Poster Presentation

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AIn_2S_4 (A= Mn-Ni): New synthesis methods and structural characterization

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Ternary chalcogenides with the spinel crystal structure have been widely studied for the last 60 years. These compounds are more covalent and allow different interactions between ions when compared to corresponding oxides while maintaining the versatility of the spinel structure. Particularly, spinels with formula AIn_2S_4 (A= Mn-Ni) are found to be semiconductors with a large band gap (~2.0 eV), showing mainly antiferromagnetic interactions at temperatures below 100 K. These properties are dependent on the distribution of cations between octahedral and tetrahedral sites in the structure and also on the synthesis method. Syntheses of these compounds have been extensively reported, involving long heating periods of mixtures of elements or binary sulfides inside evacuated quartz ampoules, lasting for up to two weeks or longer. We report two new, faster synthesis methods for polycrystalline samples of indium thiospinels avoiding evacuated ampoules. Polycrystalline $FeIn_2S_4$ and $MnIn_2S_4$ samples were synthesized from stoichiometric mixtures of binary sulfides, heating in a constant gas flow of 1% H_2 in Ar at 1073 K for 6 and 24 hours respectively. Polycrystalline samples of $FeIn_2S_4$, $CoIn_2S_4$ and $NiIn_2S_4$ have also been synthesized in a piston-cylinder press, from stoichiometric mixtures of the binary sulfides, at a pressure of 3.5 GPa at 1173 K for 1 hour. From x-ray powder diffraction data all crystal structures were refined by means of Rietveld analysis. Refined cell parameters are in agreement with previous reports. Different degrees of inversion were obtained for each sample. $NiIn_2S_4$ and both $FeIn_2S_4$ samples are in accordance with previous reports, while $MnIn_2S_4$ and $CoIn_2S_4$ differ from reported values [1]. $FeIn_2S_4$ and $MnIn_2S_4$ synthesized in H_2/Ar flux were characterized by Raman spectroscopy to further assess cation distribution. In addition, their thermal stability in air was tested by Thermogravimetric Analysis (TGA).

[1] *W. Schlein, A. Wold, Journal of Solid State Chemistry, 1972, 4, 286-291*

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