces a random Te/Se occupation of the 3*a* site.



In addition to the experiments in the proposal (as outlined above), we also managed to study a sample with the stoichoimetry $Bi_2Te_{0.5}Se_{2.5}$ (i.e., x = 2.5, or alternatively "$Bi_{0.8}Te_{0.2}Se$") and the structurally different BiTe and BiSe compounds (although these were not part of the original proposal). We chose these compositions because the molar ratios of (Bi+Te) : Se are 1:1. Thus, the ordering in the cubic high pressure phase would most likely be due to the very similar ionic size of Bi and Te at these conditions. BiSe and BiTe crystallize in crystal structures with a different stacking of layers which includes double-layers of Bi and in their structures. To our knowledge, neither BiSe nor BiTe have been studied under pressure. At the highest pressure we expected that similar cubic structures form, but that the smaller Se would lead to a higher degree of ordering, while BiTe would be randomly distributed. This behavior was indeed observed. At intermediate pressures new polymorphs formed and we are currently investigating these structures.

Experimetal details & Summary of collected data

We performed measurements on a total of 7 diamond anvil cells (DACs) during 9 shifts. All samples were measured in LeToullec DACs with 250 to 300 μm culet diamonds. Re gaskets (200 μm thickness) were indented to approx. 40 μm thickness and a 150 μm hole was made using laser drilling. Foils of very fine-grained polycrystalline powder was compressed to a thickness of 10-15 μm in a DAC and a disc of 20-40 μm diameter was isolated and mounted in the DAC together with a similar sized piece of polycrystalline Cu (diffraction pressure standard) and 1-2 ruby spheres (spectroscopic standard). We used Neon gas as pressure medium loaded at 1400 bar. Typical starting pressure after loading was 0.2 GPa.

Powder diffraction was collected with 10 second exposures during a small rotation of the cell (typically ± 1 degree) to improve the homogeneity of diffraction rings. The pressure was increased fine steps (0.2 GPa to 3 GPa) to maximum pressures in the range 43 to 61 GPa.

Exp. 1, Bi_2Te_3, (hydrothermal powder[5]), Compression/decompression: 56/7 pressure points. P_{max} = 48 GPa
Exp. 2, Bi_2Te_2Se (zone-melted crystal[6]), Compression/decompression: 79/28 pressure points, P_{max} = 61 GPa
Exp. 3, Bi_2Te_2Se (quenched melt), Compression/decompression: 48/80 pressure points, P_{max} = 50 GPa
Exp. 4, BiTe (melt-quenched), Compression/decompression: 45/90 pressure points, P_{max} = 51 GPa
Exp. 5, Bi_2Te_2Se (single crystals zone melt), crystals were too strained and the experiment was abandoned
Exp. 6, BiSe (quenched melt), Compression/decompression: 51/40 pressure points, P_{max} = 50 GPa
Exp. 7*, $Bi_2Te_{0.5}Se_{2.5}$ (quenched melt), Compression/decompression: 18/12 pressure points, P_{max} = 43 GPa
* We loaded two additional samples in this cell, CsW_2O_6 and RuP.

Preliminary Analysis

Only three months has passed since the beamtime and the data analysis is still ongoing. Here, we show only few examples of the data and preliminary refinements. Figure 1 shows a graphical overview of the collected data on Bi_2Te_3 and zone-melted Bi_2Te_2Se.

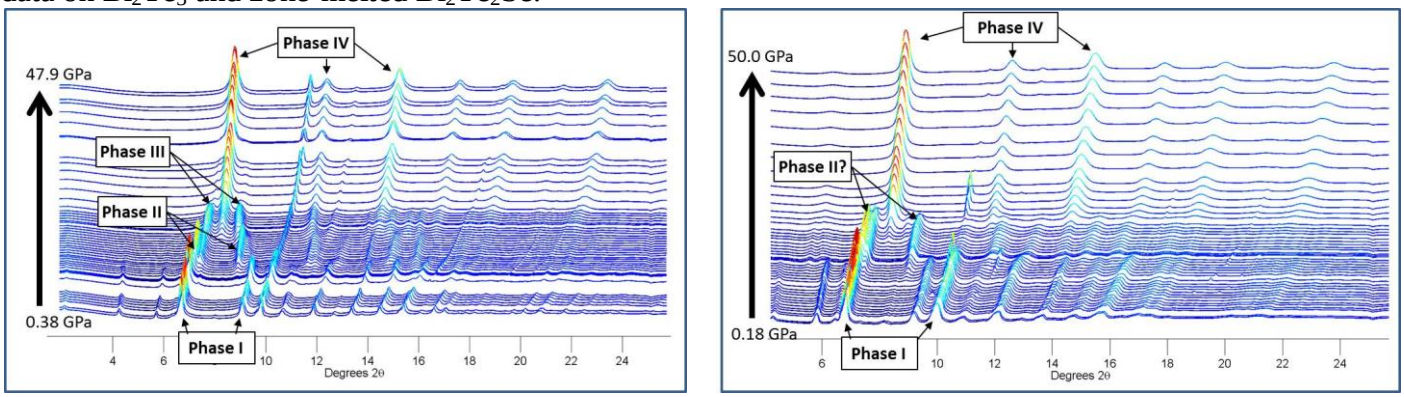


Figure 1. (Left) Bi_2Te_3 upon compression to 47.9 GPa. (Right) Zone-meltet Bi_2Te_2Se upon compression to 50.0 GPa.

The data collected on Bi_2Te_3 confirms three phase transformations although at slightly different pressures than previously reported [1]. We have collected a lot more pressure points than any of the previous study and will be able to characterize the coexistence of phases and volume changes in greater detail.

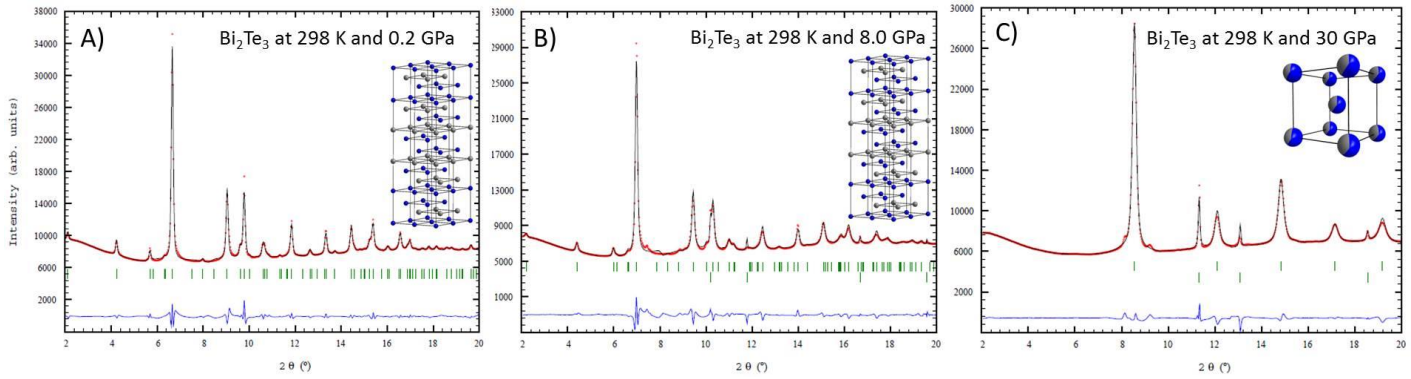


Figure 2. Rietveld refinements of tetradymite Bi_2Te_3 at A) 0.2 GPa, B) 8.0 GPa and C) 30 GPa. (The 2nd row of reflections in B and C is from the crystalline Ne medium)

In analogy to studies of the isostructural binary Bi_2Te_3, we hypothesized that Bi_2Te_2Se forms a substitutional alloy at the highest pressures [1]. This is indeed the case, but as expected the significantly smaller Se leads to partial ordering in the cubic structure. In the data the degree of ordering can be quantified by the intensity of the reflection at $2\theta \approx 6^o$, which is extinct in the random cubic phase of Bi_2T_3 (*Im-3m*). By lowering the space group symmetry to *Pm-3m*, the degree of ordering can be refined.

Scientific output & Impact in the field

Being the best known topological insulator, there is a tremendous interest in improvements of crystal growth in combination with very detailed studies of structure-property relations, which include control of the Se-Te site ordering and defect and carrier concentration. Recently, the first study of the physical properties of Bi_2Te_2Se under pressure showed that even low pressures (0-2.7 GPa) have a strong effect on its properties [3] and in analogy to Bi_2Te_3 superconductivity is expected at higher pressure. Here, however we focus on the structural characterization.

We anticipate that at least two manuscripts will be prepared based on these data. One paper on Bi_2Te_3 and the two different samples of $Bi_2Te_{3-x}Se_x$. The second paper will be about about BiTe and BiSe, and "$Bi_{0.8}Te_{0.2}Se$" (or $Bi_2Te_{0.5}Se_{2.5}$), where the latter acts as a bridge between the two studies. The results will have a broad appeal, particular for the high pressure, materials chemistry and condensed matter physics communities.

Conclusion and Outlook

Since the data analysis is still ongoing, we can only make a preliminary conclusion on the findings already apparent from the data analysis. Our data appears to support the findings for Bi_2Te_3 reported by Zhu [1] and the new system of Bi_2Te_2Se appears to behave in a rather similar way. Intermediate phases with powder patterns resembling those observed for Bi_2Te_3 intermediates are observed. For pressures above approx. 20 GPa a pure cubic phase is formed, in which partial ordering occurs in the Bi_2Te_2Se case. To some extent we anticipated such behavior and had also prepared a sample of BiSe, which with the 1:1 stoichiometry would result in the highest degree of ordering in the cubic cell, although the ambient crystal structures and compositions differ. At intermediate pressures of BiTe and BiSe we found HP polymorphs, which we believe have not been observed before.

The many results obtained as a new user group at ID27 by far exceeds our expectations for this beamtime. The success and high productivity during the beamtime is to a large extend due to very dedicated support from our local contact during the beamtime and in general a very well managed beamline with experienced staff. We wish to continue our studies of related Bi-Te-Se phases and other topological insulators and therefore submit this report simultaneously with a new proposal to continue these studies.

References

[1] L. Zhu, *et al.*, *Substitutional Alloy of Bi and Te at High Pressure*, PRL 106, 145501, 2011.
[2] J. L. Zhang *et al.*, *Pressure-induced superconductivity in topological parent compound Bi_2Te_3*, PNAS, 108 (1), 24-28, 2011.
[3] Y. Luo, *et al.*, *Effect of hydrostatic pressure on transport in the topological insulator Bi_2Te_2Se*, arXiv:1110.1081v1.
[4] Hamlin, *et al.*, *High pressure transport properties of the topological insulator Bi_2Se_3*, J. Phys.: Condens. Matter 24, 035602, 2012. [**5]** J.-L. Mi *et al, Glucose-assisted continuous flow synthesis of Bi_2Te_3 nanoparticles in supercritical/near-critical water*, J. of Supercritical Fluids 67 (2012) 84-88. **[5]** J.-L. Mi *et al, Phase Separation and Bulk p-n Transition in Single Crystals of Bi_2Te_2Se Topological Insulator*, Adv. Mater. 25(6), 889-893, 2013.