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# Exsolution Process as a Route Towards Extremely Low Thermal Conductivity in

## $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$ Tetrahedrites

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### ABSTRACT

Achieving extremely low lattice thermal conductivity is an essential requirement to improving the performance of thermoelectric materials. Engineered nanostructures in bulk materials and the search for complex crystal structures that inherently poorly conduct heat are the two main areas of research being currently pursued to achieve this objective. Tetrahedrites, a class of widely-studied minerals, show intrinsically very low thermal conductivity values of the order of  $0.5 \text{ W m}^{-1} \text{ K}^{-1}$  at 300 K leading to interesting thermoelectric properties around 700 K. Here, we report on the low-temperature transport properties of a series of synthetic tetrahedrites  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  and demonstrate that, at low Te concentrations, an exsolution process sets in near 250 K resulting in the coexistence of two tetrahedrite phases, likely at the sub-micron length scale. Remarkably, this mechanism triggers a significant reduction of  $\sim 40 \%$  in the thermal conductivity, which drops to  $0.25 \text{ W m}^{-1} \text{ K}^{-1}$  below 200 K. This exceptionally low value ranks these materials among the least conductive structures reported so far. Because this mechanism is not restricted to low temperatures and has also been shown to occur in the ternary tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  around 373 K, these results suggest a new avenue for achieving extremely low lattice thermal conductivity in minerals.

## INTRODUCTION

Thermoelectric materials, that enable direct solid-state conversion of a temperature gradient into a voltage, have proven to reliably power deep-space probes over long time periods.<sup>1,2</sup> In addition, thermoelectric generators hold great promise as energy harvesters, converting waste heat into useful electricity without pollution for the environment.<sup>2</sup> This technology also finds applications as solid-state coolers for a wide variety of electronic instruments.<sup>2</sup> The efficiency of thermoelectric materials is governed by the dimensionless thermoelectric figure of merit defined as  $ZT = \alpha^2 T / \rho \kappa$ , where  $T$  is the absolute temperature,  $\alpha$  is the thermopower or Seebeck coefficient,  $\rho$  is the electrical resistivity and  $\kappa$  is the total thermal conductivity which is the sum of a lattice  $\kappa_L$  and an electronic contribution  $\kappa_e$  in non-magnetic solids.<sup>1</sup>

In order to maximize the energy conversion in thermoelectric devices, high  $ZT$  values at the operating temperature must be reached. This requires a fine-tuning of the three transport properties to obtain simultaneously high thermopower, low electrical resistivity, and low thermal conductivity. However, the inability to optimize independently these properties provides a difficult challenge to overcome. The necessity to tailor the electronic and the thermal transport led to the development of different strategies for either increasing the power factor  $\alpha^2 / \rho$  or for lowering the lattice thermal conductivity  $\kappa_L$ . In this last research area, the search and identification of compounds that inherently show very low  $\kappa_L$  values and the introduction of nanoscale precipitates able to scatter the heat-carrying acoustic phonons are the two main directions currently under scrutiny. Over the last years, the former led to the discovery of several families of promising thermoelectric materials such as, among others, the Zintl phases  $\text{Yb}_{14}\text{MnSb}_{11}$  and  $\text{Ca}_5\text{Al}_2\text{Sb}_6$ ,<sup>3-6</sup> Ge- and Si-based type-I clathrates,<sup>7-10</sup> Mo-based cluster compounds (e.g.  $\text{Ag}_x\text{Mo}_9\text{Se}_{11}$  with  $3.4 \leq x \leq 3.9$  or  $\text{Ag}_2\text{Tl}_2\text{Mo}_9\text{Se}_{11}$ )<sup>11-14</sup> or Tl-based compounds (e.g.  $\text{Ag}_9\text{TlTe}_5$  or  $\text{Tl}_{10-x}(\text{Sn,Pb})_x\text{Te}_6$ ).<sup>15-18</sup> The second approach has been

successfully applied to mainly lead chalcogenides,<sup>19-27</sup> and more recently extended to half-Heusler alloys for which phase separation provides a novel route to enhancing the  $ZT$  values.<sup>28-31</sup>

Mineralogy is another area in materials science where phase separation has been widely observed. In many cases, minerals unmix into two (or more) phases in the solid state upon cooling from high temperatures. This process, referred to as exsolution, often leads to the growth of lamellae or to the formation of Widmanstätten precipitates.<sup>32-34</sup> A particularly important class of natural minerals where this mechanism occurs is tetrahedrites whose general chemical formula can be written as  $A_{10}B_2X_4Y_{13}$  with  $A = \text{Cu}$  or  $\text{Ag}$ ,  $B =$  transition metals such as  $\text{Fe}$ ,  $\text{Ni}$ ,  $\text{Zn}$ ,  $\text{Mn}$ ,  $\text{Co}$  or  $\text{Hg}$ ,  $X = \text{Sb}$  or  $\text{As}$  and to a lesser extent  $\text{Bi}$  or  $\text{Te}$  and  $Y = \text{S}$  that can be partially substituted by a few percent of  $\text{Se}$ .<sup>35-37</sup>

These materials are the subject of an important ongoing research in thermoelectricity due to their compelling characteristics making them promising thermoelectric materials.<sup>35-45</sup> They are composed of relatively non-toxic and earth-abundant elements and a large variety of transition metals can substitute for  $\text{Cu}$ , providing several degrees of freedom for optimizing the power factor as demonstrated in recent studies on synthetic tetrahedrites  $\text{Cu}_{12-x}\text{B}_x\text{Sb}_4\text{S}_{13}$  ( $0 \leq x \leq 2$ ).<sup>38-48</sup> One of the most remarkable feature of these materials is their extremely low, glass-like thermal conductivity with values of the order of  $0.55 \text{ W m}^{-1} \text{ K}^{-1}$  above 300 K. This intriguing property has been recently shown to arise from the peculiar chemical environment of the  $\text{Cu}_2$  atoms (Figure 1) coordinated in a planar sulfur triangle along with active lone-pair electrons of  $\text{Sb}$  from either side of these atoms.<sup>49-51</sup> The large out-of-plane thermal vibrations of the  $\text{Cu}_2$  atoms give rise to a low-energy, strongly-anharmonic excess of vibrational modes in the phonon density of states, which is at the core of the glass-like thermal conductivity observed in these minerals.<sup>49</sup> The combination of both properties leads to good thermoelectric performances at high temperatures with maximum  $ZT$  values around 0.8 at 700 K. These

investigations have been extended to composite materials composed of a mixture of synthetic and natural tetrahedrites resulting in a peak  $ZT$  of 1.0 at 700 K in  $(\text{Cu}_{12}\text{Sb}_4\text{S}_{13})_{0.5}(\text{Cu}_{9.7}\text{Zn}_{1.9}\text{Fe}_{0.4}\text{As}_4\text{S}_{13})_{0.5}$ , which raises interesting prospects as for the direct use of natural ores in thermoelectric generators.<sup>41</sup>

With very few exceptions, the compounds investigated so far are quaternary derivatives of the ternary tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  that show significant deviations from this ideal stoichiometry and undergoes an exsolution process at  $\sim 403$  K resulting in a mixture of Cu-poor and Cu-rich phases stable at room temperature.<sup>35-37</sup> In recent investigations, we showed that the crystal structure and chemical composition of the  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  tetrahedrites depend sensitively on sample processing.<sup>47</sup> Likewise the ternary compound that exhibits deviations from the ideal stoichiometry, our results suggested the existence of off-stoichiometry in samples prepared with precursor materials, in contrast to samples synthesized directly from elemental powders that did not show any sign of such deviations. However, the influence of off-stoichiometry on the thermoelectric properties remained elusive above room temperature. Further, to the best of our knowledge, the influence of exsolution on the transport properties has never been addressed.

Herein, we provide compelling experimental evidence that an exsolution process develops near 250 K in quaternary synthetic tetrahedrites  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  and investigate its influence on the transport properties by means of low-temperature transport properties measurements and X-ray diffraction experiments. This phase separation upon cooling, which results in the coexistence of two tetrahedrite phases of close compositions, opens an additional phonon scattering channel that leads to an exceptionally low thermal conductivity value of  $0.25 \text{ W m}^{-1} \text{ K}^{-1}$  at 200 K, representing an impressive  $\sim 40$  % decrease over the values measured so far in tetrahedrites.

## EXPERIMENTAL

**Synthesis.** All synthetic procedures were carried out under controlled atmosphere in a dry, argon-filled glove box. All reactions and annealing steps were performed in evacuated quartz ampules, systematically preheated at 1173 K for several hours under dynamic vacuum to ensure dry conditions.

Two series of bulk polycrystalline samples  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  were prepared by distinct metallurgical routes. The first series, denoted S1 hereafter, with nominal compositions  $x = 1.0, 1.25, 1.50$  and  $1.75$  was prepared by using elemental powders of Cu (99.99%, ChemPur), S (99.999%, Strem Chemicals), Sb (99.999%, 5N Plus) and Te (99.999%, 5N Plus) as starting materials. In a first step, CuS and  $\text{Sb}_2\text{S}_3$  precursors were prepared from stoichiometric amounts of the above-mentioned elemental powders placed in quartz tubes sealed under secondary vacuum. The ampules were slowly heated up to 723 K and 843 K for CuS and  $\text{Sb}_2\text{S}_3$ , respectively, dwelt at those temperatures for 48h and 10h, respectively, and finally quenched in room-temperature water. The phase purity was verified via powder X-ray diffraction (PXRD) prior to use. The resulting ingots were thoroughly ground and, together with additional Cu and Te powders, were loaded in stoichiometric amounts into quartz ampules. These ampules were held at 923 K for 12h followed by a final quenching in room-temperature water.

The second series, labeled S2 hereafter, with nominal compositions  $x = 0.5, 1.0, 1.5$  and  $1.75$  was synthesized directly from elemental Cu, Sb, Te and S powders weighed in stoichiometric amounts. The mixed powders were transferred into quartz ampules sealed under secondary vacuum. The ampules were heated to 923 K at  $0.3 \text{ K}\cdot\text{min}^{-1}$ , then maintained at this temperature for 12h and eventually cooled down to room temperature at a rate of  $0.4$

K.min<sup>-1</sup>. These low heating and cooling rates were applied in order to avoid an excessive sulfur vapor pressure inside the tubes.

For both series, the resulting ingots were crushed into fine powders, cold-pressed into pellets and further annealed in quartz tubes at 723 K for at least 14 days and at 673 K for at least 7 days for the series S1 and S2, respectively. This long annealing time was found to be necessary to improve the crystallinity of the samples and to minimize the presence of secondary phases. After confirmation of the phase purity by PXRD and Rietveld refinements, the final product was ground into fine powders and densified in graphite dies by spark plasma sintering (SPS) at 723 K under 80 MPa for 10 min. The consolidated cylinders were 1 – 1.5 mm thickness and 10 mm in diameter. PXRD analyses were further performed on consolidated pellets to probe for possible thermal decomposition. The experimental density of all samples, determined from the mass and geometry of the pellets, was above 93% of the theoretical density.

**X-ray Diffraction.** Powder X-ray diffraction was carried out to assess phase purity with a Bruker D8 Advance X-ray diffractometer with monochromatic CuK $\alpha_1$  radiation ( $\lambda = 1.54056$  Å). Rietveld refinements against the data were performed with the Fullprof software. To follow the evolution of the crystal structure in temperature, PXRD experiments were conducted under vacuum between 300 and 100 K with steps of 50 K with an Xpert Pro MPD diffractometer (CuK $\alpha_1$   $\lambda = 1.54056$  Å and CuK $\alpha_2$   $\lambda = 1.54439$  Å, ratio K $\alpha_2$ / K $\alpha_1$  = 0.5).

**Chemical Homogeneity and Elemental Analysis.** The spatial distribution of the elements was assessed by element mapping using a Quanta FEG (FEI) scanning electron microscope (SEM). Images of the surface of the samples were collected in backscattered electron mode (BSE) to contrast the tetrahedrite phase from the impurity phases. Elemental analysis was performed on polished surfaces of bulk pieces by energy- and wavelength-dispersive spectroscopy (EDS/WDS) using a JEOL J7600F instrument. The chalcopyrite CuFeS<sub>2</sub>, ZnS,

Sb and Te were used as standards to probe the Cu, S, Sb and Te contents, respectively. Both CuFeS<sub>2</sub> and ZnS were chosen due to the similar atomic environments of Cu and S in these structures with respect to those in tetrahedrites, which allow minimizing matrix effects. The actual compositions were obtained from an average of 15 spots measured for each samples and by normalizing the chemical formulae to 13 sulfur atoms. Hereafter, we use the actual Te content to label the samples (see Table 1).

**Transport Properties.** The dense pellets were cut with a diamond wire-saw into bar-shaped samples of typical dimensions 2.5×3.0×8.0 mm<sup>3</sup>. Electrical resistivity, thermal conductivity and thermopower were simultaneously measured between 5 and 300 K with the thermal transport option (TTO) of a physical property measurement system (PPMS, Quantum Design). The contacts were realized by attaching four coppers leads on the samples using conducting silver epoxy. To ensure mechanically-stable contacts, the ensembles (sample + copper leads) were maintained for 20 minutes at 130°C. The data were corrected for thermal radiations by a model implemented in the TTO option software by Quantum Design. Despite this correction and the use of geometries favoring a high conductance, thermal radiations still give rise to a slight additional contribution to the measured thermal conductivity values above 250 K (estimated to ~ 0.1 W.m<sup>-1</sup>.K<sup>-1</sup> when comparing these data with those measured at high temperatures and presented in Ref. 44).

## RESULTS AND DISCUSSION

**Structural and Chemical Characterizations.** The variations with  $x$  in the crystal structure and chemical compositions of both series have been already discussed in detail in our prior study.<sup>47</sup> For this reason, we restrict this part to the information relevant for the discussion of the exsolution process and transport properties that follows.



The main difference observed between the samples of the two series is related to the evolution and the values of the lattice parameters  $a$ . In the series S1,  $a$  trends anomalously with the Te content, specifically in the  $x = 0.61$  and  $0.80$  samples for which, very high values are observed (Figure S1, Supporting Information). In contrast, the lattice parameters in the S2 series (Figure S1, Supporting Information) tend to increase monotonically with  $x$  up to  $x = 1.41$  before slightly decreasing for  $x = 1.85$ . Both the values and the overall increase in  $a$  with  $x$  with respect to  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  are consistent with prior investigations on tetrahedrites containing transition metals.<sup>38-48</sup>

These differences between the two series of samples are related to deviations of the actual chemical compositions from the nominal stoichiometry, which were revealed by EDX/WDX experiments. The measured compositions, listed in Table 1, show that significant deviations exist in the  $x = 0.61$  and  $0.80$  samples of the first series, the sum of the Sb and Te atomic concentrations largely exceeding the expected 4 atoms per formula unit. Such large values are not observed for the samples of the second series for which the sum is closer to 4 atoms per formula unit. Note that these deviations are not an artifact of the normalization to 13 sulfur atoms per formula unit. The high values of  $a$  in the  $x = 0.61$  and  $0.80$  samples reflect these deviations, which might be at the origin of the exsolution process. Although the exact reasons of these deviations remain unclear, the quenching process used in the series S1 might help stabilize non-stoichiometric compositions formed at high temperatures. Alternatively, we cannot rule out the possibility that the different chemical reactions between the series S1 and S2 result in a similar effect.

**Low-Temperature X-ray Diffraction.** The strongest experimental evidence of an exsolution process is provided by a comparison of the PXRD data collected at 300 and 100 K for the  $x = 0.61$  (series S1) and  $x = 0.52$  (series S2) specimens (Figure 2 and Figure S2 in the Supporting Information file). No significant changes in the  $x = 0.52$  sample are seen except for an overall

slight shift towards higher diffraction angles as a result of the unit cell contraction upon cooling. The situation is strikingly different in the  $x = 0.61$  sample for which all the reflections are doubled in the patterns collected at 100 K. All these additional reflections can be indexed to the  $I\bar{4}3m$  space group of tetrahedrites (Figure S2 in Supporting Information) and are thus not due to a decomposition of the main tetrahedrite phase into impurity phases. This peak splitting is a clear evidence of a separation of the room-temperature tetrahedrite phase into two tetrahedrite phases of distinct compositions. Additional data collected for the  $x = 0.61$  sample from 300 to 100 K with steps of 50 K indicates that the exsolution temperature lies between 200 and 250 K (Figure S3 in Supporting Information). This phase separation is also visible in the  $x = 0.80$  sample but no longer present at higher Te contents (Figure S4 in Supporting Information). A comparison of these patterns with those collected for the  $x = 1.01$  and 1.41 samples (Figure S5 in Supporting Information) clearly indicate the absence of exsolution in the series S2. Interestingly, among all the samples investigated, only the two samples ( $x = 0.61$  and  $x = 0.80$ ) that show large lattice parameters and thus, significant deviation from stoichiometry, exsolve. This difference in behavior suggests a direct link between off-stoichiometry and exsolution process in these compounds.

Rietveld refinements of the 100 K patterns for the  $x = 0.61$  sample revealed lattice parameters of 10.4035(2) and 10.3432(3) Å with an estimated ratio of the two phases of 75-25%. As revealed by data taken upon warming back to room temperature, the second series of peak completely disappear leaving the initial PXRD pattern as the only one visible. The reversibility of this transition together with the presence of two tetrahedrite phases of different lattice parameters is consistent with an exsolution process similar to that demonstrated in  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  near 400 K.<sup>35-37</sup> In this ternary compound, the lowest and highest values of the lattice parameters were assigned to Cu-poor and Cu-rich phases, respectively. In the present

case, a definitive conclusion about the two compositions could not be drawn as, in these quaternary compositions, the exsolution might impact both the Cu and Sb/Te concentrations.

We further tried to directly image the two tetrahedrite phases by performing SEM experiments at low temperatures. Unfortunately, BSE images did not enable us to clearly distinguish the two phases, of likely very close compositions, at 130 K. Nevertheless, these experiments did not evidence the disappearance of the small amount of Cu-rich secondary phases, which could have acted as a source of additional Cu atoms for the matrix. These results thus suggest that the resulting microstructure is likely composed of fine details at the sub-micron length scale. Further transmission electron microscopy experiments at low temperatures might help to get relevant information on the microstructure below the exsolution temperature.

**Transport properties.** In the following, we restrict our investigations to three samples of each series ( $x = 0.61, 0.80, 1.81$  and  $x = 0.52, 1.41, 1.85$  for the series S1 and S2, respectively) with the aim of highlighting the influence of the exsolution process on the transport properties. The temperature dependences of the electrical resistivity and thermopower are shown in Figures 3 and 4, respectively. Simple counting rules of valence electrons suggest that the stoichiometric tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$  is a *p*-type metal with two holes per formula unit, a result confirmed experimentally and theoretically by electronic band structure calculations.<sup>38,39,47</sup> Recently, the expected charge balance in tetrahedrites, that can be written as  $(\text{Cu}^{+1})_{10}(\text{Cu}^{2+})_2(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$  for  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ , has been experimentally confirmed by X-ray photoelectron spectroscopy.<sup>46</sup> In addition, prior investigations on Te-containing tetrahedrites have shown that Te atoms exhibit a +4 oxidation state.<sup>52,53</sup> Hence, the substitution of  $\text{Te}^{4+}$  for  $\text{Sb}^{3+}$  is expected to provide additional electrons that gradually drive the system from a metal to a semiconducting state that should develop for  $x = 2.0$ . The  $\rho(T)$  and  $\alpha(T)$  data of both series indeed show trends typical of heavily-doped semiconductors. At

300 K, the change in  $\rho$  and  $\alpha$  faithfully reflects the expected trend with a gradual increase with the Te content. For  $x \geq 1.40$ , the electrical resistivity increases over several orders of magnitude upon cooling indicative of semiconducting behavior. In the  $x = 0.61$  and  $0.80$  samples (series S1), the  $\rho$  values rise by one order of magnitude between 250 and 200 K *i.e.* in the temperature range where the exsolution process sets in. Measurement of the specific heat performed on the  $x = 0.61$  sample (Figure S6, Supporting Information) did not indicate the presence of an electronic phase transition that could be responsible for the sudden change observed in  $\rho(T)$ . The variations in  $\rho$  below 250 K can be thus solely attributed to the exsolution process. This is further corroborated by the transition which is clearly visible for  $x = 0.61$  but less pronounced in the  $x = 0.80$  sample in agreement with the low-temperature X-ray diffraction data (see Figure 2 and Figure S2 in Supporting Information).  $\alpha(T)$  is also impacted by this phase separation since, in these two samples, a significant deviation from linearity at 250 K is visible.

The most remarkable effect of the exsolution is seen in the thermal conductivity as a function of temperature (Figure 5). Regardless of the synthetic method used, all samples exhibit glass-like thermal conductivity and very low values of the order of  $0.6 \text{ W m}^{-1} \text{ K}^{-1}$  at 300 K. In the series S1, the upper limit of the electronic contribution  $\kappa_e$  (estimated by the Wiedemann-Franz law using a Lorenz number  $L = 2.44 \times 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$ ) amounts to  $0.1 \text{ W m}^{-1} \text{ K}^{-1}$  above 250 K in the  $x = 0.61$  and  $0.80$  samples. This contribution is thus negligible below this temperature due to the high electrical resistivity values measured in these samples. We can thus safely conclude that the measured  $\kappa$  almost entirely reflect the lattice contribution in the series S1 below 250 K. In the second series S2, the electronic contribution is however more significant in the  $x = 0.52$  and  $1.01$  samples due to their more pronounced metallic character. For the two other samples of this series, the higher  $\rho$  values yield a negligible  $\kappa_e$  component. Of note, a marked decrease occurs around 250 K for  $x = 0.61$  and  $x = 0.80$  (series S1) *i.e.* near

the exsolution temperature, while  $\kappa(T)$  smoothly decreases upon cooling for higher Te contents. At 200 K,  $\kappa$  reaches an extremely low value of  $0.25 \text{ W m}^{-1} \text{ K}^{-1}$  that remains nearly constant down to 75 K. As expected from the absence of exsolution in the series S2, the  $\kappa(T)$  curves do not show any sign of anomalous behavior besides the glass-like dependence inherent to these compounds.

The extreme values achieved at 200 K in the  $x = 0.61$  specimen represent a decrease of  $\sim 40 \%$  compared to those measured at 250 K and in the samples of the second series. This ranks this tetrahedrite among the best bulk, crystalline thermal insulators known to date  $\text{Ag}_9\text{TlTe}_5$  and  $\text{Gd}_{117}\text{Co}_{56}\text{Sn}_{112}$ , both exhibiting room-temperature  $\kappa_L$  values of 0.23 and  $0.28 \text{ W m}^{-1} \text{ K}^{-1}$ , respectively.<sup>16,54</sup> The separation below 250 K of the main tetrahedrite phase into two phases thus provides an additional and effective source of phonon scattering besides the strong anharmonicity present in tetrahedrites. Interestingly, the  $\kappa$  values reached below the exsolution threshold are lower than the theoretical minimum of the lattice thermal conductivity  $\kappa_m$  estimated to  $\sim 0.5 \text{ W. m}^{-1}.\text{K}^{-1}$  at 300 K using the model developed by Cahill.<sup>47,55,56</sup> This difference suggests that the phase separation results in a drastic reduction in the elastic moduli below 250 K and hence, in the transverse and longitudinal sound velocities used to estimate  $\kappa_m$ .

The present results demonstrate that an exsolution help to significantly lower the lattice thermal conductivity and one may naturally wonder whether this process can lead to enhanced thermoelectric performances. In the present case, owing to the rise in the electrical resistivity in the exsolved phase that counterbalances the drop in the thermal conductivity, this phase separation does not give rise to enhanced  $ZT$  values. Yet, this is not to say that this process does not deserve further attention since an exsolution is neither restricted to low temperatures nor to tetrahedrites. Besides the pyroxene minerals for which this process occurs at high temperatures,<sup>32-34</sup> another family of minerals with interesting thermoelectric properties named

colusites shows similar phase separation.<sup>57,58</sup> Because rapid quenching of the high-temperature melt can prevent the exsolution in some systems, comparison between exsolved and single-phase materials may provide useful insights into the role played by this mechanism on the thermal transport of minerals and may tell us whether an increase in  $ZT$  can be achieved thanks to this mechanism.

## CONCLUSION

We reported on the basic crystallographic features and the low-temperature transport properties of two series of synthetic tetrahedrites  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  that harbor interesting thermoelectric properties at high temperatures. The low-temperature transport properties depend on the synthesis method used to prepare the samples, the use of precursor materials resulting in significant off-stoichiometry in the final composition. Our experimental findings suggested a possible link between off-stoichiometry and exsolution process that occurs below 250 K for tetrahedrites with low Te contents. PXRD experiments carried out down to 100 K clearly evidenced the separation of the main phase into two tetrahedrite phases below 250 K in a way similar to that observed in early studies on the ternary tetrahedrite  $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ . The presence of this phase separation has a profound influence on the thermal transport. Our results revealed a significant reduction in the thermal conductivity values of  $\sim 40\%$  once the tetrahedrite phase has exsolved. The coexistence of the two phases gives rise to enhanced phonon scattering that naturally explains the remarkable drop observed. Because this mechanism is general and is restricted neither to a particular temperature range nor to tetrahedrites, these results might be applicable to other families of minerals, possibly providing an avenue for optimizing their thermoelectric performances.

## ASSOCIATED CONTENT

**Supporting Information.** Lattice parameter as a function of the Te content in both series; Rietveld analyses of the PXRD patterns of the  $x = 0.61, 0.80$  (series S1) and  $x = 0.52, 1.01$  and  $1.41$  (series S2) at 100 and 300 K; evolution of the PXRD pattern of the  $x = 0.61$  sample from 300 to 100 K; temperature dependence of the specific heat of the  $x = 0.61$  sample. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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## TABLE

Table 1. Nominal and actual compositions determined on the series S1 and S2 of polycrystalline  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  tetrahedrites. The chemical formulae were normalized to 13 sulfur atoms per formula unit.

<i>Series S1</i>		<i>Series S2</i>	
<i>Nominal composition</i>	<i>Actual composition</i>	<i>Nominal composition</i>	<i>Actual composition</i>
$\text{Cu}_{12}\text{Sb}_3\text{Te}_1\text{S}_{13}$	$\text{Cu}_{12.24}\text{Sb}_{3.78}\text{Te}_{0.61}\text{S}_{13}$	$\text{Cu}_{12}\text{Sb}_{3.5}\text{Te}_{0.5}\text{S}_{13}$	$\text{Cu}_{12.37}\text{Sb}_{3.50}\text{Te}_{0.52}\text{S}_{13}$
$\text{Cu}_{12}\text{Sb}_{2.75}\text{Te}_{1.25}\text{S}_{13}$	$\text{Cu}_{12.44}\text{Sb}_{3.73}\text{Te}_{0.80}\text{S}_{13}$	$\text{Cu}_{12}\text{Sb}_3\text{Te}_1\text{S}_{13}$	$\text{Cu}_{12.39}\text{Sb}_{3.16}\text{Te}_{1.01}\text{S}_{13}$
$\text{Cu}_{12}\text{Sb}_{2.5}\text{Te}_{1.5}\text{S}_{13}$	$\text{Cu}_{12.51}\text{Sb}_{2.82}\text{Te}_{1.40}\text{S}_{13}$	$\text{Cu}_{12}\text{Sb}_{2.5}\text{Te}_{1.5}\text{S}_{13}$	$\text{Cu}_{12.41}\text{Sb}_{2.73}\text{Te}_{1.41}\text{S}_{13}$
$\text{Cu}_{12}\text{Sb}_{2.25}\text{Te}_{1.75}\text{S}_{13}$	$\text{Cu}_{11.98}\text{Sb}_{1.96}\text{Te}_{1.81}\text{S}_{13}$	$\text{Cu}_{12}\text{Sb}_{2.25}\text{Te}_{1.75}\text{S}_{13}$	$\text{Cu}_{11.97}\text{Sb}_{2.40}\text{Te}_{1.85}\text{S}_{13}$



## FIGURE CAPTIONS

**Figure 1.** (Left figure) Crystal structure of the  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  tetrahedrites that crystallize in the  $I\bar{4}3m$  space group. The Cu1 and Cu2 atoms are in red and yellow, respectively. The S1 and S2 atoms are in light grey and black, respectively, while the Sb atoms are in blue. (Right figure) Chemical environment of the Cu2 atoms drawn in ellipsoid representation (at the 95 % probability level) according to the thermal displacement parameter of each atom.

**Figure 2.** Rietveld refinements of the PXRD data collected at 100 and 300 K for  $x = 0.61$  (series S1, panels a and b) and  $x = 0.52$  (series S2, panels c and d). The full spectra are provided in Supporting Information.

**Figure 3.** (a) Temperature dependence of the electrical resistivity  $\rho$  of the synthetic  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  tetrahedrites for  $x = 0.61, 0.80$  and  $1.40$  (series S1). The panel (b) shows a magnification to highlight the rise in the electrical resistivity at the exsolution temperature. (c)  $\rho$  data measured for  $x = 0.52, 1.01$  and  $1.41$  (series S2).

**Figure 4.** Thermopower  $\alpha$  as a function of temperature for the  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  series S1 (a) and S2 (b).

**Figure 5.** Thermal conductivity  $\kappa$  as a function of temperature for the  $\text{Cu}_{12}\text{Sb}_{4-x}\text{Te}_x\text{S}_{13}$  series S1 (a) and S2 (b).

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