MS18-O2 Inhomogeneity and anisotropy of chemical bonding in thermoelectric materials

Yuri Grin[1]

1. Max-Planck-Institut für Chemische Physik fester Stoffe

email: Juri.Grin@cpfs.mpg.de

Two different strategies are employed to enhance the thermoelectric ability of materials in general and intermetallic compounds in particular. The electron-engineering approach deals with the effecting the electronic structure around the Fermi level in order to maximize the thermopower and/or to enhance the charge carrier mobility. The 'phonon engineering' utilizes the phonon glass-electron crystal concept creating centers scattering more strongly phonons than electrons. When the electron-engineering approach in the development of the thermoelectric materials is well established technique, the phonon-engineering part - the interconnection between the low thermal conductivity and crystal structures - is still offering a play yard for new chemical thoughts. Precise information about atomic ordering in the crystal structures of thermoelectrica allows better description and calculation of the electronic structure. The obtaining of this information requires often combination of spectroscopic techniques in addition to the diffraction ones. To get more insight into the thermoelectric behavior, the chemical bonding descriptors were found to be suitable analytical tool. Spatial separation of the regions with different atomic interactions in the crystal is an indicator for enhanced thermoelectric ability. For the compounds with the characteristic structural and bonding features, structural and bonding complexity opens an opportunity to influence more directly the thermal conductivity separating - at least partially – its lattice and electronic parts.

Keywords: Crystal structure; atomic ordering; chemical bonding

MS18-O3 Thermoelectric properties of Cu-doped germanium antimony tellurides

Stefan Schwarzmüller[1], Daniel Souchay[1], Gerald Wagner[1], Oliver Oeckler[1]

1. Leipzig University, IMKM, Scharnhorststr. 20, 04275 Leipzig, Germany.

email: stefan.schwarzmueller@uni-leipzig.de

The high mobility of Cu atoms in thermoelectric materials like $Cu_{2-x}Se$,[1] $Cu_{2-x}S$[2] or Cu_7PSe_6[3] leads to low thermal conductivities due to effective phonon scattering, as described by the phonon-liquid electron-crystal (PLEC) concept.[1] However, these materials often lack high electrical conductivities, so that thermoelectric figures of merit (ZT) do not exceed 1 at temperatures up to 500 °C.

Inspired by thermoelectric chalcogenides with the group 11 element Ag (TAGS-materials),[4,5] this issue was addressed by replacing Ag by Cu in samples with the compositions $Cu_{2-x}Ge_{11+x/2}Sb_2Te_{15}$ ($0 \leq x < 2$). For $1 \leq x$, homogeneous samples were obtained. They show phase transitions between metastable quenched pseudocubic and layered phases as well as NaCl-type high-temperature phases, similar to germanium antimony tellurides without Cu.[6] Higher copper concentrations (e.g. x = 0) lead to a minority phase of Cu_2Te. HRTEM investigations reveal endotactically intergrown Cu_2Te precipitates ranging from 50 to 500 nm in a matrix which corresponding to $x \approx 1$. Temperature-dependent synchrotron powder diffraction (ID11, ESRF Grenoble) enables the detection of such precipitates and their structures, until they dissolve in the matrix at 425 °C during heating and reform at 350 °C during subsequent cooling. Samples with x = 0 show a lattice thermal conductivity of 0.35 W m^{-1} K^{-1} at 500 °C, which is similar to that of Cu_7PSe_6 and thus below the theoretical glassy limit.[3] The thermal conductivity as well as the Seebeck coefficient increase with increasing x. The maximum value for the electrical conductivity is similar for all compositions at around 650 S cm^{-1} but is shifted to lower temperatures with increasing x (500 °C for x = 0; 300 °C for x = 1.66). The materials show high figures of merit (ZT), approaching 2.0 for x = 1.33 at 480 °C.

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