Experimental report

31/01/2019

Proposal: **5-21-1112** **Council:** 4/2017

Title: Crystal structure determination byhigh resolution NPD of thermoelectric sulfides: Cu8+xFe3-xSn2-yS12 (x<= 0.5; y <= 1) and Cu26V2Sn6S32

Research area: Materials

This proposal is a new proposal

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Samples:
Cu8+xFe3-xSn2-yS12 (x <= 0.5; y <= 1)
Cu26V2Sn6S32

Instrument	Requested days	Allocated days	From	To
D2B	4	4	24/05/2018	28/05/2018

Abstract:

Following the discovery of promising thermoelectric (TE) properties among copper-containing sulfides such as tetrahedrite Cu12Sb4S13, colusite Cu26V2Sn6S32, and bornite Cu5FeS4, we are now focusing on stannoidite Cu8+xFe3-xSn2-yS12 (x <= 0.5; y <= 1) compounds, reaching a ZT of 0.4@650K. In order to draw conclusion on the TE properties of these materials and to explain the anomalous high content of Fe3+ detected by 57Fe Mössbauer spectroscopy and the vacancies on the Sn site suggested by preliminary NPD data, long duration patterns of high resolution NPD data are indispensable. On another hand, an unusual 57Fe Mössbauer spectra was recorded at 4K on Cu8Fe3Sn2S12, suggesting a complex magnetic ordering that seems interesting to investigate. Moreover, we have shown recently that the TE properties of colusite Cu26V2Sn6S32 phase can be strongly increase (ZT = 0.9@673K instead of 0.56@663K) by using an alternative preparation route. Such improvement appears to be related to local stoichiometry element and sites occupancy modifications. Precise crystallographic structure determination by high resolution NPD is now necessary to explain the crystal structure-properties relationships.

Experimental report on the proposal 5-21-1112: *Crystal structure determination by high resolution NPD of thermoelectric sulfides: $Cu_{8+x}Fe_{3-x}Sn_{2-y}S_{12}$ (x ≤ 0.5; y = ≤ 1) and $Cu_{26}V_2Sn_6S_{32}$.*

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1. Introduction

The increasing needs for renewable energy sources have made thermoelectric (TE) materials, which allow the conversion of waste heat into clean electricity, the object of extensive investigations in last fifteen years.[1,2] Among the various possibilities offered by the periodic table, copper-rich sulfides represent a formidable source for the discovery of low cost and environmentally benign TE materials. These sulfides form an important class where univalent copper is the dominant element, giving the possibility of creating hole carriers in the "Cu-S" network for the generation of *p*-type TE materials, as exemplified by bornite Cu_5FeS_4,[3-5] tetrahedrite $Cu_{12-x}T_xSb_4S_{13}$ (T = Mn, Fe, Ni, Zn),[6-12] stannoidite $Cu_{8.5}Fe_{2.5}Sn_2S_{12}$,[13] germanite $Cu_{22}Fe_8Ge_4S_{32}$,[14] and colusite $Cu_{26}T_2M_6S_{32}$ (T = V, Nb, Ta; M = Sn, Ge).[15-21] The potential of these materials in term of TE application is related to their low thermal conductivities arising from their complex crystal structures. On the contrary, the power factors ($PF = S^2/\rho$, where S is the Seebeck coefficient and ρ the electrical resistivity) of these materials remain modest and significantly lower than the state-of-art intermetallic TE compounds.[1,22] Enhancement of the PF should be done by metallic substitution, which leads to an increase of the crystal structure complexity, through local stoichiometry element and/or sites occupancy modifications. Consequently, for an understanding of the crystal structure-properties relationships, with the aim to optimize the PFs of these TE materials, precise crystallographic structure determination is necessary. In this context, the crystal structures of colusite, germanite and stannoidite compounds, all derived from the more symmetric cubic structure of sphalerite (Figure 1), have been studied from high resolution neutron powder (NPD) diffraction data.

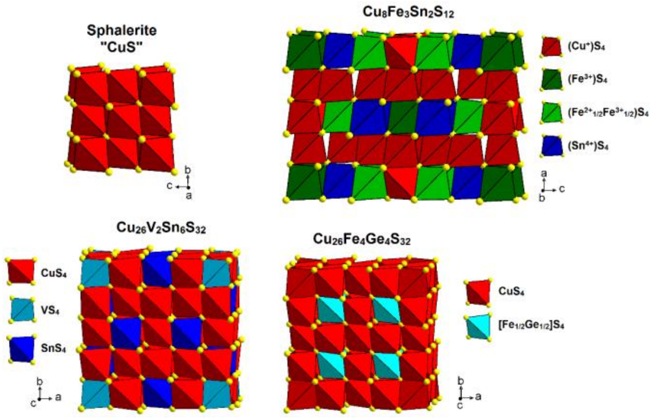

Figure 1: Representations of the crystal structure of "CuS" cubic sphalerite, $Cu_{26}V_2Sn_6S_{32}$ colusite, $Cu_{26}Fe_4Ge_4S_{32}$ natural germanite, and $Cu_8Fe_3Sn_2S_{12}$ stannoidite.

2. High resolution neutron diffraction results

2.1. colusites

Recently, we have shown that the introduction of hexavalent T^{6+} cations in the *p*-type TE colusite $Cu_{26}T_2Ge_6S_{32}$ (T = Cr, Mo, W) leads to the highest power factors among copper-rich sulfides, ranging from 1.15 mW m^{-1} K^{-2} at 700 K for W to 1.94 mW m^{-1} K^{-2} for Cr, this latter value being comparable to that of the best of state-of-the-art TE materials. A detailed structural analysis of these colusites was performed by combined Rietveld refinements of high resolution NPD (λ = 1.594 Å, D2B, Figure 2) and XRD data (λ = 1.5406 Å). This shows that the distortion of the conductive "Cu-S" network (Figure 3) is influenced by the presence in the structure of mixed octahedral-tetrahedral $[TS_4]Cu_6$ complexes (Figure 4) where the T cations are underbonded to sulfur and form metal-metal interactions with copper. The interactions between these complexes are responsible for the outstanding electronic transport properties, without affecting significantly the thermal conductivity. This study is accepted for publication in Advanced Energy Materials.[23]

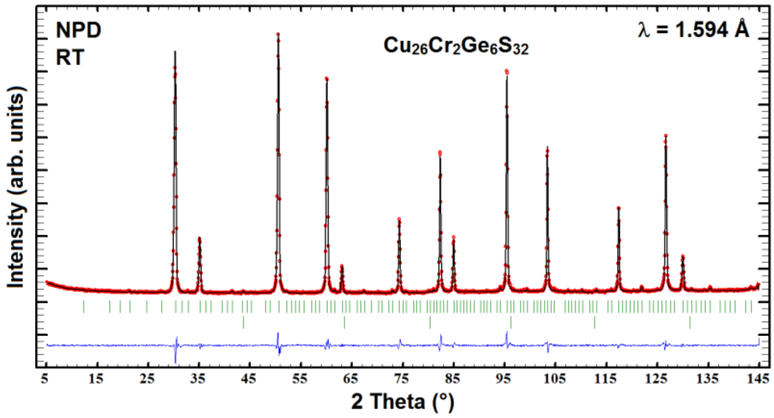

Figure 2: Rietveld refinement of the high resolution NPD data (λ = 1.594 Å, D2B) of $Cu_{26}Cr_2Ge_6S_{32}$ colusite: R_{wp} = 7.52, R_{Bragg} = 2.58, Chi^2 = 1.17. Second sets of diffraction peaks are related to vanadium sample holder.

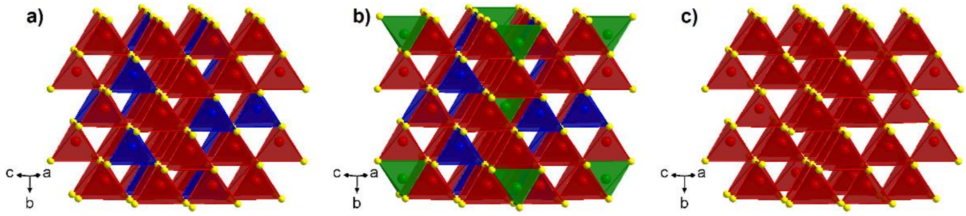

Figure 3: Crystal structure representation of a) ordered sphalerite framework "$Cu_{26}Ge_6S_{32}$" built up of corner-sharing CuS_4 (red) and GeS_4 (blue) tetrahedra, b) $Cu_{26}T_2Ge_6S_{32}$ colusite showing the insertion of additional T cations (green) in the tetrahedral cavities of the ordered sphalerite framework, and c) conductive "$Cu_{26}S_{32}$" framework deduced from the sphalerite framework by omitting Ge atoms.

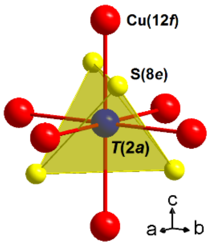

Figure 4: Representation of the mixed tetrahedral-octahedral complexes $[TS_4]Cu_6$ encountered in colusite.

In addition to this study, high resolution NPD data were recorded on the $Cu_{26}V_2Sn_6S_{32}$ colusite samples studied in reference [20]. These data will be used to perform maximum entropy method (MEM) analyses with the aim to obtain extra information on the disordered regions as well as point defects observed on HAADF-STEM images of the sample sintered at 1023 K.[20]

2.2. germanites

Recently, we have shown from single-crystal X-ray diffraction data on synthetic $Cu_{22}Fe_8Ge_4S_{32}$ germanite specimen that the cationic distribution over the metallic sites is different to that reported for natural $Cu_{26}Fe_4Ge_4S_{32}$ germanite.[24] However, due to the isoelectronic character of Cu^+ and Ge^{4+}, it is very difficult to discriminate these atoms from XRD data only. This leads to diverse possible cationic distributions. Thank to slightly different neutron scattering lengths between Cu, Ge and Fe, we expect to determine the exact cationic distribution in synthetic germanite. Rietveld refinements of the high resolution NPD data recorded on $Cu_{22}Fe_8Ge_4S_{32}$ sample as well as Sn for Ge substituted samples are in progress. The crystallographic results will be completed by theoretical calculations and will be the subject of a future scientific publication.

2.3. stannoidites

High resolution NPD data recorded on pristine $Cu_8Fe_3Sn_2S_{12}$ stannoidite at 300 K and 4 K reveal the absence of (i) structural transition and (ii) either extra magnetic peaks or magnetic contribution to the nuclear peaks, despite magnetic ordering at low temperature highlighted by magnetic susceptibility and ^{57}Fe Mössbauer measurements (see Fig. 3 of the title proposal). Absence of magnetic signal on the NPD pattern recorded at 4 K should be the consequence of a spins delocalization over the cationic network, as supported by the decrease in the intensity of the low-angle diffuse scattering (Figure 5). Moreover, crystal structure resolution of stannoidites as well as theoretical calculations are in progress and will be the subject of a future scientific publication.

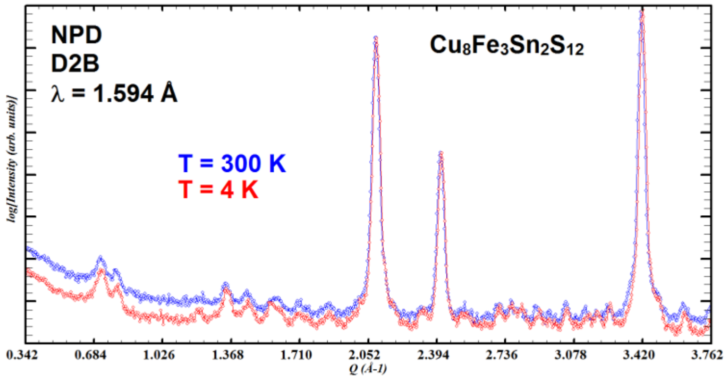

Figure 5: High resolution NPD patterns at 300 K and 4 K of pristine $Cu_8Fe_3Sn_2S_{12}$ stannoidite.

3. References

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