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Synthesis and structural properties of Cu_2MnSnS_4 – a synthetic analogue of stannite

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The structure of stanninte Cu_2FeSnS_4 allows for numerous substitutions including replacement of Fe by Mn. A pure manganese analog of stannite, Cu_2MnSnS_4(CMTS), does not exist in nature but may be acknowledged in photovoltaic technology as an alternative to traditional p-type semiconductors. The crystal structure of this material is similar to the established photovoltaic materials of CGIS ($Cu_2GaInSe_4$) type.

Cu_2MnSnS_4 has been synthesized by modified hydrothermal method developed for kesterite Cu_2ZnSnS_4 by Jiang et al. (2012). The phase was precipitated from aqueous solution (a mixture of $SnCl_2$, $MnCl_2$, $CuCl_2$, and thiocarbamide in presence of ethylene glycol) reacted in autoclave at 180^oC for one and for seven days. The effect of synthesis time on morphology, composition, and structure of the product has been studied in detail with electron microscopy SEM/EDS, powder X-ray diffraction and Raman spectroscopy.

Both syntheses resulted in Cu_2MnSnS_4 precipitating in the form of spherical aggregates of fine crystals. Prolonged synthesis time results in improved purity: traces of rhodochrosite $MnCO_3$ have been detected in 1-day sample. 7-days synthesis resulted in larger crystallite aggregates (up to 1.5 μm) than 1-day product (below 1 μm). Moreover, sharper and narrower diffraction peaks indicate better crystallinity allowing for calculation of unit cell parameters: a = b = 5.51 ?, c = 10.80 ? (orthorhombic system).

This improved method will be applied for synthesis of Cu_2MnSnS_4 - Cu_2FeSnS_4 solid solution series which will allow for better understanding of cationic substitutions in natural stannite. The more crystalline structure resulting from prolonged synthesis is promising in technology and may allow for improvement of photoelectric and photocatalytic properties of this alternative photovoltaic material.

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