Experimental report

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Proposal: 5-21-1181 **Council:** 4/2023

Title: Crystal and magnetic structure studies of Ag4MnSb2S6 antiferromagnetic materials

Research area: Materials

This proposal is a new proposal

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Samples: Ag4MnSb2S6
K10Zr2(SO4K2)9

Instrument	Requested days	Allocated days	From	To
D2B	1	1	18/09/2023	19/09/2023
D20	1	0		

Abstract:

The Samsonite phase, with the general composition of Ag4MnSb2S6, which has never been synthesized so far through lab conditions, has been single-phase obtained via two non-conventional synthesis processes: the polyol and the hydrothermal processes. This compound, which exhibits promising thermoelectric properties, has therefore never been accurately studied. Preliminary magnetic characterizations highlighted a transition from paramagnetic to antiferromagnetic at around 7 K. Performing high-resolution neutron diffraction acquisitions at low and room temperature shall assess both the accurate crystal and magnetic structure of the Ag4MnSb2S6 phase.

Experimental Report

Crystal and Magnetic Structure Studies of $Ag_4MnSb_2S_6$ antiferromagnetic materials

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Introduction:

The Samsonite phase, with the general composition of $Ag_4MnSb_2S_6$, has never been synthesized under laboratory conditions. However, we successfully obtained it as a single phase using two non-conventional synthesis methods: the polyol process, which resulted in 100 wt.% of the samsonite phase, and the hydrothermal process, which led to 97.2 wt.% of the targeted phase. As a result, this compound, which exhibits promising thermoelectric properties, has yet to be thoroughly studied. Preliminary magnetic characterizations revealed a transition from paramagnetic to antiferromagnetic behavior at approximately 6 K.

Preliminary Results from In-house Data

Before the ILL experiments, X-ray diffraction measurements were conducted to preliminary assess the sample's purity. These acquisitions were performed using a Bruker D8 diffractometer. Additionally, PPMS measurements were carried out to determine the magnetic temperature transition temperature, which was found to be around 7 K.

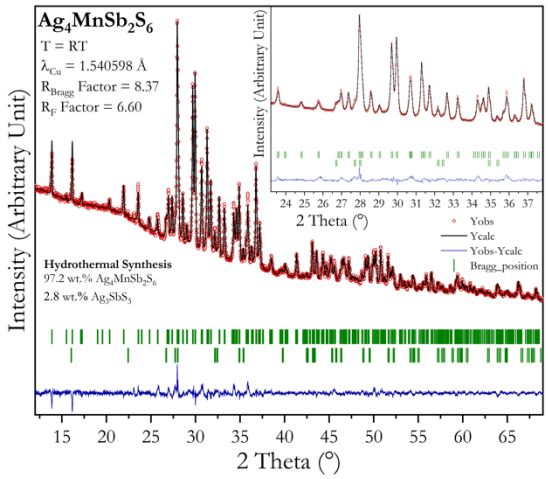

Figure 1: X-ray diffraction pattern of $Ag_4MnSb_2S_6$ synthesized using the hydrothermal process

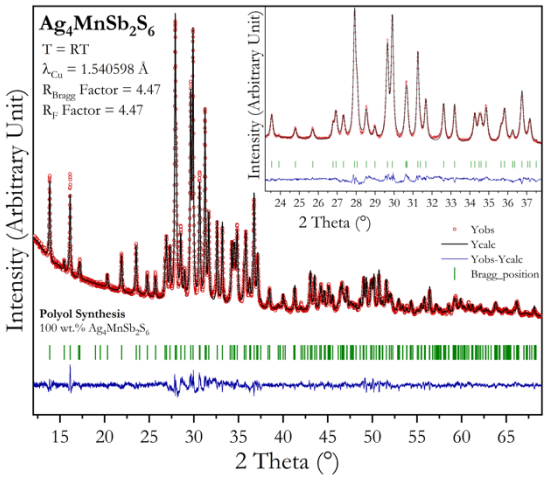

Figure 2: X-ray diffraction pattern of $Ag_4MnSb_2S_6$ synthesized using the polyol process

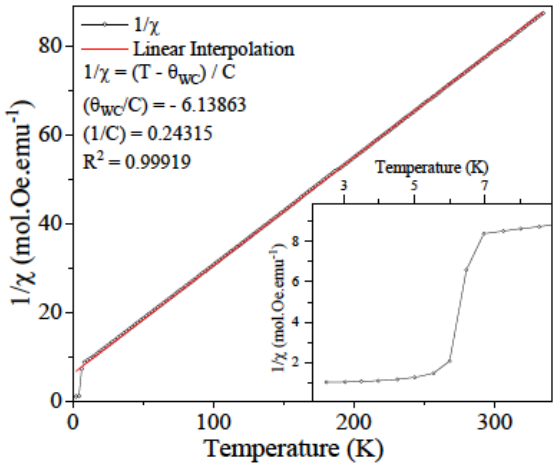

Figure 3: Magnetic susceptibility of the Samsonite phase according to temperature with a constant field of 100 Oe.

Experiments at ILL and Results

Since the Samsonite phase had never been synthesized under laboratory conditions, room-temperature neutron diffraction on D2B was chosen to accurately determine its crystallographic features using a 1.54 Å wavelength. Measurements were conducted at room temperature, 15 K, and at 0.5 K intervals between 15 K and 3.5 K to precisely determine the transition temperature.

Both the hydrothermal and polyol samples were preliminarily measured to quickly evaluate their quality. Both samples showed similar levels of noise in the initial scans. Given the comparable noise levels, we decided to focus on the hydrothermal sample for the extensive acquisition.

Figures 4 and 5 show the neutron diffraction patterns obtained at room temperature and 3.5 K, respectively, for the hydrothermal sample. These patterns were collected over a 12-hour acquisition on D2B.
Despite extensive TG/DSC analyses and thermodiffraction studies, our samples may still contain water. This conclusion arises from the significant discrepancy between laboratory X-ray diffraction data and neutron diffraction results, which were marred by a high level of noise. The noise level was substantial enough to prevent the data from being used to accurately determine the crystallographic parameters of the Samsonite phase. The only plausible explanation for the unusually low intensity observed in the neutron diffraction data is the presence of water in the samples (hydrogen pollution).

It is easy to understand why the compound synthesized through the hydrothermal process contains water molecules, as the process itself uses water as a solvent. However, it is more difficult to explain the presence of water molecules in the polyol-synthesized compound. The explanation may lie in the powder precursors, some of which were hydrated. Furthermore, the flux on the D2B line was not intense enough to provide useful information for both samples especially due to the presence of hydrogen atoms.

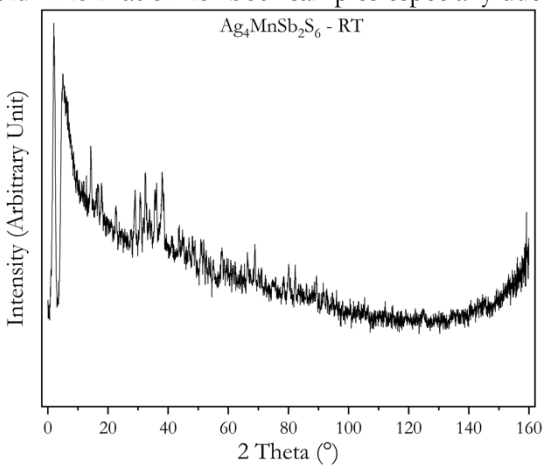

Figure 4: Room temperature neutron diffraction pattern of $Ag_4MnSb_2S_6$ synthesized using the hydrothermal process – D2B, 12h acquisition

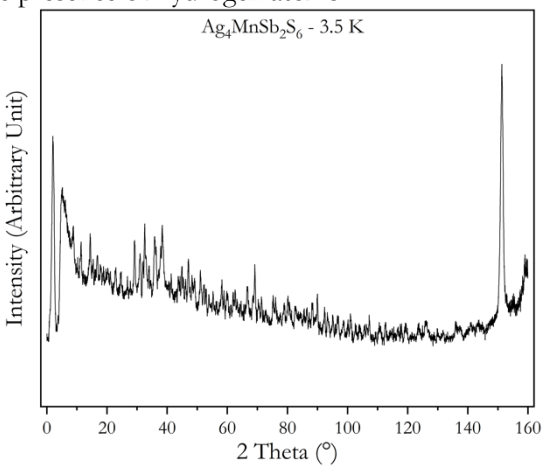

Figure 5: 3.5 K neutron diffraction pattern of $Ag_4MnSb_2S_6$ synthesized using the hydrothermal process – D2B, 12h acquisition

Conclusion:

The Samsonite phase had never been synthesized under laboratory conditions. Our hydrothermal and polyol synthesis protocols successfully yielded compounds of high purity. However, despite the high purity, the samples synthesized by both methods showed significant discrepancies between laboratory X-ray diffraction data and neutron diffraction results, likely due to the presence of water in the samples. The hydrothermal process, which uses water as a solvent, easily accounts for this, while the presence of water in polyol-synthesized samples remains less clear, possibly originating from hydrated precursors.
Further refinement of the synthesis protocols, including the use of anhydrous precursors and careful control of the reflux setup, will be essential to obtain a completely anhydrous Samsonite phase which is essential to accurately determine its crystallographic parameters through neutron diffraction.