

# Materials for Energy Technology

## MS.4.P105

### Real-structure effects of quaternary and quinary germanium antimony telluride thermoelectrics caused by doping with silver and indium

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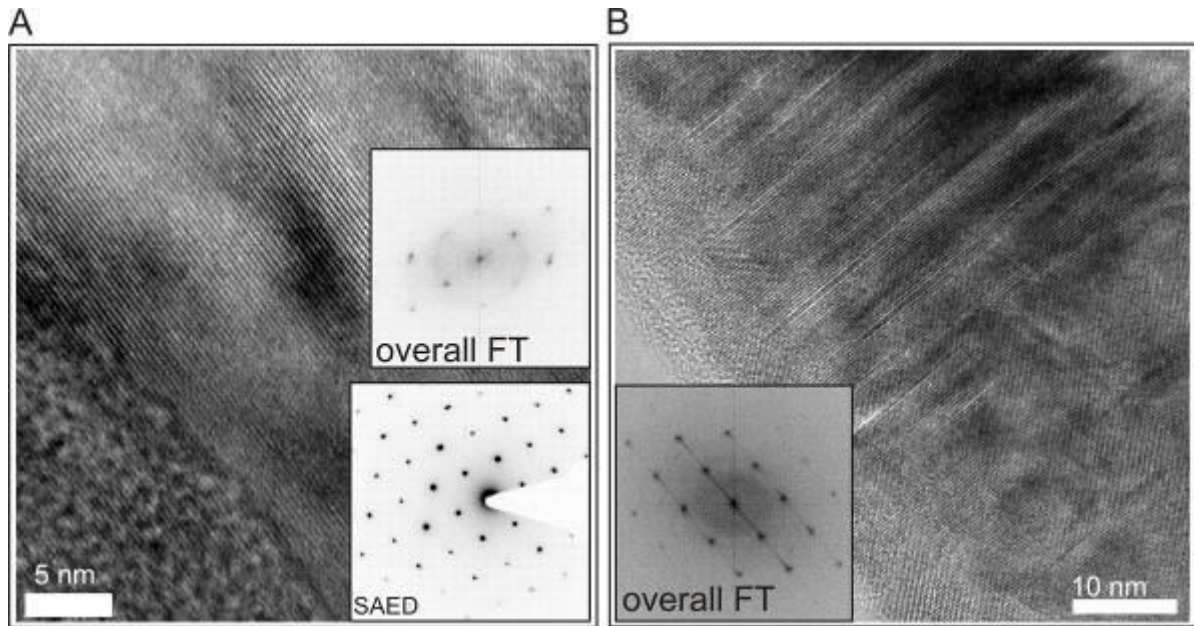
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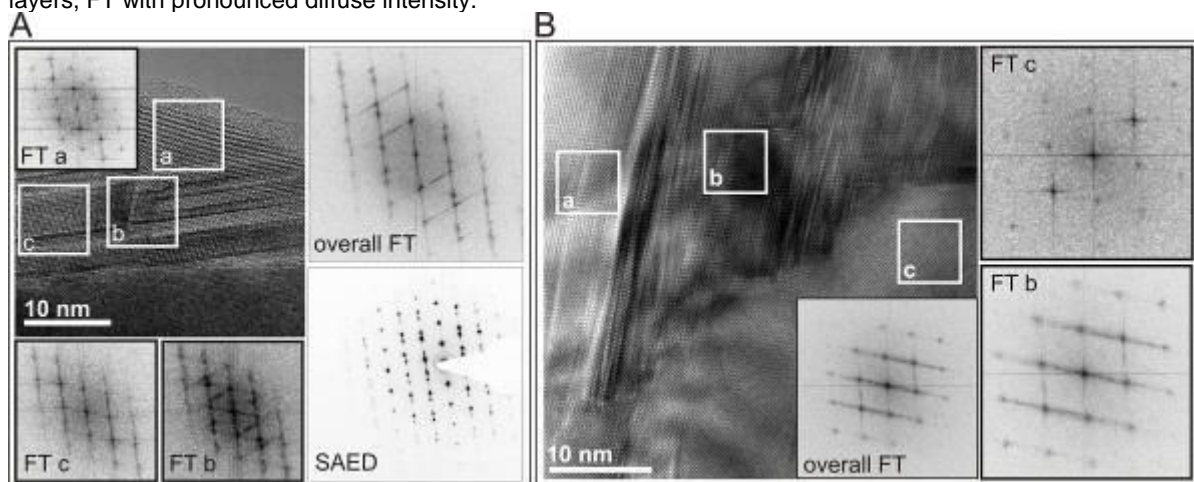
Keywords: real structure, thermoelectrics, tellurides

(GeTe)<sub>n</sub>Sb<sub>2</sub>Te<sub>3</sub> (GST) materials doped with silver or indium exhibit a high concentration of defects, which leads to pronounced real-structure effects and influences the thermoelectric properties. The occurrence of defect layers depends on *n*; their extension and relative orientation have been investigated by electron diffraction and HRTEM. The chemical composition was determined by EDX with spatial resolution. In the rocksalt-type high-temperature phase of GST materials, Te<sup>2-</sup> occupies the anion position, whereas Ge<sup>2+</sup>, Sb<sup>3+</sup> and optionally In<sup>3+</sup> and/or vacancies are randomly disordered on the cation position. Quenching the cubic high-temperature phase leads to metastable pseudo-cubic samples with layer-like defect ordering. Annealing at temperatures below the stability range of the cubic phase yields trigonal layered structures which are stable at ambient conditions and characterized by van der Waals gaps instead of cation defect layers in a fcc anion arrangement [1]. The efficiency of thermoelectrics is quantified by the figure of merit ( $ZT = S^2\sigma T/\kappa$ ), depending on the Seebeck coefficient *S*, the electrical conductivity  $\sigma$ , the total thermal conductivity  $\kappa$  and the temperature *T*. Quenched ingots of (GeTe)<sub>n</sub>Sb<sub>2</sub>Te<sub>3</sub> with *n* = 12, 19 yield *ZT* values up to 1.3 [2]. The substitution of one Ge<sup>2+</sup> cation by two monovalent cations such as Li<sup>+</sup> or Ag<sup>+</sup> can be used to reduce the vacancy concentration and thus to stabilize the quenched modification. The nanostructure of the metastable pseudo-cubic phase can be tuned with a precise concentration of vacancies, simultaneously optimizing *ZT* by decreasing the thermal conductivity. For (GeTe)<sub>11</sub>Li<sub>2</sub>Sb<sub>2</sub>Te<sub>4</sub>, the rocksalt-type phase stable above 250 °C shows a low total thermal conductivity of 1.4 W/Km, yielding *ZT* = 1.0 at 450 °C. The chemical variation of compounds Ge<sub>n-x</sub>Ag<sub>2x</sub>In<sub>y</sub>Sb<sub>1-y</sub>Te<sub>1.5+n</sub> (with 0 ≤ *n* ≤ 9, 0 ≤ *x* ≤ 0.5 and 0 ≤ *y* ≤ 1) involves pronounced structural changes on various length scales, including the exsolution of tellurides like Ag<sub>2</sub>Te or In<sub>2</sub>Te<sub>3</sub>. TEM investigations indicate a randomly disordered structure for quenched Ge<sub>5.5</sub>AgSb<sub>0.5</sub>In<sub>0.5</sub>Te<sub>7.5</sub> with no vacancies and no short-range cation ordering (cf. Fig. 1A). In contrast, quenched Ge<sub>3.25</sub>Ag<sub>0.5</sub>SbTe<sub>5</sub> exhibits pronounced nanostructure with predominantly layer-like ordered vacancies (cf. Fig. 1B). Both X-ray and electron diffraction indicate that the rocksalt-type unit cell is slightly distorted. In the GeTe-type trigonal phase Ge<sub>7</sub>AgIn<sub>0.5</sub>Sb<sub>0.5</sub>Te<sub>9</sub> (*a* = 4.20679(4) Å; *c* = 10.4595(2) Å, *R*3*m*), there are In- and Ag-rich nanodomains in a "matrix" with disordered defect layers (Fig. 2) which occasionally intersect and, in general, are randomly distributed. Since the volume of these nanodomains is very small, the overall structure as obtained by Rietveld refinement on X-ray powder data shows an "average" GeTe-type. The nano-scale inclusions or precipitates, respectively, should affect thermoelectric properties, e. g. by increasing phonon scattering [3]. The presence of twin domains in Ge<sub>7</sub>AgIn<sub>0.5</sub>Sb<sub>0.5</sub>Te<sub>9</sub> as verified by electron diffraction (cf. Fig. 2A) results in real structures with a low thermal conductivity, additional vacancies may further improve it.

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**Figure 1.** A:  $\text{Ge}_{5.5}\text{AgSb}_{0.5}\text{In}_{0.5}\text{Te}_{7.5}$  with average GeTe-type structure with no apparent short-range order (no diffuse intensity in FT and SAED); B:  $\text{Ge}_{3.25}\text{Ag}_{0.5}\text{SbTe}_5$  crystallite ( $\langle 110 \rangle$  zone axis) with irregularly stacked defect layers, FT with pronounced diffuse intensity.



**Figure 2.** A:  $\text{Ge}_7\text{AgIn}_{0.5}\text{Sb}_{0.5}\text{Te}_9$  crystallite (pseudocubic  $\langle 110 \rangle$  zone axis) with differently oriented defect layers, diffuse streaks in the overall FT along  $\langle 111 \rangle$ ; the SAED indicates an obverse-reverse twinning of R-lattice; B: Ge- (a) or In-rich (c) sections show no defect layers (no diffuse streaks in the FT) whereas in region b (containing Ge and In) there is layer-like defect ordering perpendicular to  $\langle 111 \rangle$ .