

**MS34-03 Ternary metastable rocksalt-type tellurides.** Oliver Oeckler,<sup>a,b</sup> Thorsten Schröder,<sup>b</sup> Tobias Rosenthal,<sup>b</sup> Stefan Schwarzmüller,<sup>b</sup> Christian Petermayer,<sup>b</sup> Daniel Souchay,<sup>b</sup> Sebastian Grott,<sup>b</sup> <sup>a</sup>Leipzig University, IMKM, Scharnhorststr. 20, 04275 Leipzig, Germany, <sup>b</sup>LMU Munich, Department of Chemistry, Butenandtstr. 5-13, 81377 Munich, Germany.  
E-mail: [oliver.oeckler@gmx.de](mailto:oliver.oeckler@gmx.de)

Ternary and multinary cubic tellurides play an important role in phase-change memory devices, where phase transitions in germanium antimony tellurides (GST materials) or silver indium antimony tellurides (AIST materials) are used to store binary codes. Compounds  $(\text{GeTe})_n\text{Sb}_2\text{Te}_3$  exhibit rocksalt-type high-temperature phases (for  $n > 2$ ) with a high degree of disorder (Ge, Sb, vacancies) on the cation positions. These are metastable in thin films at ambient conditions, whereas in quenched bulk material, various nanostructures are obtained by diffusion-controlled vacancy ordering processes. Like other disordered rocksalt-type tellurides such as  $\text{AgSbTe}_2$ , these quenched GST phases are intriguing thermoelectrics with rather high figures of merit.[1]

However, for low values of  $n$ , the rocksalt-type phases are not stable at any temperature or only in a small temperature interval as almost all atoms would have incomplete coordination spheres. Due to the high concentration of vacancies, short-range diffusion is sufficient to reach stable layered phases. By replacing one  $\text{Ge}^{2+}$  by two  $\text{Li}^+$ , the amount of vacancies can be reduced and the rocksalt-type phases become stable even at room temperature. The distribution of Li and Ge has been elucidated by neutron diffraction, which shows that a small percentage of Ge atoms occupy tetrahedral sites. For  $n > 5$ , a rhombohedral distortion is observed at room temperature, which is not present in high-temperature phases. The corresponding phase transition yields twin domains and twin boundaries combined with very pronounced cation disorder that should yield promising thermoelectric properties.

Rocksalt-type phases of AIST materials cannot be obtained by conventional synthesis as In (like in chalcopyrite-type  $\text{AgInTe}_2$ ) prefers tetrahedral coordination. However, at high pressure (e. g. 2.5 GPa), In becomes octahedrally coordinated. In contrast to the high-pressure phase of  $\text{AgInTe}_2$ , [2] most representatives of the high-pressure solid solution series  $\text{Ag}(\text{In,Sb})\text{Te}_2$  can be quenched and are inert at ambient pressure up to 100 - 200 °C. Short-range ordering and partial decomposition yield nanostructured thermoelectrics as evidenced by HRTEM; they exhibit figures of merit up to  $ZT = 0.15$  at room temperature. Comparable nanomaterials have also been obtained by a top-down approach, i. e. by annealing mixtures of small particles.

$\text{In}_3\text{SbTe}_2$  [3] is a high-temperature phase suitable for the generation of heterogeneous nanostructured bulk material as it decomposes to InSb and InTe below 420 °C. HRTEM and single-crystal X-ray studies on quenched rocksalt-type material reveal pronounced short-range order and a tendency to form superstructures. The formation of crystalline rocksalt-type  $\text{In}_3\text{SbTe}_2$  with random Sb/Te disorder from amorphous material could be observed in situ by means of HRTEM.

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**MS34-04 Low melting point of alkali metals under pressure: electronic origin.** Valentina F. Degtyareva, *Institute of Solid State Physics Russian Academy of Sciences, Russia*  
E-mail: [degtyar@issp.ac.ru](mailto:degtyar@issp.ac.ru)

Group I elements – alkali metals Li, Na, K, Rb and Cs – are examples of *simple* metals with  $1s$  electron in the valence band. Under pressure these elements display unusually complex behaviour transforming first from bcc to fcc and then to low symmetry open structures including an incommensurate host-guest structure in Na, K and Rb [1]. Unexpectedly complex form was found for melting curves of alkalis under compression with initial increasing and further decreasing to very low melting point. The lowest point of melting was found to be 300K at 120 GPa for sodium and 200K at 50 GPa for lithium [2,3]. Heavier alkalis have also non-monotonic behaviour of the melting curve on T - P diagrams. To understand complex and low symmetry structures in compressed alkalis a transformation of the energy levels was suggested which involves an overlap between the valence band and outer core electrons [4,5]. Within the model of the Fermi sphere – Brillouin zone interaction the Na-*oP8* structure above 117 GPa can be stabilized assuming that sodium is divalent metal at such compression [5]. Similar electron transfer may occur also in liquid state and even at lower pressure, leading to the increase of stability for the liquid state. The well known example of the only one liquid metal at ambient conditions is mercury – the divalent metal. Experimental diffraction data on liquid alkalis display non-simple behaviour on compression suggesting the essential changes of the electron state in the valence band.

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