Experimental report

16/12/2021

Proposal: **CRG-2585** **Council:** 10/2018

Title: Study of the synthesis conditions of theroelectric Cu-based sulphidesby in situ NPD

Research area:

This proposal is a new proposal

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Samples: CuVSnS
Cu22Fe8Ge4S32
Cu22Fe8Sn4S32
Cu26Cr2Ge6S32
[Mo4S4Cl6]136
CuFeCrGeS

Instrument	Requested days	Allocated days	From	To
D1B	2	2	24/07/2019	26/07/2019

Abstract:

Experimental report on the proposal CRG-2585: **Study of the synthesis conditions of thermoelectric Cu-based sulphides by *in situ* NPD**

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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

Following a preliminary test done during the ILL experience doi:10.5291/ILL-DATA.5-24-615, we have studied, during this CRG experience, 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 (**Fig. 1**). This experience, monitored by *in situ* time-resolved neutron powder diffraction 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. 2**). 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.

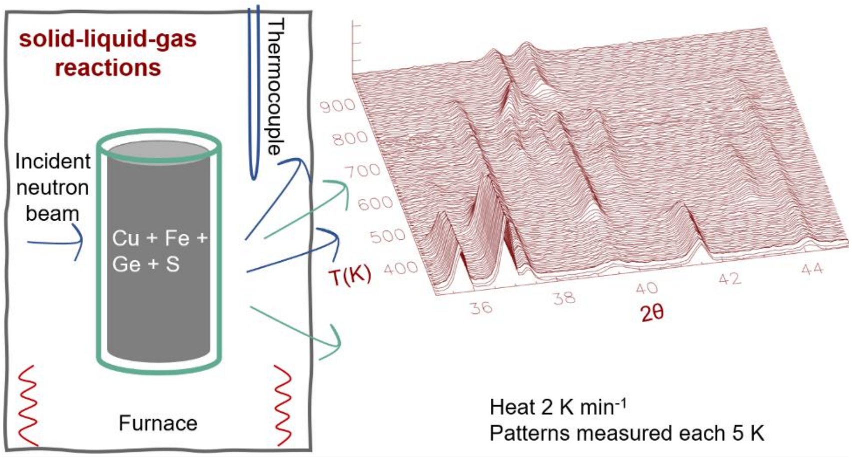

Fig. 1. Schematic representation of the *in situ* time-resolved high-temperature neutron powder diffraction experiment performed on D1B.

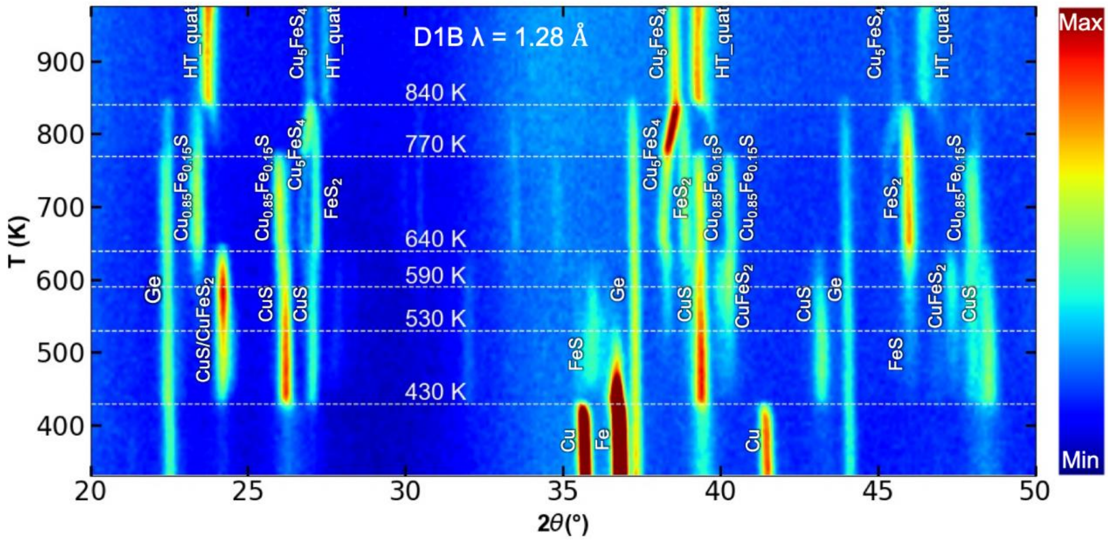

Fig. 2. 2D contour plot showing the NPD patterns of the *in situ* sealed tube reaction of $Cu_{22}Fe_8Ge_4S_{32}$ germanite from elemental precursors.

3. References

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