Experimental report

31/01/2022

Proposal: EASY-766 **Council:** 4/2020

Title: Cation and anion distribution in the new sulfide chloride AgInSCl2 with cation-deficient spinel structure

Research area: Chemistry

This proposal is a new proposal

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Experimental team:

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Samples: AgInSCl2

Instrument	Requested days	Allocated days	From	To
D2B	8	8	01/03/2021	02/03/2021

Abstract:

A new sulfide chloride with a chemical composition of AgInSCl2 was synthesized using a procedure of ball-milling followed by annealing at elevated temperatures. X-Ray diffraction experiments show the reflection pattern of a spinel type structure, which is supported by Rietveld refinement. The stoichiometry indicates a cation-deficient spinel structure with different possible cation occupations and distributions on the two cation positions 8b and 16c. Rietveld refinement suggests a fully occupied position 16c and an underoccupied position 8b. Due to identical electron configurations neither the cations Ag+ and In3+ can be distinguished with X-Ray diffraction experiments, nor the anions S2¿ and Cl¿. Neutron scattering experiments are therefore necessary to unravel not only the distribution of silver and indium on the cation positions, but also the distribution of sulfide and chloride on the anion position 32e. In addition to the proposed experiment, quantum-chemical calculations in cooperation with the group of Thomas Bredow (Bonn) are planned.

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A new compound with the formula $AgInSCl_2$ was synthesized by a two-step process of mechanochemical synthesis and annealing at 300 °C.

X-ray scattering data indicated that the compound crystallizes in a cation-deficient spinel-type structure in space group $Fd\bar{3}m$. Since both cations as well as both anions exhibit the same electron configuration, they cannot be distinguished by conventional X-ray scattering experiments. However, the distribution of the cations on the two possible cation positions (8*b* and 16*c*) can be examined using neutron diffraction methods.

Simulations of neutron scattering diffractograms showed that different cation distributions on the two possible positions lead to changes in the resulting diffractograms, although the differences are small.

As a result of the sample's sensitivity to air and moisture, poor crystallinity, silver and indium being neutron absorbers, and insufficient sample quantity, the quality of the neutron scattering data is not ideal for Rietveld refinement.

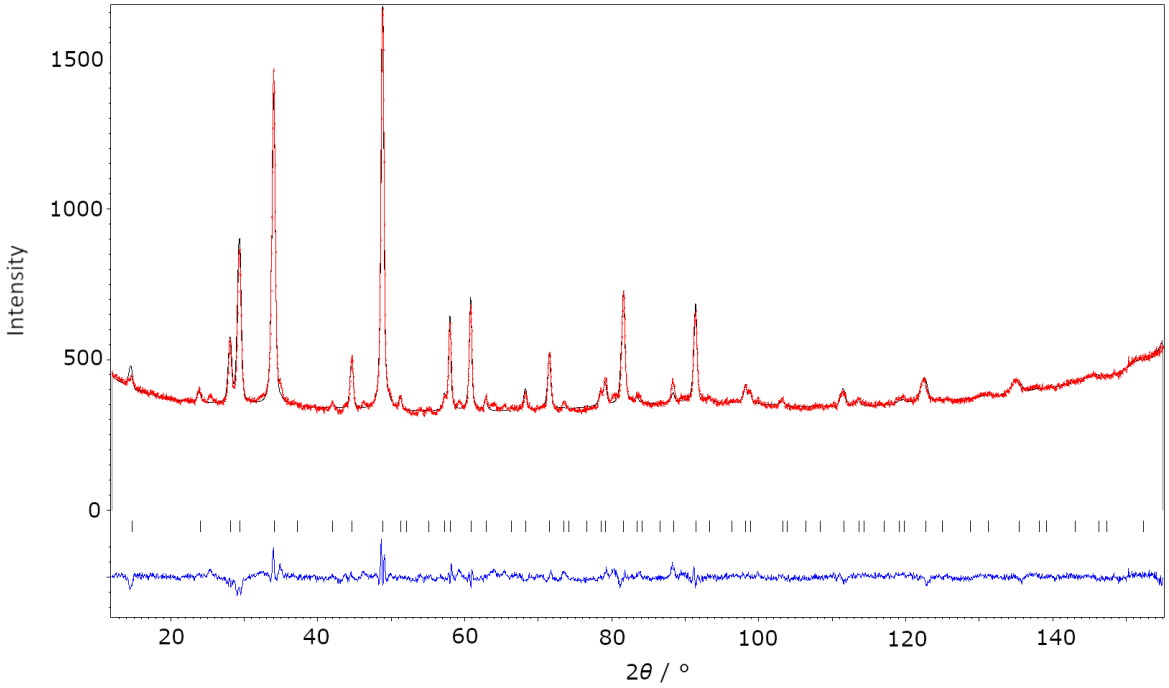

Figure 1: Diffractogram of $AgInSCl_2$ from neutron scattering with the results of the Rietveld refinement (red = observed diffractogram, black = calculated diffractogram, blue = difference plot).

Due to the experimental conditions (low annealing temperature of only 300 °C) the anion distribution was assumed to be statistical. Therefore, the coordinates of sulfide and chloride, as well as the Debye-Waller-factors for both anions were kept identical and the occupation factors were set to their ideal values.

Several possible cation distributions were tried to be refined, but all lead to the same *R*-values. For the determination of ion distribution, the first reflections of a diffractogram are important. In this case, especially the first reflection is problematic: the form of that reflection is not ideal, since it is very broad. In all refinements the first reflection was always poorly fitted. Leaving out the first reflection from refinement did not lead to better *R*-values or changes between the refinements of different cation distributions. Therefore, a cation distribution could not be derived from the presented data.