

MS16-02 Exotic unmixing processes in columbite-tapiolite minerals from the Nordic countries. [Serena C. Tarantino](#),^a Michele Zema,^a *^aDept. of Earth and Environmental Sciences, University of Pavia, Italy*
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Oxides with formula AB_2O_6 , where A is a divalent cation (typically Fe^{2+} or Mn^{2+}) and B a pentavalent cation (Nb^{5+} or Ta^{5+}), form a family of minerals including columbite (tri- \bar{a} - PbO_2 structure, orthorhombic $Pbcn$) and tapiolite (Fe,Ta-rich terms, trirutile structure, tetragonal $P4_2/mnm$). Here we present different unmixing processes occurring in such minerals: a columbite sample from Kragero (Norway) and a tapiolite sample from Kimito (Finland).

Cation ordering processes at high temperature in columbite hide a complex scenario which could be unravelled by combining structural information at different length. A novel mechanism of microstructure formation associated to cation ordering under non-equilibrium conditions has been found: a fully coherent and regular array of nanosized domains develops in columbite crystals through separation into two discrete phases which have the same composition but different degrees of long-range cation order. Such pattern of microstructure can be created by high temperature annealing of crystals which grew with a metastable state of cation disorder. Size and distribution of such domains remain more or less constant over a prolonged period of annealing, as revealed by synchrotron X-ray powder diffraction and TEM analyses [1].

High-temperature treatment of tapiolite above 750 °C causes a significant and progressive contraction of unit-cell parameters and volume. Such phenomenon is interpreted on the basis of a progressive oxidation of Fe^{2+} with consequent formation of $FeTaO_4$, associated to unmixing of Ta_2O_5 . $FeTaO_4$ has the rutile structure and crystallizes in the same space group as $FeTa_2O_6$ with similar (but for the tripling of the c -axis in tapiolite due to cation ordering) but slightly shorter lattice parameters. As the transformation proceeds, a significant broadening, but not a clear splitting, of the reflections is observed. Unit-cell parameters values, which after the beginning of the transformation may represent a weighted average of those of the two coexisting phases, were measured also under “cooling-down” conditions. While the diffraction patterns collected down to RT on the recovered crystals are still indexable by a trirutile-type unit-cell, intensity data are not refinable using the tapiolite or the $FeTaO_4$ structural models. Local probes such as $\bar{\epsilon}$ -Raman and XANES spectroscopies have then been used and allowed to distinguish the two phases in the HT-treated tapiolite and to determine their relative amounts.

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MS16-03 Substituted Ge-Sb-Te materials: structure, element distribution and thermoelectric properties. [Simon Welzmler](#),^a Tobias Rosenthal,^b Thorsten Schröder,^b Philipp Urban,^a Felix Fahrnbauer,^b Christian Stiewe,^c Oliver Oeckler,^{a,b} *^aLeipzig University, IMKM, Scharnhorststr. 20, 04275 Leipzig, Germany, ^bLMU Munich, Dept. of Chemistry, Butenandtstr. 5-13, 81377 Munich, ^cDLR, Linder Höhe, 51147 Cologne, Germany*
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Quenched GST compounds, i. e. $(GeTe)_n(Sb_2Te_3)$, exhibit nanostructures that depend on the thermal treatment and the GeTe content n . They are due to a diffusion controlled phase transition from a cubic high-temperature (HT) phase to a trigonal layered phase at ~ 500 °C. Quenching the disordered HT phase, which is characterized by a high concentration of cation vacancies, yields a metastable pseudocubic phase with promising thermoelectric figures of merit $ZT = S^2\sigma T/k$ of up to 1.3 at 450 °C for $n = 12$ or 19. However, most of these nanostructures are not long-term stable due to diffusion processes that set in at ~ 300 °C and lead to the stable trigonal phase [1, 2]. The characteristics of the phase transitions can be influenced by substitution of either anions or cations with e.g. Sn, In, Li, or Se. In case of lacking X-ray scattering contrast, resonant X-ray and neutron diffraction provide unambiguous models.

The nanostructures of $(Ge_{1-x}Sn_xTe)_n(Sb_2Te_3)$ samples are more pronounced than those of GST. Domain structures with intersecting defect layers appear at lower GeTe contents and the stability range of the cubic phase extends to lower temperatures. The element distribution in the layered structure was determined by a joint refinement on 5 datasets, including resonant data at all K edges involved; $\Delta f''$ was calculated from fluorescence spectra. Whereas the Te substructure is ordered, the cation distribution involves modulated site occupancies. The thermal conductivity κ remains constant up to 450 °C, whereas in GST it increases with temperature. In contrast, the electrical conductivity rises analogous to that of GST. Substitution of Te against Se also leads to samples with very pronounced nanostructures, what may enhance the thermoelectric properties in analogy with the favourable effect of Se substitution in $AgSbTe_2$ [3]. Compounds in the series $(GeTe)_n(Sb_{2-x}In_xTe_3)$ show less pronounced nanostructures; however, κ is rather low but increases with the temperature as with GST. The electrical conductivity shows an unusual change at ~ 300 °C where the metastable cubic to trigonal phase transition takes place. Resonant X-ray diffraction has shown how indium is distributed over the cation position.

The cubic HT phase can be stabilized at lower temperatures by filling the vacancies, what be achieved by substituting one Ge atom by two Li atoms. This leads to a solid solution series $Ge_nLi_2Sb_2Te_{4+n}$. For $n < 6$, the compounds form a disordered rocksalt type from RT up to the melting point whereas for $n > 6$, a phase transition from a trigonal - cubic phase occurs at 250 °C. Neutron diffraction shows that in such disordered rocksalt-type structures, a small percentage of the tetrahedral voids are occupied by Ge.

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[2] Rosenthal, T., Schneider, M. N., Stiewe, C., Döblinger, M., Oeckler, O. (2011). *Chem. Mater.* **23**, 4349.
[3] Schmidt, M., Zybala, R., Wojciechowski, K. (2010). *Ceramic Materials* **62**, 465.

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