[MS16 - 03] Combining TEM and synchrotron microdiffraction – a novel lead antimony sulfide telluride, and more examples.

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Electron microscopy and electron diffraction in combination with EDX spectroscopy are excellent tools for discovering new compounds that are minority phases in complex reaction products; this is an intriguing task when metastable phases in quenched samples are important to understand reaction pathways. However, the precise determination of the crystal structure is often not straight-forward by electron crystallography. Therefore, crystallites were investigated by SAED and EDX to ensure that the combination of unit cell and composition proves the novelty. The preselected crystallites have been transferred to ID11's (ESRF, Grenoble) micofocus beamline and localized on TEM grids by fluorescence scans which also made a reliable centering possible. "Normal" single-crystal X-ray datasets were collected that allow us to dis¬cuss the precise crystal structures in detail. Quenching Pb/Sb/S/Te melts affords $Pb_8Sb_8S_{15}Te_5$ ($P4_1$, a = 8.003 Å, c = 15.02 Å, Z = 1, R1 = 0.043) as a minority phase whose complicated Tl_3PbCl_5-type [1] structure has been determined by the method outlined. As the ionic radii of S and Te differ by more than 20%, mixed crystals are exceptional and expected to be metastable at room temperature. The structure is not related with those of typical compounds in the systems Pb/Sb/S (chain structures) or Pb/Sb/Te (layer structures) but characterized by interconnected heterocubane-like entities. The cations, whose coordination spheres are irregular with CN = 8, form a sequence of nets built up from distorted squares and rhombi. Pb/Sb and S/Te are statistically distributed on the cation and anion positions, respectively. Preferred occupancies are reflected in the averaged bond lengths and can be understood by bond valence calculations. Pseu-dosymmetry leads to twinning around [110]. The structure was confirmed by HRTEM image simulations, which highlight the synergism between electron and synchrotron methods. The method was further applied to various layer structures derived from Ge/Sb/Te materials which are interesting because of their thermoelectric properties and to other classes of materials such as oxonitridophosphates.

[1] Keller, H.-L. (1977). *Z. Anorg. Allg. Chem.* **432**, 141.

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