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High temperature neutron powder diffraction study of the Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ phases

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Abstract

Ternary copper-containing sulfides Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ have attracted considerable interest since few years due to their high-efficiency conversion as absorbers for solar energy and promising thermoelectric materials. We report therein on the decomposition study of Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ phases using high temperature in situ neutron powder diffraction. Our results obtained at a heating rate of 2.5 K/min indicate that: (i) Cu$_{12}$Sb$_4$S$_{13}$ decomposes above ≈ 792 K into Cu$_3$SbS$_3$, and (ii) Cu$_4$Sn$_7$S$_{16}$ decomposes above ≈ 891 K into Sn$_2$S$_3$ and a copper-rich sulfide phase of sphalerite ZnS-type structure with an assumed Cu$_3$SnS$_4$ stoichiometry. Both phase decompositions are associated to a sulfur volatilization. While the results on Cu$_{12}$Sb$_4$S$_{13}$ are in fair agreement with recent published data, the decomposition behavior of Cu$_4$Sn$_7$S$_{16}$ differs from other studies in terms of decomposition temperature, thermal stability and products of reaction. Finally, the crystal structure refinements from neutron powder diffraction data are reported and discussed for the Cu$_4$Sn$_7$S$_{16}$ and tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ phases at 300 K, and for the high temperature form of skinnerite Cu$_3$SbS$_3$ at 843 K.

Keywords: Sulfide material; Neutron powder diffraction; Thermal decomposition; Thermoelectric; Photovoltaic absorber

1. Introduction

In the past few years, several copper-containing sulfides have been reported as high-efficiency absorbers for solar energy conversion applications and promising thermoelectric materials [1-10]. Among them, ternary tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ compounds have attracted considerable interest due to their complex crystal structures (Figure 1) characterized by an intrinsically low thermal conductivity [11-13].

Cu$_{12}$Sb$_4$S$_{13}$ crystallizes in the non-centrosymmetric cubic space group $I4_3m$ (No. 217) with copper atoms localized on 12d ($\frac{1}{4}, \frac{1}{4}, 0$) and 12e ($x, 0, 0$) crystallographic sites, antimony atoms localized on 8c ($x, x, x$) site, and sulfur atoms localized on 2a ($0, 0, 0$) and 24g ($x, x, z$) sites [14,15]. One of the complex feature of tetrahedrite crystal structure is related to copper atoms on the 12e site, which are in a trigonal plane environment formed by the sulfur atoms (two on the 24g site and one on the 2a site). This trigonal plane environment induces an important anisotropic atomic motion of the Cu...
of tetrahedrite was proposed by Makovicky and Skinner [22]. Indeed, the authors have claimed that a split of the Cu 12e site into two lower symmetry 24g sites, statistically occupied, may described the anisotropic atomic motion as well [18,23,24]. Such structural description decreases the magnitude of the displacement parameters, and consequently improves the crystal structure refinement when isotropic (instead of anisotropic) displacement parameters are considered. Moreover, synthetic Cu$_{12}$Sb$_4$S$_{13}$ exhibits at low temperature a metal-semiconductor (also reported as a paramagnetic-nonmagnetic) transition around 85 K [11,20,25-27], which was recently associated to a concomitant structural transition from the well-known cubic structure to tetragonal structure [28,29]. Finally, synthetic Cu$_{12}$Sb$_4$S$_{13}$ sample evidences exsolution at low-temperature leading to Cu-poor and Cu-rich compounds. Consequently, the unit cell parameter ranges from 10.32 Å (Cu-poor) to 10.45 Å (Cu-rich) at room temperature [22,30,31].

Cu$_4$Sn$_3$S$_{16}$ crystallizes in the centrosymmetric trigonal space group $R\bar{3}m$ (No. 166) with copper atoms localized on the 3$a$ (0, 0, 0) site and two 6$c$ (0, 0, z) sites, tin atoms localized on the 3$g$ (0, 0, $\frac{1}{2}$) site and one 18$h$ (x, -x, z) site, and sulfur atoms localized on two 6$c$ (0, 0, z) sites and two 18$h$ (x, -x, z) sites [32]. All crystallographic sites are fully occupied, excepted one of the 6$c$ copper site (i.e. z $\approx$ 0.188), which is half occupied [32]. Similarly to the tetrahedrite structure, one of the complex feature of the crystal structure of Cu$_4$Sn$_3$S$_{16}$ is related to copper atoms on the 6$c$ site (i.e. z $\approx$ 0.295), in a trigonal plane environment formed by sulfur atoms (all on the 18$h$ (x $\approx$ 0.507, -x, z $\approx$ 0.376) site). This leads to an important anisotropic atomic motion of Cu atoms perpendicularly to the trigonal plane defined by sulfur atoms (Figure 1). Likewise, copper atoms on the 3$a$ site are in an octahedral environment formed by sulfur atoms (all on the 18$h$ (x $\approx$ 0.507, -x, z $\approx$ 0.376) site) and also evidence an anisotropic atomic motion of disk-like shape perpendicular to the c-axis (Figure 1). This former anisotropic atomic motion was described by Jemetio et al. [33] through a structural disorder considering a splitting of Cu 6$c$ site atom (i.e. z $\approx$ 0.295) into two 6$c$ sites (i.e. z $\approx$ 0.302 and z $\approx$ 0.290) statistically occupied. Finally, as in tetrahedrite, the aforementioned anisotropic atomic motions of copper atoms may contribute to the very low lattice thermal conductivity measured in Cu$_4$Sn$_3$S$_{16}$ [13].

While complex crystal structures of Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_3$S$_{16}$ compounds are now well-known, the thermal stability and phase decomposition of these materials remains ambiguous and not fully understood. The decomposition of pure synthetic tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ phase, studied from differential thermal analysis (DTA) and/or differential scanning calorimetry (DSC), has been examined by different authors [24,34-37]. Skinner et al. reported a phase decomposition of tetrahedrite around 816 K into famatinite Cu$_4$Sb$_4$S$_6$, skinnerite Cu$_4$Sb$_3$S$_3$, and a cation-disordered face-centered cubic phase [34]. Tatsuka and Morimoto mentioned the decomposition of the copper-poor tetrahedrite Cu$_{12.30}$Sb$_{4.05}$S$_{13}$ phase at about 816 K into famatinite Cu$_4$Sb$_4$S$_6$, chalcostibite CuSbS$_2$ and the high-temperature form of skinnerite Cu$_4$Sb$_3$S$_3$ [35]. Di Benedetto et al. attributed the endothermic effect on DTA curve starting at $\approx$ 813 K to the decomposition of pure copper synthetic tetrahedrite [36]. Braga et al. pointed out a phase decomposition of Cu$_{12}$Sb$_4$S$_{13}$ into Cu$_4$Sb$_3$S$_3$ at 795 K [37], and more recently Barbier et al. shown that synthetic tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ phase decomposes into Cu$_4$Sb$_3$S$_3$ (associated with sulfur volatilization) at a temperature starting from 791 K [24]. From X-ray powder diffraction data (XRPD), Barbier et al. highlighted that synthetic Cu$_{12}$Sb$_4$S$_{13}$ is stable up to 673 K and
decomposes at higher temperatures into Cu$_3$SbS$_3$ passing through CuSbS$_2$ as intermediate phase [24]. Finally, it could be mentioned that some studies relate on the breakdown below $\approx$ 634 K of skinnerite Cu$_3$SbS$_3$ into tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$, antimony, and sometimes chalcostibite CuSbS$_2$ phases [30,34,38,39].

The ternary phase diagram Cu-Sn-S was studied totally or partially by several authors [40-43]. A state of the art of the ternary phases in this system can be found in reference [44]. According to the authors, different chemical formulas were assigned to describe the same crystalline phase. This is the case of Cu$_4$Sn$_7$S$_{16}$ for which chemical formulas ranging from Cu$_2$Sn$_3$S$_7$ to Cu$_2$Sn$_4$S$_9$ were reported. Among the publications on Cu-Sn-S ternary compounds, only few addressed on the melting or decomposition temperature of Cu$_4$Sn$_7$S$_{16}$, and the results obtained from DTA, DSC and XRPD experiments are strongly incoherent one to the others. Khanafer et al. mentioned the decomposition of cubic "Cu$_2$Sn$_4$S$_9$" (i.e. Cu$_4$Sn$_7$S$_{16}$) phase into "Cu$_4$Sn$_3$S$_8$" (which was discredited by Piskach et al. [42]) and Sn$_2$ at 938 K [40], Piskach et al. pointed out the formation of "Cu$_2$Sn$_4$S$_9$" through peritectoid reaction of Cu$_2$Sn$_3$ and Sn$_2$ at 943 K [42], and Fiechter et al. reported on the melting temperature at 1076 K of the wide stoichiometry range Cu$_2$Sn$_{3+2x}$S$_{7+2x}$ ($0 \leq x \leq 1$) phase after three solid-solid phase transitions at 948 K, 958 K, and 1043 K [43].

Finally, the knowledge of the thermal phase stability/instability is fundamental for large scale applications, especially regarding thermoelectric materials. For this reason, we have investigated for the first time the temperature and phase decomposition of the ternary Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ compounds using in situ neutron powder diffraction (NPD) data recorded from room temperature up to 843 K and 1010 K, respectively. Moreover, we report, from long duration NPD data, on the crystal structure refinements of Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ compounds at 300 K and of the high temperature form of skinnerite Cu$_3$SbS$_3$ at 843 K.

2. Experimental methods

2.1. Synthesis

Cu$_{12}$Sb$_4$S$_{13}$ powder has been synthesized in a three-step process. Firstly, stoichiometric mixture of high purity powder elements ($\geq$ 99.5 wt.%, Alfa Aesar) were sealed in evacuated silica tubes, heated up to 973 K for 3 h (rate of 100 K/h), then cooled down to 793 K (rate of 45 K/h), held for 25 h, before cooling to room temperature at the rate of 50 K/h. Resulting powder was then ground, sieved down to 200 $\mu$m, shaped into pellets using a hydraulic press, and sealed into an evacuated silica tube for a second annealing of 25 h at 793 K with heating and cooling rate of 100 K/h. The sample was finally crushed and sieved down to 200 $\mu$m before spark plasma sintering (SPS – FCT HPD 25) process at 793 K for 30 min (heating and cooling rate of 50 K/min and 200 K/min, respectively) under a pressure of 75 MPa using graphite dies of 15 mm diameter and a slight over pressure of argon (+20 hPa) to prevent oxidation and sulfur volatilization.

Cu$_4$Sn$_7$S$_{16}$ powder was synthesized in a two-step process. Firstly, stoichiometric mixture of high purity powder elements (Cu, S: $\geq$ 99.5 wt.%, Alfa Aesar; Sn: $\geq$ 99.9 wt.%, Merck) were sealed in evacuated silica tubes, heated up to 973 K at the rate of 100 K/h, held for 72 h and then cooled down to room temperature at the rate of 50 K/h. Secondly, the sample was ground, sieved down to 200 $\mu$m and densified by SPS (FCT HPD 25) at 973 K for 30 min (heating and cooling rate of 100 K/min) under a pressure of 64 MPa using graphite dies of 10 mm diameter and a slight over pressure of argon (+50 hPa) to prevent oxidation and sulfur volatilization.
The densified Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$ pellets were crushed and sieved down to 200 μm prior to X-ray and neutron powder diffraction analyzes.

Remark: Similar synthesis processes were already performed to produce high density pellets of these materials. These pellets were then cut in several ingots used for thermoelectric properties measurements (i.e. Seebeck coefficient, electrical resistivity, thermal diffusivity). The thermoelectric properties of these materials, not reported here, are presented and discussed in references [24] and [13] for Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$, respectively.

2.2. X-ray and neutron powder diffraction

The purity of the samples and the crystallographic structure of the phases were checked at room temperature by XRPD using a PANalytical X’Pert Pro diffractometer equipped with a Cu Kα X-ray tube. NPD experiments were carried out at the Institut Laue Langevin (ILL), Grenoble, France. The data were collected from room temperature up to 1010 K under dynamical secondary vacuum using the high-flux neutron two-axis powder diffractometer D1B (λ = 2.52 Å) equipped with a one-dimensional curved multidetector. The analysis of the diffraction patterns was performed by Rietveld profile refinement using the FullProf and WinPlotr software packages [45,46].

3. Results and discussion

3.1. Cu$_{12}$Sb$_4$S$_{13}$

NPD pattern recorded at T = 300 K on the Cu$_{12}$Sb$_4$S$_{13}$ sample (Figure 2) evidences the diffraction peaks of the cubic tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ phase (space group $I\bar{4}3m$, No. 217) as majority phase (81.5(8) wt.%) and of the tetragonal Cu$_{1.5}$Sb$_{0.5}$S$_2$ (CuFeS$_2$-type structure, space group $I\bar{4}2d$, No.122) and Cu$_3$SbS$_4$ (space group $I\bar{4}2m$, No. 121) phases (13.1(2) wt.% and 5.4(3) wt.%, respectively). These results are in fair agreement with previous X-ray diffraction analyses performed on similar sample [24]. Extra diffraction peaks observed around 75.6° and 90.1° on the neutron pattern are attributed to the thermocouple and were refined by pattern matching considering a simple fcc crystal structure of cell parameter $a \approx 3.56$ Å (space group $Fm\bar{3}m$, No. 225). The refinement of the tetrahedrite phase was performed using the crystal structure description proposed by Makovicky and Skinner [22]. Due to the limited number of observed diffraction peaks, only the profile peak-shape parameters, lattice parameters and the fractional atomic coordinates of the tetrahedrite phase were refined, while the fractional atomic coordinates of Cu$_{1.5}$Sb$_{0.5}$S$_2$ and Cu$_3$SbS$_4$ phases were fixed according to the structural data found in references [47,48]. The sites occupancies of the three phases were fixed to the theoretical values. The results of the crystal structure refinement of tetrahedrite phase are gathered in Table 1.

In order to carried out quantitative phase analysis of the Cu$_{12}$Sb$_4$S$_{13}$ phase decomposition under the same thermal conditions than those used by Barbier et al. during DSC and thermogravimetric analyses (TGA) [24], NPD patterns of 2 minutes were recorded continuously from 300 K up to 843 K at the rate of 2.5 K/min. The fractional atomic coordinates of the tetrahedrite phase refined at 300 K (Table 1) were used as fixed parameters in the refinement of the high temperature in situ neutron diffraction patterns.

NPD patterns recorded from 300 K up to 787 K show only a weak shift to the lower angles of the diffraction peaks of Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_{1.5}$Sb$_{0.5}$S$_2$ phases in relation with the thermal expansion of their unit cells. The transformation of Cu$_{1.5}$Sb$_{0.5}$S$_2$ into CuSbS$_2$ (space group $Pnma$, No. 62 [49]) around 673
K noted by Barbier et al. [24] is not confirmed by NPD. Due to lower signal to noise ratio compared to the long duration 300 K neutron pattern, the existence of weak proportion of Cu$_3$SbS$_4$ as secondary phase is not confirmed at high temperature.

From T = 792 K, the intensity of the Cu$_{12}$Sb$_4$S$_{13}$ diffraction peaks decreases while concomitantly extra diffraction peaks appear (Figure 3). Those peaks are characteristic of the high temperature form of the orthorhombic skinnerite Cu$_3$SbS$_3$ phase (space group Pnma, No. 62) [50]. The diffraction peaks of the Cu$_{12}$Sb$_4$S$_{13}$ phase are not observed anymore above 836 K, while those of the Cu$_{1.5}$Sb$_{0.5}$S$_2$ phase \( (i.e. 47.6^\circ, 55.4^\circ, 55.8^\circ, \text{Figure 2}) \) are observed up to 841 K (Figure 3). These results indicate that Cu$_{12}$Sb$_4$S$_{13}$ decomposes into Cu$_3$SbS$_3$ starting from 792 K up to 836 K (at the heating rate of 2.5 K/min), which is in good agreement with the results reported by Braga et al. [37] and Barbier et al. [24].

The unit cell parameters, occupancies of copper sites and fractional atomic coordinates (excepted those of Cu(4) and Cu(5) sites, which were fixed to those determined by Pfitzner at T = 493 K [50]) of the high temperature form of the orthorhombic skinnerite Cu$_3$SbS$_3$ phase were refined from long duration NPD pattern recorded at T = 843 K (Figure 4). The results are gathered in Table 2 and were used as fixed parameters in the refinement of the high temperature NPD patterns. The refined atomic coordinates are in fair agreement with those given by Pfitzner [50], while refined copper site occupancies evidence some differences, more especially concerning Cu(1), Cu(2), and Cu(5) sites. The refined occupation factors of copper sites lead to the stoichiometry Cu$_{2.99}$SbS$_3$ for the high temperature form of the skinnerite phase, which differs from the copper deficient stoichiometry Cu$_{2.922}$SbS$_3$ reported by Pfitzner [50].

Quantitative phase analysis data determined from Rietveld refinements of the NPD patterns recorded between 723 K and 841 K are displayed in Figure 5(a). They are compared with DSC and TGA results reported by Barbier et al. [24] (Figure 5(b)). The quantitative phase analysis highlights that the Cu$_{12}$Sb$_4$S$_{13}$ phase decomposes into Cu$_3$SbS$_3$ in two-step. Firstly, in the temperature range of 792 to 816 K, the majority of the Cu$_{12}$Sb$_4$S$_{13}$ phase decomposes into Cu$_3$SbS$_3$ and Cu$_{1.5}$Sb$_{0.5}$S$_2$ phases as expressed by the thermal evolution of the weight fraction of these phases (Figure 5(a)). Secondly, the weight fraction of the Cu$_{1.5}$Sb$_{0.5}$S$_2$ phase decreases above 816 K, while that of Cu$_3$SbS$_3$ continues to increase (Figure 5(a)). Considering that CuSbS$_2$ melts congruently around 826 K [34,37,51,52], we can conclude that the second step, between 816 K and 836 K, corresponds to the melting of Cu$_{1.5}$Sb$_{0.5}$S$_2$ associated with the end of the decomposition of Cu$_{12}$Sb$_4$S$_{13}$ into Cu$_3$SbS$_3$. It could be mentioned that the diffraction peaks of Cu$_{1.5}$Sb$_{0.5}$S$_2$ have totally disappeared after a dwell time of 8 minutes at 843 K.

The quantitative phase analysis results and starting/ending temperatures of phase decomposition determined from NPD are in excellent agreement with the DSC results (Figure 5). Moreover, considering that the transformation of Cu$_{12}$Sb$_4$S$_{13}$ into Cu$_3$SbS$_3$ requires sulfur loss, the mass loss observed on the thermogravimetric curve (Figure 5(b)) can then be attributed to a sulfur volatilization coming from the Cu$_{12}$Sb$_4$S$_{13}$ phase decomposition. The present results corroborate the study of Barbier et al. performed with the same thermal treatment [24]. Finally, the origin of the weak inflection around 835 K on the DSC curve (Figure 5(b)) can be attributed to the end of the Cu$_{12}$Sb$_4$S$_{13}$ phase decomposition (Figure 5(a)).

The phase stability of Cu$_{12}$Sb$_4$S$_{13}$ is then confirmed up to \( \approx 792 \) K. It is important to note that considering the heating rate of 2.5 K/min, this value is probably slightly overestimated. It implies that
the physical properties of the Cu$_{12}$Sb$_4$S$_{13}$ tetrahedrite phase should evolve, and consequently have to be considered carefully, if the material is exposed at a temperature higher or close to 790 K. For higher temperature applications, Ni to Cu substituted tetrahedrite samples can be privileged. Indeed, it was demonstrated by Barbier et al. [24] that Ni for Cu substitution enhances the phase stability of the tetrahedrite phase at high temperature. In situ neutron powder diffraction performed on Cu$_{10.4}$Ni$_{1.6}$Sb$_4$S$_{13}$ sample up to 843 K (heating rate of 2.5 K/min) evidences the absence of structural modifications (data not shown) and then confirm the beneficial effect of Ni substitution on the thermal stability of tetrahedrite phase.

3.2. Cu$_4$Sn$_7$S$_{16}$

NPD pattern recorded at T = 300 K on the Cu$_4$Sn$_7$S$_{16}$ sample (Figure 6) evidences only the diffraction peaks of the rhombohedral Cu$_4$Sn$_7$S$_{16}$ compound (space group R̃3m, No. 166). The refinement has been performed considering the crystal structure description reported by Jemetio et al. [33], where Cu(2) atoms are statistically distributed on two 6c sites instead of only one 6c site as reported by Chen et al. [32]. The lattice parameters and the fractional atomic coordinates were refined while the site occupancies were fixed to those reported by Jemetio et al. [33]. The results are gathered in Table 3.

In order to perform in situ quantitative phase analysis of the Cu$_4$Sn$_7$S$_{16}$ phase decomposition, NPD patterns of 2 minutes were recorded continuously from 300 K up to 823 K at the rate of 20 K/min and then from 823 K up to 1010 K at the rate of 2.5 K/min. The fractional atomic coordinates refined at 300 K (Table 3) were used as fixed parameters in the refinement of the high temperature NPD patterns. Intensities of the diffraction peaks are constant between 300 K and 823 K, indicating the absence of crystal structure evolution on this temperature range. Therefore, only NPD patterns recorded from 823 K to 1010 K have been carefully analyzed.

The neutron thermogram of Cu$_4$Sn$_7$S$_{16}$ recorded between 823 K and 1010 K is shown in Figure 7(a). The temperature dependence of the independent (2 0 8) reflection (2θ = 57.4°) intensity of Cu$_4$Sn$_7$S$_{16}$ and of one diffraction peak (2θ = 81.2°) corresponding to a secondary phase is displayed in Figure 7(b). Up to 891 K, the NPD patterns evidence only the diffraction peaks of the Cu$_4$Sn$_7$S$_{16}$ phase, indicating that this phase is chemically stable up to this temperature. Above 891 K, extra diffraction peaks appear on the NPD patterns, and concomitantly, the intensity of the diffraction peaks of Cu$_4$Sn$_7$S$_{16}$ decreases. These results indicate that Cu$_4$Sn$_7$S$_{16}$ starts to decompose above 891 K at the heating rate of 2.5 K/min. The extra diffraction peaks related to the thermal decomposition of Cu$_4$Sn$_7$S$_{16}$ are characteristic of the Sn$_2$S$_3$ phase (space group Pnma, No. 62) [53] and of a copper-rich sulfide phase for which several crystal structure descriptions can be considered (see below). Above 960 K, the intensity of all of the diffraction peaks strongly decreases (Figure 7). Above 976 K the diffraction peaks of Sn$_2$S$_3$ are no more observed and from 990 K only the signal of the copper-rich sulfide phase is still detected. It could be related with the experimental observation (after cooling) of a reaction between the sample and the vanadium sample holder. From thermodynamic study of the S-Sn system, Lindwall et al. [54] reported about the decrease of the melting temperature of Sn$_2$S$_3$ with the decrease of the gas pressure. Taking into account that the measurement was performed under dynamical secondary vacuum, the reaction of the sample with vanadium is likely the result of the melting of Sn$_2$S$_3$ at a lower temperature than the expected one (i.e. $T_m = 1031$ K [54]). Moreover, Lindwall et al. [54] concluded that, due to its lower sulfur content, Sn$_2$S$_3$ is more thermally stable than SnS$_2$ at low pressure (i.e. < 1 bar), which is confirmed by our neutron powder diffraction results.
In order to determine more accurately the crystal structure of the copper-rich sulfide phase, Rietveld refinements have been performed on the NPD pattern recorded at 990 K by considering: (i) the monoclinic form of mohite Cu$_3$SnS$_4$ (space group $Cc$, No. 9) [40,55,56], (ii) the tetragonal form of Cu$_3$SnS$_4$ in the stannite Cu$_2$FeSnS$_4$-type structure (space group $I\bar{4}2m$, No. 121) [32], (iii) the tetragonal form of kuramite Cu$_3$SnS$_4$ in the stannite Cu$_2$FeSnS$_4$-type structure (space group $I\bar{4}2m$, No. 121) reported with a sulfur deficiency by Goto et al. [57], (iv) the cubic form of Cu$_3$SnS$_4$ in the sphalerite ZnS-type structure (space group $F\bar{4}3m$, No. 216) [58], and (v) the cubic form of kuramite Cu$_3$SnS$_4$ in the sphalerite ZnS-type structure (space group $F\bar{4}3m$, No. 216) [59]. All of these crystal structures lead to equivalent quality of refinements. It is important to note that the crystal structure of the high-temperature form of digenite Cu$_4$Sn$_2$S$_7$ (space group: $F\bar{4}3m$, No. 216 or $Fm\bar{3}m$, No. 225), does not fit correctly the intensity of the observed diffraction peaks.

According to Di Benedetto et al. [59], the tetragonal crystal structure of Cu$_3$SnS$_4$ (iii) generates reflections which are absent in the experimental neutron pattern (i.e. $(0 \ 0 \ 2)$, $(1 \ 0 \ 1)$, $(1 \ 1 \ 0)$), but consistent with the cubic sphalerite-type structure (iv) and (v). Similar interpretation can be done with the monoclinic form (i) and tetragonal form (ii) of mohite Cu$_3$SnS$_4$. Hence, we can concluded that the copper-rich sulfide phase detected by neutron powder diffraction crystallizes in the cubic sphalerite-type structure (space group $F\bar{4}3m$) with refined cell parameter $a = 5.483(2)$ Å at 990 K. To this point, the cubic form of mohite Cu$_3$SnS$_4$ (iv) and the cubic form of kuramite Cu$_3$SnS$_4$ (v) cannot be distinguished. However, considering that the cubic form of Cu$_3$SnS$_4$ (iv) is known to be stable above 1053 K [32,56], we can assume that, at 990 K, the copper-rich sulfide phase is the cubic form of Cu$_3$SnS$_4$ (v). Refinement of the 990 K neutron pattern considering the Cu$_3$SnS$_4$ stoichiometry is displayed in Figure 8.

In the sphalerite ZnS-type structure, the $4a$ $(0, \ 0, \ 0)$ and $4c$ $(\frac{1}{4}, \ \frac{1}{4}, \ \frac{1}{4})$ crystallographic sites are fully occupied by zinc and sulfur atoms, respectively. Thus, in the cubic form of kuramite Cu$_3$SnS$_4$, it implies that copper and tin atoms are randomly distributed on the $4a$ $(0, \ 0, \ 0)$ site [59]. From magnetic characterization of the cubic form of kuramite nanopowders, Di Benedetto et al. concluded to the expected stoichiometry of Cu$_3$SnS$_4$ [59]. In our case, a different Cu/Sn ratio is not excluded. Unfortunately, the quality of the neutron diffraction data recorded at 990 K is too weak to allow the refinement of the Cu/Sn ratio. For this reason, the exact chemical composition of the present sphalerite-type phase cannot be confirmed. Nevertheless, the impact on NPD refinement of a different Cu/Sn ratio is very weak, and the cubic form of kuramite Cu$_3$SnS$_4$ well describes the copper-rich sulfide phase.

Due to the reaction of the sample with the vanadium sample holder above 960 K, the quantitative phase analysis has been done from Rietveld refinement of the NPD patterns recorded between 852 K and 960 K. The results, shown in Figure 9, indicate that Cu$_4$Sn$_7$S$_{16}$ decomposes progressively above 891 K into Sn$_7$S$_{16}$ (space group $Pnma$, No. 62) [53] and a copper-rich sulfide phase of sphalerite ZnS-type structure (space group $F\bar{4}3m$, No. 216) assumed to have the stoichiometry Cu$_3$SnS$_4$ [59]. Considering that the measurements have been done at a heating rate of 2.5 K/min, the starting temperature of decomposition of Cu$_4$Sn$_7$S$_{16}$, comprised between 891 K and 896 K, is probably slightly overestimated. Finally, during this decomposition, sulfur volatilization is assumed in order to balance the stoichiometry, leading to the following reaction: Cu$_4$Sn$_7$S$_{16}$ → 17/6 Sn$_7$S$_3$ + 4/3 Cu$_3$SnS$_4$ + 13/6x S_{x\geq1} (2 \leq x \leq 10).

Our results highlight that the decomposition of Cu$_4$Sn$_7$S$_{16}$ starts at a temperature ≈ 40 K lower than that reported up to now [40,42], and leads to the formation of Sn$_7$S$_3$ instead of SnS$_2$ [40,42]. Moreover our results indicate the formation of a cubic sphalerite ZnS-type structure with assumed Cu$_3$SnS$_4$ stoichiometry. As already mentioned, the Cu$_3$SnS$_4$ stoichiometry reported by Piskach et al.
is however not excluded. Finally, our results are in deep disagreement with those published by Fiechter et al. [43], where three solid-solid phase transitions of the Cu$_{2}$Sn$_{3+x}$S$_{7+2x}$ (0 ≤ x ≤ 1) phase are reported at 948 K, 958 K, and 1043 K, followed by the melting of the phase at 1076 K.

These results highlight that the Cu$_{4}$Sn$_{7}$S$_{16}$ phase is stable up to ≈ 891 K. Consequently, if the material is exposed at a temperature higher or close to 890 K the physical properties of the Cu$_{4}$Sn$_{7}$S$_{16}$ phase should evolve, and then have to be considered carefully.

4. Conclusion

High resolution neutron powder diffraction data collected from room temperature up to 1010 K under dynamical secondary vacuum have been analyzed to determine the temperatures and chemical reactions associated with the phase decompositions at the heating rate of 2.5 K/min of the ternary Cu$_{12}$Sb$_{4}$S$_{13}$ tetrahedrite and Cu$_{4}$Sn$_{7}$S$_{16}$ phases. The results highlight that (i) Cu$_{12}$Sb$_{4}$S$_{13}$ tetrahedrite phase decomposes above 792 K (and up to 836 K) into the high temperature form of skinnerite Cu$_{3}$Sb$_{3}$ and Cu$_{1.5}$Sb$_{0.5}$S$_{2}$ phases, this later being instable above 816 K, and (ii) Cu$_{4}$Sn$_{7}$S$_{16}$ phase decomposes above 891 K into Sn$_{2}$S$_{3}$ and a cubic phase of sphalerite ZnS-type structure. During these phase decompositions, sulfur volatilization likely occurs in order to balance the overall stoichiometry. While, high temperature in situ neutron powder diffraction results obtained on Cu$_{12}$Sb$_{4}$S$_{13}$ tetrahedrite phase confirm previous conclusions reported by Barbier et al. [24], the data obtained on Cu$_{4}$Sn$_{7}$S$_{16}$ lead to significant differences in comparison to previous thermal studies. In particular the temperature of decomposition is ≈ 40 K lower than previously reported values [40,42]. Our results also indicate that the interpretations of the data related to the Cu$_{2}$Sn$_{3+x}$S$_{7+2x}$ (0 ≤ x ≤ 1) phase in the pseudobinary Cu$_{2}$S – SnS$_{2}$ phase diagram proposed by Fiechter et al. [43] are not fully correct. These updates on the thermal stability/instability of the ternary Cu$_{12}$Sb$_{4}$S$_{13}$ and Cu$_{4}$Sn$_{7}$S$_{16}$ phases are new information that scientific community have to take into account for potential high temperature applications, especially in thermoelectricity.

Acknowledgements

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References

[34] B.J. Skinner, F.D. Luce, E. Makovicky, Econ. Geol. 67 (1972) 924-938.

**Figure captions**

Figure 1: Crystal structure representations of Cu$_{12}$Sb$_4$S$_{13}$ and Cu$_4$Sn$_7$S$_{16}$.

Figure 2: Refinement of the neutron diffraction pattern of Cu$_{12}$Sb$_4$S$_{13}$ recorded at 300 K ($\lambda = 2.52$ Å).

Figure 3: Neutron diffraction patterns of Cu$_{12}$Sb$_4$S$_{13}$ sample recorded between 743 K and 841 K ($\lambda = 2.52$ Å).

Figure 4: Refinement of the neutron diffraction pattern of Cu$_3$Sb$_3$ recorded at 843 K ($\lambda = 2.52$ Å).

Figure 5: Quantitative phase analysis from Rietveld refinement of the NPD patterns (a) and DSC and TGA data (b) from ref. [24] of Cu$_{12}$Sb$_4$S$_{13}$ phase decomposition.

Figure 6: Refinement of the neutron diffraction pattern of Cu$_3$Sn$_7$S$_{16}$ recorded at 300 K ($\lambda = 2.52$ Å).

Figure 7: (a) Neutron thermogram of Cu$_3$Sn$_7$S$_{16}$ sample recorded between 823 K and 1010 K and (b) thermal evolution of the intensity of the independent (2 0 8) reflection of Cu$_3$Sn$_7$S$_{16}$ and of the (2 2 0) reflection of the cubic form of Cu$_3$Sn$_3$.

Figure 8: Refinement of the neutron diffraction pattern recorded at 300 K ($\lambda = 2.52$ Å) considering the sphalerite-type structure form of kuramite Cu$_3$Sn$_3$.

Figure 9: Quantitative phase analysis of the Cu$_4$Sn$_7$S$_{16}$ phase decomposition at the heating rate of 2.5 K/min from Rietveld refinement of the neutron diffraction patterns.
Table 1: Crystallographic parameters of Cu$_{12}$Sb$_4$S$_{13}$ deduced from Rietveld refinement of neutron powder diffraction pattern recorded at 300K.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>12d</td>
<td>¾</td>
<td>¾</td>
<td>0</td>
</tr>
<tr>
<td>Cu(2)</td>
<td>24g</td>
<td>0.218(5)</td>
<td>0.023(4)</td>
<td>-0.023(4)</td>
</tr>
<tr>
<td>Sb</td>
<td>8c</td>
<td>0.271(5)</td>
<td>0.271(5)</td>
<td>0.271(5)</td>
</tr>
<tr>
<td>S(1)</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>S(2)</td>
<td>24g</td>
<td>0.113(6)</td>
<td>0.113(6)</td>
<td>0.366(8)</td>
</tr>
</tbody>
</table>

$\chi^2 = 914$, $R_{Bragg} = 4.58$, $R_f = 3.18$

Table 2: Crystallographic parameters of Cu$_3$SbS$_3$ deduced from Rietveld refinement of neutron powder diffraction pattern recorded at 843 K.

<table>
<thead>
<tr>
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<th>y</th>
<th>z</th>
<th>Occ.</th>
</tr>
</thead>
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<td>0.010(2)</td>
<td>0.166(4)</td>
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<tr>
<td>Cu(2)</td>
<td>8d</td>
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<td>0.108(2)</td>
<td>0.388(2)</td>
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<tr>
<td>Cu(3)</td>
<td>8d</td>
<td>0.121(2)</td>
<td>0.073(2)</td>
<td>0.327(4)</td>
</tr>
<tr>
<td>Cu(4)</td>
<td>4c</td>
<td>0.0805</td>
<td>¾</td>
<td>0.4585</td>
</tr>
<tr>
<td>Cu(5)</td>
<td>4c</td>
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</tr>
<tr>
<td>Sb</td>
<td>4c</td>
<td>0.270(1)</td>
<td>¾</td>
<td>0.889(1)</td>
</tr>
<tr>
<td>S(1)</td>
<td>4c</td>
<td>0.053(2)</td>
<td>¾</td>
<td>0.151(2)</td>
</tr>
<tr>
<td>S(2)</td>
<td>8d</td>
<td>0.172(2)</td>
<td>0.067(2)</td>
<td>0.677(3)</td>
</tr>
</tbody>
</table>

$\chi^2 = 75.5$, $R_{Bragg} = 3.49$, $R_f = 3.55$

Table 3: Crystallographic parameters of Cu$_4$Sn$_7$S$_{16}$ deduced from Rietveld refinement of neutron powder diffraction pattern recorded at 300 K.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(1)</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.189(1)</td>
</tr>
<tr>
<td>Cu(2a)</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.305(1)</td>
</tr>
<tr>
<td>Cu(2b)</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.288(1)</td>
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<tr>
<td>Cu(3)</td>
<td>3a</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Sn(1)</td>
<td>18h</td>
<td>0.502(1)</td>
<td>0.498(1)</td>
<td>0.251(1)</td>
</tr>
<tr>
<td>Sn(2)</td>
<td>3b</td>
<td>0</td>
<td>0</td>
<td>¾</td>
</tr>
<tr>
<td>S(1)</td>
<td>18h</td>
<td>0.494(1)</td>
<td>0.506(1)</td>
<td>0.124(1)</td>
</tr>
<tr>
<td>S(2)</td>
<td>18h</td>
<td>0.502(1)</td>
<td>0.498(1)</td>
<td>0.375(1)</td>
</tr>
<tr>
<td>S(3)</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.123(1)</td>
</tr>
<tr>
<td>S(4)</td>
<td>6c</td>
<td>0</td>
<td>0</td>
<td>0.378(1)</td>
</tr>
</tbody>
</table>
\[\chi^2 = 58.9, R_{Bragg} = 3.36, R_i = 3.00\]

Figure 1

![Figure 1](image1)

Figure 2

![Figure 2](image2)
Figure 5

Figure 6
Figure 9

Temperature (K)

Wt.%

- $\text{Cu}_4\text{Sn}_7\text{S}_{16}$
- $\text{Cu}_3\text{SnS}_4$
- $\text{Sn}_2\text{S}_3$
In situ neutron powder diffraction data (heating rate of 2.5 K/min) indicates that (i) the ternary Cu$_{12}$Sb$_4$S$_{13}$ phase is stable up to 792 K and decomposes at higher temperature into Cu$_3$SbS$_3$ and Cu$_{1.5}$Sb$_{0.5}$S$_2$, and (ii) the Cu$_4$Sn$_7$S$_{16}$ phase is stable up to 891 K and decomposes at higher temperature into Sn$_2$S$_3$ and a cubic phase of sphalerite ZnS-type structure. Sulfur volatilization likely occurs in order to balance the overall stoichiometry.