ESRF	**Experiment title:** Low temperature structural behaviour of stannite and kesterite	**Experiment number**: MA4234
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Shifts: 9	**Local contact(s)**: Mashikoane Wilson Mogodi	*Received at ESRF:*

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Report:

In the present experiment, four samples of natural specimens and synthetic analogues of members of the stannite-kesterite pseudobinary joins were investigated by means of high quality X-ray Powder Diffraction. The experimental set up included the use of a cryostat, in order to obtain a full structural characterisation in the range of temperature values between 5 and 275 K. XRPD patterns were registered every 5 or 10 K interval, and longer acquisitions, dedicated to extract the pdf function, were operated at 5 and 275 K. The materials were analysed inserted in borosilicate capillary tubes, in contact with the cryogenic gas, i.e. vapours of He (**Fig. 1**).
The median chemical composition of the investigated samples is listed herer below:

Sample	**label**	**origin**	**formula**
#1	1495	natural	$Cu_2Fe_{0.9}Zn_{0.1}SnS_4$
#2	1499	natural	$Cu_2Fe_{0.75}Zn_{0.25}SnS_4$
#3	1496	natural	$Cu_2Fe_{0.5}Zn_{0.5}SnS_4$
#4	kes500	synthetic	Cu_2ZnSnS_4

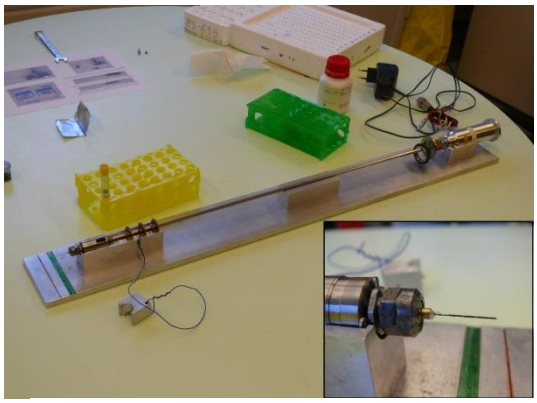

Figure 1- sample holder and capillary tube in the inset

In a previous experiment a further sample, i.e. a synthetic stannite Cu_2FeSnS_4 has been already analysed. The experiments were successful, with a almost complete utilisation of the beamtime.

The preliminary results achieved during this experiment can be included in the long debated scientific question concerning the Fe-Zn replacement in this pèseudobinary join. On one hand, Zn can replace Fe starting from the nominal stannite composition, up to the kesterite one, without necessity of changing the space group.
This mechanism would occur by simple intrsa-site replacement. On the other hand, the replacement of Fe by Zn is not simple, involving two cation sites, with a combined change of metal occupancy. This mechanism produces

a decrease in symmetry, and a change of space group (**Fig. 2**). Obvious consequences in the physical properties (as e.g. band gap and magnetism) and of thermodynamic stability (with the necessity of a miscibility gap) can be devised.

Exemplar results of the XRPD experimental data achieved in this experiment are shown in the **Figure 3**, where the temperature dependence of the position of a Bragg reflection of the 1499 sample is plotted. The graph highlights the continuous shifts towards high 2θ values, and a discontinuity in the T range between 50 and 25 K.

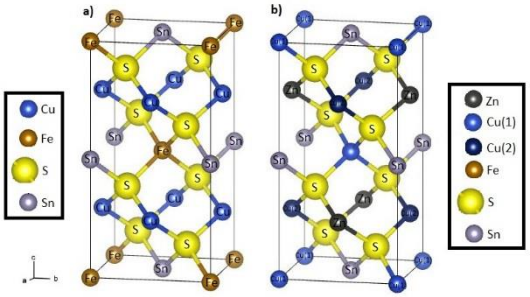

Figure 2 - structural models of stannite (left)

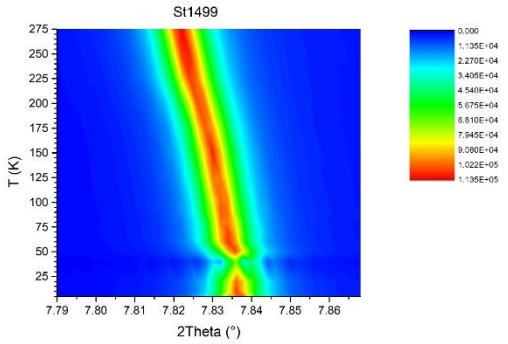

Figure 4 - plot of a reflection fo the 1499 sample vs temperature

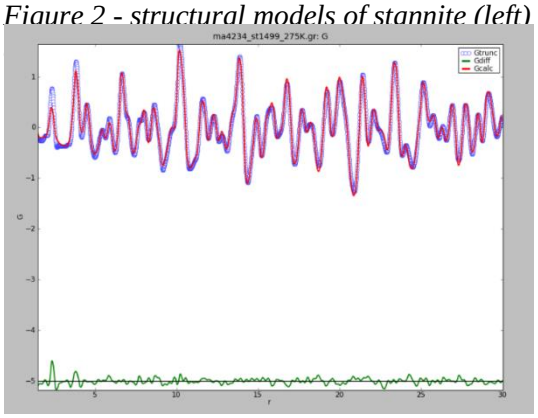

Figure 3 - plot of the best fit of the pair distribution function pf the 1499 sample

In a similar way, **Figure 4** depicts an exemplar fit of the pair distribution function analysis of the 1499 sample, revealing the excellent agreement of the structural model used to fit the experimental data, and the high coherence of the metal distribution with the proposed scheme.
Among the most impressive results, a structural transition occuring at low temperature (well highlighted by the comparison of the experimental temperature dependent cell volume data and their Grüneisen fit), also verified by independent magnetic susceptibility measurements (**Figure 5**)

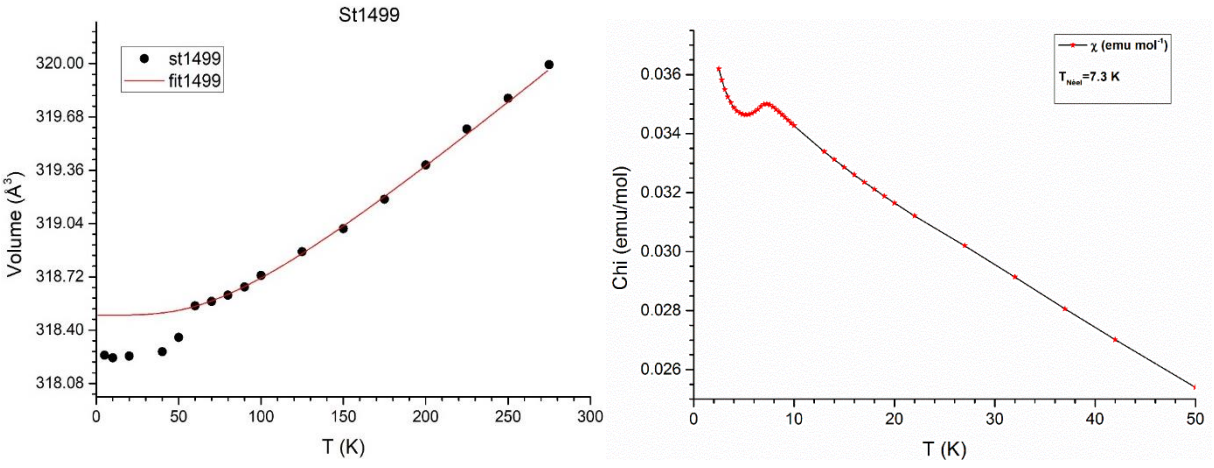

Figura 5 - Grüneisen plot of the 1499 sample (left); magnetic susceptibility versus temeprature plot of the same sample (right)