Germanium telluride GeTe forms nanostructures with twin domains when its NaCl-type high-temperature (HT) phase undergoes a phase transition to the rhombohedral GeTe type upon cooling. GeTe is not exactly stoichiometric; samples with the exact nominal composition contain precipitates of elemental Ge. Both of these nanoscale phenomena are favorable for thermoelectric materials as they may decrease lattice thermal conductivity. This can additionally be achieved by introducing vacancies whose concentration can be adjusted via substitution. This influences phase transition temperatures and the nanostructures formed upon quenching. Substitution effects can also effectively enhance electronic properties.

Germanium antimony tellurides (GeTe)xSb2Te3 [1] (GST materials) have turned out to exhibit promising thermoelectric figures of merit ZT up to 1.5 for high GeTe contents (e.g., x = 12). Crystal structures and typical phase transitions of pseudobinary GBT materials (GeTe)xBi2Te3 [2] are comparable. Both GST and GBT phases exhibit disordered NaCl-type structures at HT; the concentration of cation vacancies is determined by GeTe content x. At room temperature, the stable modifications form layered structures (with integer values of x), in which the vacancies form van der Waals gaps between rocksalt-type slabs whose thickness depends on the composition. Quenching HT phase prevents the formation of long-range ordered van der Waals gaps; instead, TEM shows finite defect layers in a metastable pseudocubic phase with a herringbone-like domain structure.

In chemically homogeneous samples, partial substitution of Ge by Sn leads to higher electrical conductivities both for GST and for GBT. For GST this is beneficial, whereas for GBT it involves a decrease of the maximum ZT values at HT due to the associated higher thermal conductivity. However, optimal combinations of substitution ratio and GeTe content yield significantly increased ZT values at low to intermediate temperatures. These remain almost constant over a wide temperature range, which is important for possible applications. Ge may also be replaced by Mn, which introduces additional magnetism and for complete replacement leads to a range of new layered compounds in the system Mn/Bi/Te (e.g. MnBi6Te10) as evidenced by TEM and electron diffraction. Replacement of Ge by monovalent ions such as Li+ influences the vacancy concentration and leads to compounds with mobile cations (phonon-liquid electron-crystal thermoelectrics). Low vacancy concentrations in combination with Li atoms as “pseudo-vacancies” afford low thermal conductivity without phase transitions caused by vacancy ordering.

Intriguing heterogeneous systems with nanoscale precipitates of a second phase include the combination of cobalt germanides with GST [3] or GeTe itself. These lead to significantly enhanced ZT values and have the advantage that the matrix phase does no incorporate Co so that the process is relatively easy to control and to understand. This is more complicated in the system Cu/Ge/Sb/Te, where Cu may replace Ge similar the way Li does, but in addition forms copper telluride nano-precipitates. Yet, this system offers superior properties, probably because the two phases intergrow endotaxially.


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