Experimental report

16/12/2021

Proposal:	**5-24-615**	**Council:**	4/2018

Title: High temperature in situ NPD studyof crystal structure and phase transitions of high thermoelectric performance quaternary sulfides

Research area: Materials

This proposal is a new proposal

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Samples:
$Cu8Fe3Sn2S12$
Cu26V2Sn6S32
Cu22Fe8Ge4S32
Cu2FeSnS4
Cu2FeGeS4
Cu22Fe8Sn4S32
Cu26M2Ge6S32 (M = V, Cr, Mo, Ta, W)

Instrument	Requested days	Allocated days	From	To
D1B	4	2	20/09/2018	22/09/2018

Abstract:

Recent studies have revealed very promissing thermoelectric (TE) properties at medium temperature for complex quaternary Cu based sulfides: colusite Cu26V2Sn6S32 (ZT ~ 0.93@675 K), germanite Cu22Fe8Ge4S32 (ZT ~ 0.17@575 K), stannoidite Cu8+xFe3-xSn2S12 (ZT ~ 0.35@630 K), Cu2ZnSnS4 (ZT ~ 0.35@700 K). These TE materials are structurally related since they are all derivate from the sphalerite ZnS cubic structure (i.e. consists of corner- and edge-sharing MS4 tetrahedra crystal structures). While their structure - TE properties relationships are relatively well understood, their stability at high temperature (HT), an essential knowledge for large scale applications, have never been studied. Following our previous studies performed by HT in situ neutron powder diffraction on ternary copper sulfides Cu5FeS4, Cu12Sb4S13 and Cu4Sn7S16, we started to investigate the phase transitions of the aforementioned quaternary Cu-containing sulfides. In order to determine precisely the crystal structures (complementarity with XRPD data) and phase transitions of these TE materials and to better understand the associated electric properties, we need HT in situ neutron powder diffraction data.

Experimental report on the proposal 5-24-615: **High temperature in situ NPD study of crystal structure and phase transitions of high thermoelectric performance quaternary sulfides**

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1. Introduction

Cu-based sulfides are reported as high-performance *p*-type thermoelectric (TE) materials at intermediate temperature. A non-exhaustive list (see Fig. 7 from ref [1]) includes *p*-type tetrahedrite $Cu_{12-x}Tr_xSb_4S_{13}$ [2,3], colusites $Cu_{26}T_2M_6S_{32}$ [4,5], germanite $Cu_{22}Fe_8Ge_4S_{32}$ [6], bornite Cu_5FeS_4 [7], stannoidite $Cu_{8+x}Fe_{3-x}Sn_2S_{12}$ [8], Cu_2SnS_3 [9], and *n*-type $Cu_4Sn_7S_{16}$ [10], $CuFeS_2$ [11] and $CuFe_2S_3$ [12]. Among these TE materials, germanite $Cu_{22}Fe_8Ge_4S_{32}$ ($P\bar{4}3n$, a = 10.593 Å), and colusites $Cu_{26}Cr_2Ge_6S_{32}$ ($P\bar{4}3n$, a = 10.552 Å) and $Cu_{26}V_2Ge_6S_{32}$ ($P\bar{4}3n$, a = 10.574 Å) are structurally related. Indeed, they are all derivate from the sphalerite ZnS cubic structure ($F\bar{4}3m$, a = 5.41 Å, V = 158 Å^3), *i.e.* corner-sharing MS_4 (M = Cu, Fe, Ge) tetrahedra, with either Fe, Cr or V atoms in interstitial positions [1]. Moreover, in this family of materials, the *p*-type conductivity, carrier concentration and power factor are governed by the Cu^+/Cu^{2+} ratio [1,4,13].

Despite the huge advances in the field of thermoelectric Cu-based sulfides [1-4,13], it remains primordial to determine accurately both crystal structure (cell parameters, atomic coordinates, site occupancy, etc), for the understanding of the structure-properties relationships, and nature of the decomposition phases of these TE materials, for determining their thermal stability for future potential applications. Moreover, the determination of the synthesis conditions to obtain single phase sample can be a long and boring procedure. Due to its high penetration depth and its specific atomic scattering lengths, NPD data can provide complementary information to XRPD data, especially in the characterization of bulk samples or compounds containing lights and/or isoelectronic elements such as germanite $Cu_{22}Fe_8Ge_4S_{32}$.

2. Neutron diffraction results

2.1. Colusites $Cu_{26}Cr_2Ge_6S_{32}$ and $Cu_{26}V_2Ge_6S_{32}$

High-temperature NPD patterns of the high-performance thermoelectric $Cu_{26}Cr_2Ge_6S_{32}$ and $Cu_{26}V_2Ge_6S_{32}$ compounds were recorded on the D1B diffractometer (ILL, Grenoble) from room temperature up to 1000 K. The data analyses shown that $Cu_{26}Cr_2Ge_6S_{32}$ colusite starts to decompose above 830 K into Cu_8GeS_6 and $CuCrS_2$ phases (**Fig. 1(a)**), leading to a Ge enrichment of the colusite phase (*i.e.*, decrease of the Cu/Ge ratio). This initial decomposition step is followed by a second one above 880 K, related to the structural modification from the cubic structure of colusite into the monoclinic Cu_2GeS_3 structure (**Fig. 1(b)**). Above 930 K, the colusite $Cu_{26}Cr_2Ge_6S_{32}$ phase is fully decomposed (**Fig. 1(b)**). Neutron data recorded on the $Cu_{26}V_2Ge_6S_{32}$ colusite reveals that this phase is stable at least up to 1000 K (**Fig. 2**). These results were published in 2020 in the ACS journal *Chemistry of Materials* (https://doi.org/10.1021/acs.chemmater.9b04378).

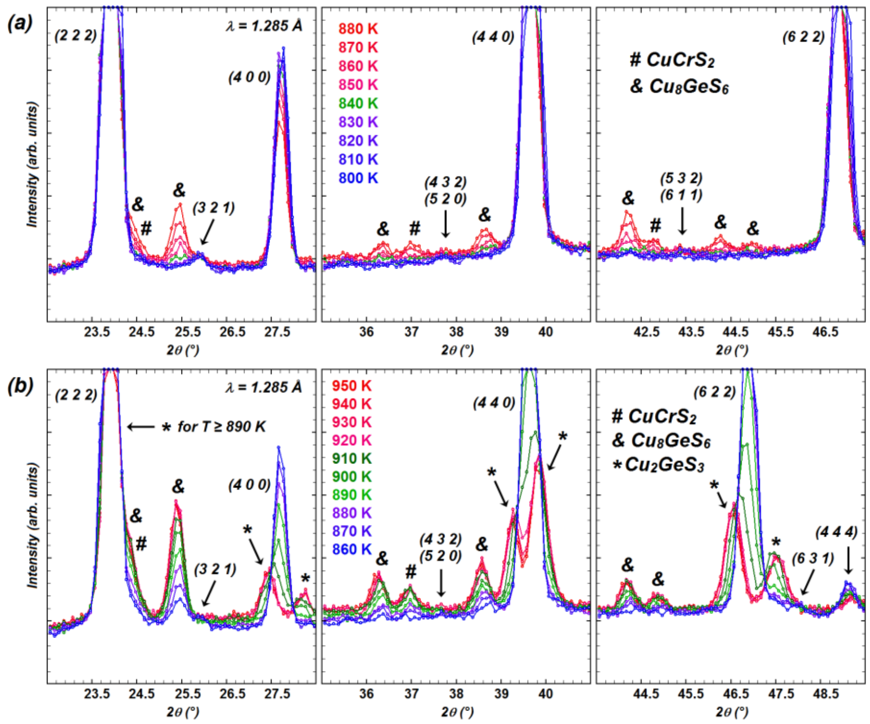

Fig. 1. Thermal evolution of the NPD patterns of the $Cu_{26}Cr_2Ge_6S_{32}$ colusite recorded between (a) 800 and 880 K, and (b) 860 and 950 K (heating rate of 2 K min^{-1}).

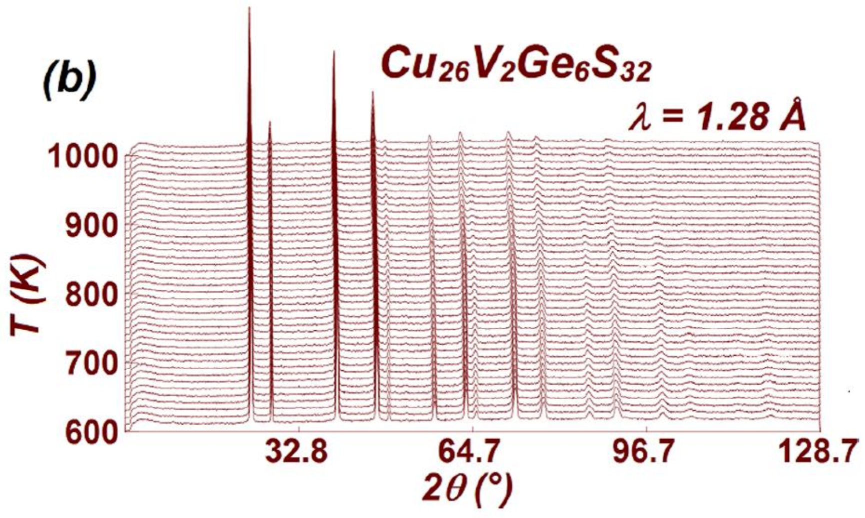

Fig. 2. High-temperature neutron thermogram of $Cu_{26}V_2Ge_6S_{32}$ colusite recorded at the heating rate of 2 K min^{-1}.

2.2. Germanite $Cu_{22}Fe_8Ge_4S_{32}$

A second type of high-temperature NPD experiment was tested during this experience and fully completed few months after during a CRG experience (doi:10.5291/ILLDATA.CRG-2585). It corresponds to the synthesis, from elementary precursors, of a polycrystalline sulfide sample of germanite $Cu_{22}Fe_8Ge_4S_{32}$ by solid−liquid−gas reaction in a sealed silica tube, monitored, for the first time, by in situ time-resolved neutron powder diffraction. These data allowed us to determine all the successive crystallization/decomposition sequences and intermediate products formed during the synthesis of the $Cu_{22}Fe_8Ge_4S_{32}$ germanite (**Fig. 3**). Moreover, the data has revealed that sealed tube synthesis is highly dynamic, with reaction times shorter than expected. Beyond new data on the complex crystal chemistry of germanite $Cu_{22}Fe_8Ge_4S_{32}$, this study demonstrates the compelling benefits of time-resolved in situ NPD in the optimization of the synthesis process for a wide range of complex chalcogenide materials. These results were published in 2020 in *Chemistry of Materials* (https://doi.org/10.1021/acs.chemmater.0c03219) and will be the subject of a scientific highlight in the ILL annual report 2021.

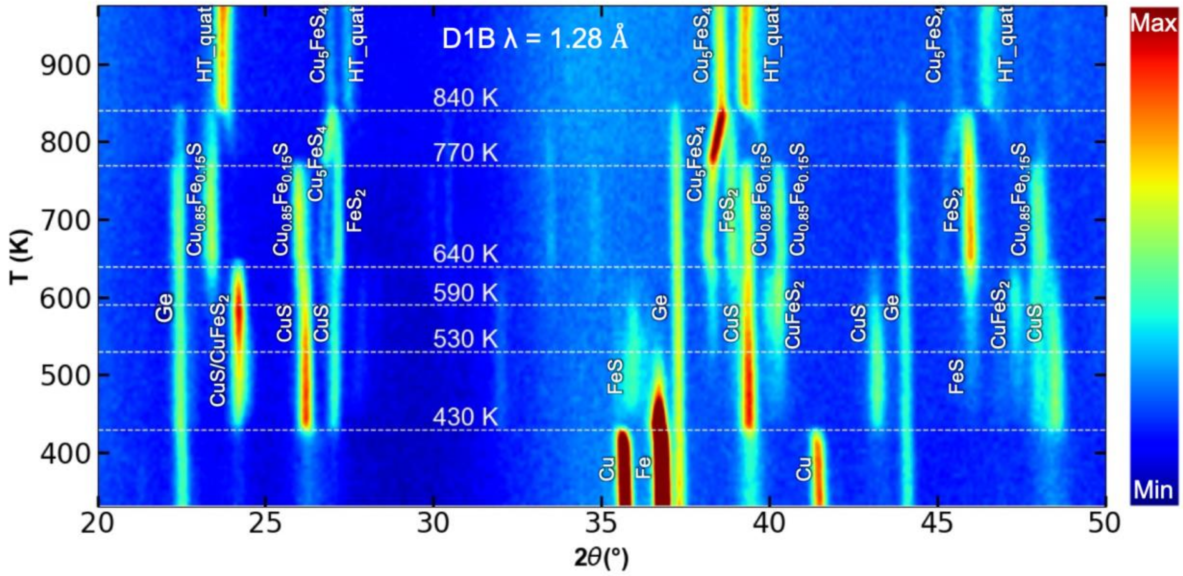

Fig. 3. 2D contour plot showing the NPD patterns of the in situ sealed tube reaction of $Cu_{22}Fe_8Ge_4S_{32}$ germanite from elemental precursors.

3. References

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