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Chapter 4

Tetrahedrites: Prospective Novel Thermoelectric Materials

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Additional information is available at the end of the chapter

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Abstract

Since their discovery in 1845, tetrahedrites, a class of minerals composed of relatively earth-abundant and nontoxic elements, have been extensively studied in mineralogy and geology. Despite a large body of publications on this subject, their transport properties had not been explored in detail. The discovery of their interesting high-temperature thermoelectric properties and peculiar thermal transport has led to numerous experimental and theoretical studies over the last 4 years with the aim of better understanding the relationships between the crystal, electronic, and thermal properties. Tetrahedrites provide a remarkable example of anharmonic system giving rise to a temperature dependence of the lattice thermal conductivity that mirrors that of amorphous compounds. Here, we review the progress of research on the transport properties of tetrahedrites, highlighting the main experimental and theoretical results that have been obtained so far and the important issues and questions that remain to be investigated.

Keywords: tetrahedrites, thermoelectric, thermal conductivity, exsolution, composite

1. Introduction

Thermoelectric effects provide a reliable way for converting waste heat into useful electricity and vice versa [1, 2]. This solid-state conversion process is realized without hazardous gas emissions and moving parts, ranking this technology among clean and sustainable energy sources. Thermoelectric generators have been successfully used to reliably power deep-space probes and rovers over several decades, and have been used as solid-state coolers for electronic devices [1, 2]. Yet, a widespread use of this versatile technology is hampered by the rather low conversion efficiency achieved. The thermoelectric efficiency, with which a

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thermoelectric device converts heat into electricity and vice versa is directly dependent of the dimensionless figure of merit ZT of the active thermoelectric legs [1, 2]. This parameter is defined at an absolute temperature T as $ZT = \alpha^2 T / \rho(\kappa_L + \kappa_e)$, where α is the thermopower (or Seebeck coefficient), ρ is the electrical resistivity, and κ_L and κ_e are the lattice and electronic thermal conductivities, respectively. Thus, a good thermoelectric material should possess a combination of high thermopower to produce a sizeable thermoelectric effect, low electrical resistivity to avoid Joule effect, and low thermal conductivity to maintain a large thermal gradient across the device [3, 4].

While quite simple at first sight, this expression however underlies a formidable material challenge since the ideal thermoelectric material should be concomitantly a thermal insulator and an electrical conductor. The question is therefore how far these two seemingly conflicting aspects can be reconciled within the same material. The quest for this long-sought ideal material has led to thousands of experimental and theoretical investigations on a large number of material's families and on the possibilities to optimize their thermoelectric performances through various strategies such as the optimization of the carrier concentration by doping or the reduction of the lattice thermal conductivity via substitutions or nanostructuring [1–4]. These studies have increased the number of known crystalline compounds that show the remarkable ability to conduct heat akin to glassy systems [5–14]. In addition to being ideal systems for improving our understanding of the physical mechanisms leading to this behavior, these materials provide interesting playgrounds to achieve high thermoelectric performances. When the lattice thermal conductivity is intrinsically lowered to a value close to the theoretical minimum value, the electrical resistivity and thermopower remain the only key properties to be optimized to reach high ZT values.

This approach has led to the identification of several new families of thermoelectric materials, some of which exhibiting thermoelectric performances that surpass those of the state-of-the-art thermoelectric materials such as PbTe or $Si_{1-x}Ge_x$ alloys at moderate and high temperatures, respectively [2, 5–14]. Among these new families, tetrahedrites have recently draw attention due to the relatively nontoxic, earth-abundant elements that enter their chemical composition [15]. These compounds are a class of copper antimony sulfosalt minerals geologically formed in hydrothermal veins at low-to-moderate temperatures making them abundant in the Earth's crust. Tetrahedrites are minor ores of copper that were first discovered in 1845 in Germany. While they were the subject of a large number of experimental and theoretical studies in geology and mineralogy, it is not until recently, however, that their transport properties have been investigated in detail [15, 16]. Both natural and synthetic tetrahedrites, i.e., synthesized in laboratory environment, have been recently studied indicating that these compounds are interesting candidates for thermoelectric applications in power generation.

This chapter provides an updated review on the experimental and theoretical results obtained and an overview of the status of the research activities on the thermoelectric properties of these materials. Our goal is to highlight the important structural and chemical aspects that influence their transport properties and thus play a role in their thermoelectric performances. This review will also cover the first experimental attempts at scaling-up the synthesis process via chemical or metallurgical approaches.

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2. Crystal structure and chemical composition

The general chemical formula of tetrahedrites can be written as $A_{12}X_4Y_{13}$, where A is mainly Cu that can be partially substituted by transition metals (Ag, Zn, Fe, Ni, Co, Mn, and Hg), X is a pnictide (Sb or As with possible partial substitution by Te or Bi), and Y is sulfur (S can be substituted in small quantities by Se). All these elements can be found in the chemical composition of natural tetrahedrites and numerous experimental and theoretical studies in geology and mineralogy focused on the link between their composition and the geological place where they were discovered.

With no exceptions, all tetrahedrites, should they be natural or synthetic, crystallize within a cubic crystal structure described in the $I\bar{4}3m$ space group with 58 atoms per unit cell (**Figure 1**) [17, 18]. The different A, X, and Y elements are distributed over five distinct crystallographic sites. Taking the ternary compound $Cu_{12}Sb_4S_{13}$ as an example, the copper atoms possess two different chemical environments. The Cu1 atoms show a tetrahedral coordination with three S and one surrounding Sb atoms. The Cu2 atoms lie within a triangular environment formed by three sulfur atoms in a nearly coplanar coordination. Twelve of the 13 S atoms exhibit a tetrahedral environment while the remaining S atom is surrounded by six Cu atoms forming an octahedron. The main peculiarity of this crystal structure is related to the Cu2 atoms that show large and anisotropic atomic thermal displacement parameters (ADPs), i.e., a strong ability to vibrate about their equilibrium position (see **Figure 1**) [19]. In addition, the tetrahedral environment of the Sb atoms lacks one sulfur atom to be complete. The presence of only three S atoms thus gives rise to 5s lone pair electrons on the Sb atoms. These "free" electrons can be oriented along the missing vertex of the tetrahedron according to the valence shell electron pair repulsion theory. Several studies have pointed out the decisive influence of lone pair electrons on the thermal conductivity, the delocalization of the lone pair away from the Sb nucleus yielding anharmonic forces in the lattice [20–22]. As we shall see below, a similar situation is probably at play in tetrahedrites, explaining their extremely low lattice thermal conductivity values.

While the crystal structure of tetrahedrites is simple to describe, their chemical composition displays some subtleties that make these compounds particularly interesting. Specifically, synthetic tetrahedrites often show deviations from stoichiometry, a characteristic usually absent in natural specimens that possess the exact 12–4–13 composition to within the detection limits of the instruments used [23–26]. The most prominent example of such behavior is provided by the ternary compound $Cu_{12}Sb_4S_{13}$, which has been the subject of thorough experimental studies in the 1970s [23–26]. These investigations have shown that the chemical composition of this compound is best described by the general chemical formula $Cu_{12+x}Sb_{4+y}S_{13}$ with $0.08 \leq x \leq 1.72$ and $0.06 \leq y \leq 0.30$ [23, 24]. This formula indicates that an excess of Cu is systematically observed together with a possible excess on the Sb sites, both of which depend on the synthesis conditions. These deviations are clearly correlated to the lattice parameter: an increase in either the Cu or Sb content always expands the unit cell from 10.327 Å for $(x, y) = (0.08, 0.06)$ up to 10.448 Å for $(x, y) = (1.72, 0.09)$. In addition to these deviations from the ideal stoichiometry, the ternary compositions undergo an exsolution process, i.e., a separation of the main tetrahedrite phase into two tetrahedrite phases of close compositions below the

so-called exsolution temperature [23, 24]. Such phase separation has been widely observed in minerals and often results in lamellar microstructures. In $Cu_{12+x}Sb_{4+y}S_{13}$, this process occurs below about 120°C, the exact value slightly varying with the chemical composition [23, 24]. Below this temperature, Cu-rich and Cu-poor phases coexist, the lattice parameters of both phases differing significantly from each other. This mechanism is reversible and disappears upon heating above 120°C to show up again upon cooling back below this temperature.

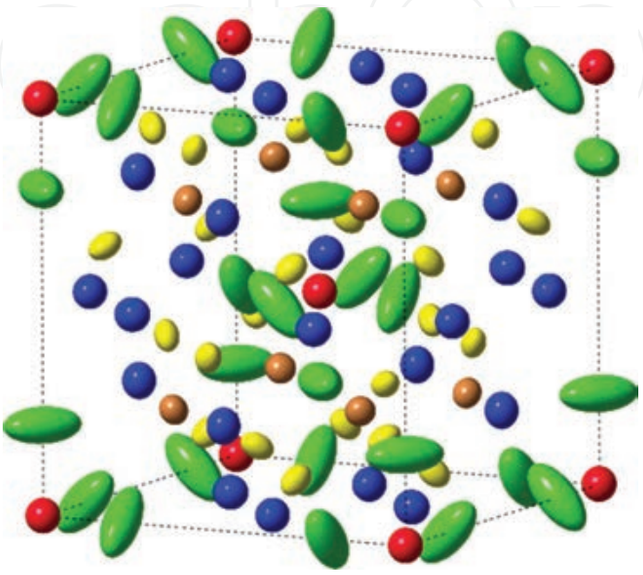


Figure 1. Perspective view of the crystal structure of $Cu_{12}Sb_4S_{13}$ in the ellipsoidal representation (drawn at the 95% probability level). The Cu1 and Cu2 atoms are in blue and green, respectively. Sb atoms are shown in brown while S1 and S2 atoms are in yellow and red, respectively.

3. Electronic properties

While the chemical and structural trends in natural and synthetic tetrahedrites are rather well understood, their transport properties have been investigated in detail only very recently [15, 16]. In order to better understand why these materials may be interesting for thermoelectric applications, it is helpful to assume that the atomic bonds are purely ionic. Within this assumption, the general chemical formula may be rewritten as $(Cu^{+})_{10}(Cu^{2+})_2(Sb^{3+})_4(S^{2-})_{13}$ which corresponds to 204 valence electrons per chemical formula [27]. From an electronic point of view, these valence electrons do not entirely fill the valence bands leaving two holes per formula unit. The ternary compound is thus predicted to behave as a *p*-type metal. This metallic state can nevertheless be driven toward a semiconducting state when two electrons per chemical formula are added (resulting in a total of 208 valence electrons per chemical formula) [27]. This progressive filling thus leads to highly doped semiconducting states more favorable to achieve high thermoelectric performances. Further, based on this simple electronic structure model, it was argued that natural tetrahedrites crystallize preferentially with a composition that corresponds to 208 valence electrons in agreement with the results based on a large survey of the literature data [27]. In particular, this model predicts that metallic compositions are energetically less favorable which might explain why $Cu_{12}Sb_4S_{13}$ tends to exsolve into Cu-poor and Cu-rich phases.

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The first experimental results on the transport properties of the ternary tetrahedrite $Cu_{12}Sb_4S_{13}$ have been reported by Suekuni et al. [15] who measured the temperature dependence of the magnetic susceptibility, electrical resistivity, thermopower, and thermal conductivity between 5 and 350 K (**Figure 2**). The results have shown that this compound exhibits several interesting features. A first one is a metal-insulator transition that sets in near 85 K and leaves clear signatures on the transport and magnetic properties. Below this temperature, the electrical resistivity significantly increases by approximately two orders of magnitude upon cooling from 85 to 5 K. A concomitant strong increase in the thermopower values from 25 μV K^{-1} at 85 K to 100 μV K^{-1} at 60 K further corroborates a semiconducting-like state of the low-temperature phase. The thermal conductivity drops below the transition temperature due to both a reduced electronic contribution as a result of the increase in ρ and to the influence of this transition on the lattice thermal conductivity. The magnetic susceptibility, indicative of paramagnetic behavior across the entire temperature range, suddenly drops below about 100 K.

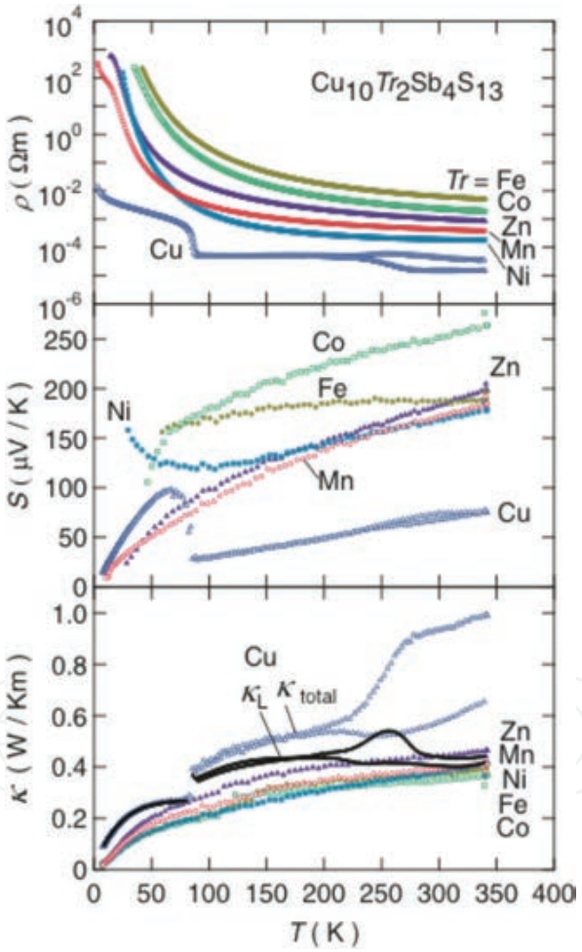


Figure 2. Temperature dependence of the electrical resistivity, thermopower, and total thermal conductivity of the tetrahedrite $Cu_{10}Tr_2Sb_4S_{13}$ (*Tr* = Cu, Fe, Co, Ni, Zn, and Mn). Copyright 2012 by the Japan Society of Applied Physics.

Using low-temperature powder X-ray diffraction measurements, May et al. [28] demonstrated that this transition is accompanied by a cubic-to-tetragonal lattice distortion characterized by an in-plane ordering that doubles the unit cell volume (**Figure 3**). The low-temperature crystal

structure has been described in the $P\bar{4}$ space group using a supercell model $\sqrt{2}a \times \sqrt{2}a \times c$. Owing to the high number of atomic position parameters to be refined (83), the crystal structure could not be entirely solved and remains to be determined in future studies.

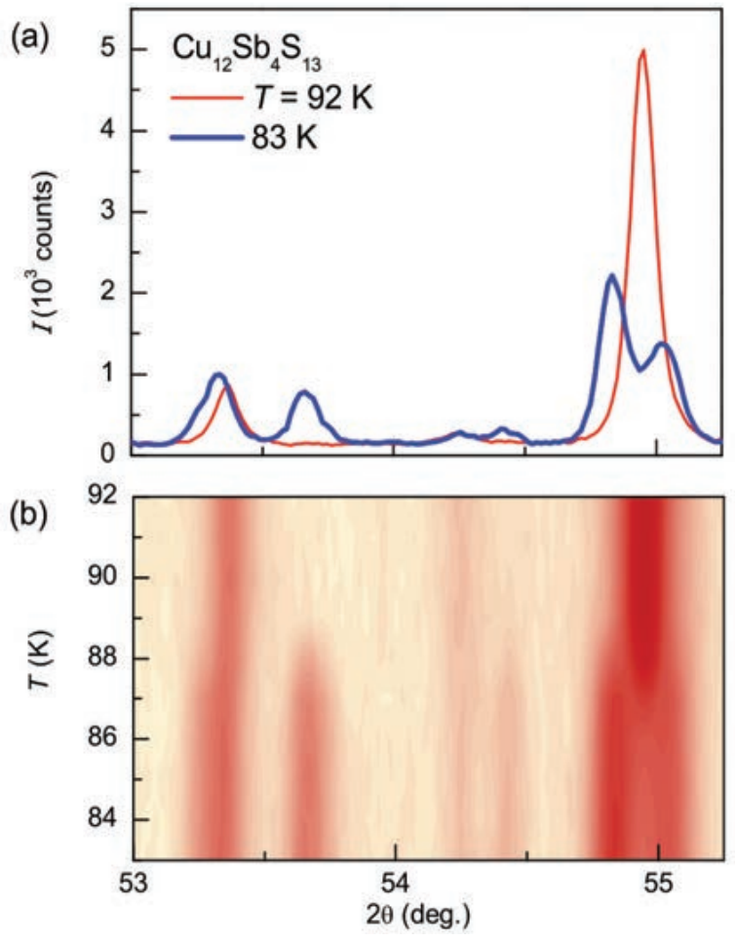


Figure 3. (Panel a) Powder X-ray diffraction pattern collected upon cooling across the 85 K phase transition in $Cu_{12}Sb_4S_{13}$. The appearance of additional Bragg reflections (Panel b) is indicative of the cubic-to-tetragonal structural transition that accompanies the metal-insulator transition. Reproduced **Figure 1** with permission from May et al. [28]. Copyright 2016 by the American Physical Society. DOI: 10.1103/PhysRevB.93.064104.

Kitagawa et al. [29] further investigated the metal-to-insulator transition through measurements of the electrical resistivity and magnetic susceptibility at high pressures (up to 4.06 GPa) and of the ^{63}Cu-NMR spectra. The results evidence a transition from a paramagnetic bad metal to a nonmagnetic insulating state below 85 K at ambient pressure. The nonmagnetic ground state evolves toward a metallic state under pressure. Tanaka et al. [30] further investigated the pressure dependence of this transition as well as its evolution upon substituting As for Sb ($Cu_{12}Sb_{4-x}As_xS_{13}$). In agreement with the study of Kitagawa et al., the transition is suppressed under pressure. The substitution of As for Sb that decreases the unit cell volume acts similarly and supresses the transition for relatively low substitution levels ($x \leq 0.5$).

In their initial study on $Cu_{12}Sb_4S_{13}$, Suekuni et al. [15] have also reported the transport properties of several tetrahedrites $Cu_{10}Tr_2Sb_4S_{13}$ with Cu substituted by various transition metals

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(*Tr* = Ni, Zn, Co, Fe, or Mn) (see **Figure 2**). In agreement with the aforementioned simple ionic model, all these quaternary tetrahedrites exhibit semiconducting-like properties characterized by an activated-like temperature dependence of the electrical resistivity and high thermopower values. Further, all samples display extremely low thermal conductivity values of the order of 0.4 W m^{-1} K^{-1} at 300 K regardless of the nature of the transition metal. However, although this study has demonstrated that a semiconducting state can be achieved thanks to substitution on the Cu site, the too high electrical resistivity values measured preclude achieving high *ZT* values. In order to optimize the thermoelectric properties, it thus appears necessary to adjust the concentration of the transition metal to optimize the hole concentration and hence, the power factor. This strategy was at the core of the study reported by Lu et al. [16] who reported high-temperature transport properties measurements on the tetrahedrites $Cu_{12-x}Fe_xSb_4S_{13}$ and $Cu_{12-x}Zn_xSb_4S_{13}$. This investigation has demonstrated for the first time that high thermoelectric performances could be achieved around 700 K with maximum *ZT* values of 0.8 for the composition $Cu_{11.5}Fe_{0.5}Sb_4S_{13}$.

These encouraging results led other groups to investigate in detail the influence of several transition metals on the crystal structure and the high-temperature thermoelectric properties [31–41]. All these studies have confirmed the main traits of these compounds, i.e., a favorable combination of intrinsically extremely low thermal conductivity values and semiconducting-like electrical properties that can be tuned by varying the concentration of the substituting element. Peak *ZT* values ranging between 0.7 and 0.9 around 700 K were achieved in Ni-, Co-, or Mn-substituted tetrahedrites. The highest *ZT* value of 1.1 at 575 K has been reported by Heo et al. [33] in Mn-substituted tetrahedrites. This value, not reproduced independently so far to the best of our knowledge, mainly originates from thermal conductivity values twice lower than usually measured in these materials. Further investigations seem necessary before drawing a definitive conclusion on the validity of this high value.

Lu et al. [39] explored the possibility to substitute Te for Sb and showed that Te also provides additional electrons that enable optimizing the power factor. As a result, a maximum *ZT* value of 0.92 at 723 K has been achieved for the composition $Cu_{12}Sb_3TeS_{13}$. Bouyrie et al. [38] further extended these investigations and synthesized Te-containing tetrahedrites by considering two different synthetic routes: using precursor compounds (CuS, Sb_2S_3, and Te) and from direct reaction of pure elemental powders, both syntheses being performed in evacuated and sealed silica tubes. Surprisingly, the results have evidenced that both routes are not strictly equivalent indicating that the final chemical compositions could be sensitive to the synthesis conditions used. The differences between the two series of samples was revealed by significantly higher lattice parameters for Te-concentrations below $x = 1.5$ in the series of samples prepared from precursors (**Figure 4**).

In the series of samples synthesized from direct reaction of the elements, the lattice parameter monotonically increases in a linear manner with increasing the Te-content. While this difference does not seem to affect the thermoelectric performances at high temperatures, the measurements of the low-temperature transport properties showed that these quaternary tetrahedrites undergo an exsolution process at 250 K [42]. This phenomenon has a drastic influence on the transport properties and more particularly on the thermal transport. Below

the exsolution temperature, the lattice thermal conductivity drops significantly by 40% reaching values as low as 0.25 W m^{-1} K^{-1} around 200 K (**Figure 5**). This behavior, which seems to be tied to the large lattice parameters of these samples, is not present in the series of samples prepared by direct reaction of the elements. The exact origin of these differences is not yet settled and requires further investigations. In addition, low-temperature transmission electron microscopy experiments on the Te-containing tetrahedrites would be helpful in determining the microstructure and perhaps the chemical composition of the two exsolved phases.

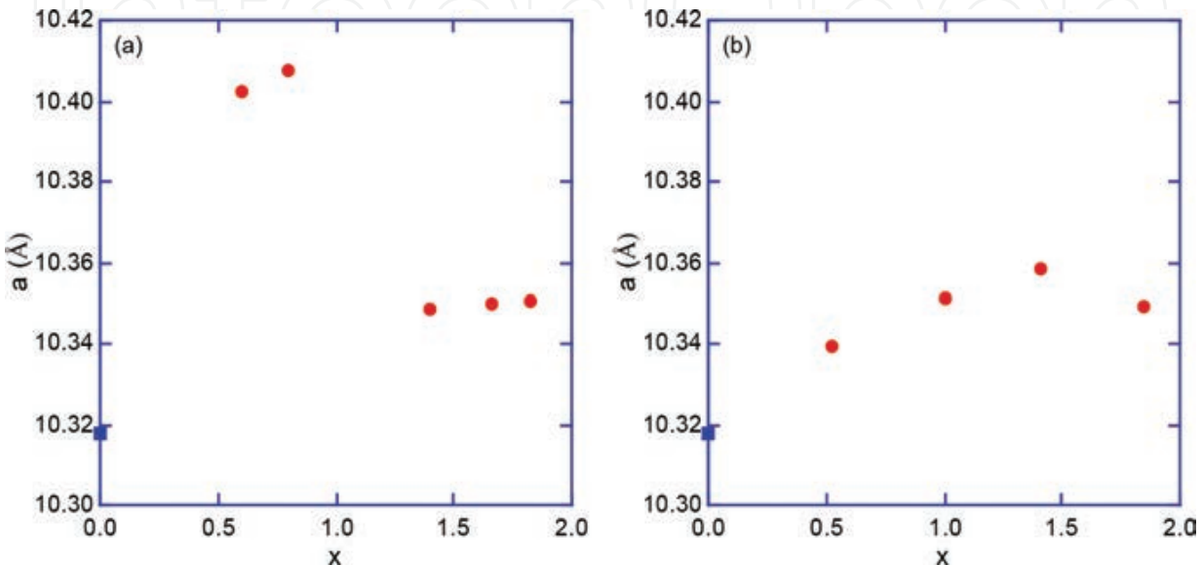


Figure 4. Lattice parameter *a* as a function of the actual Te content *x* for the series of samples prepared from precursors (a) and directly from reaction of elemental powders (b). As a reference, the lattice parameter of the ternary compound $Cu_{12}Sb_4S_{13}$ (filled blue square) has been added. Reproduced from Ref. [38] with permission from The Royal Society of Chemistry.

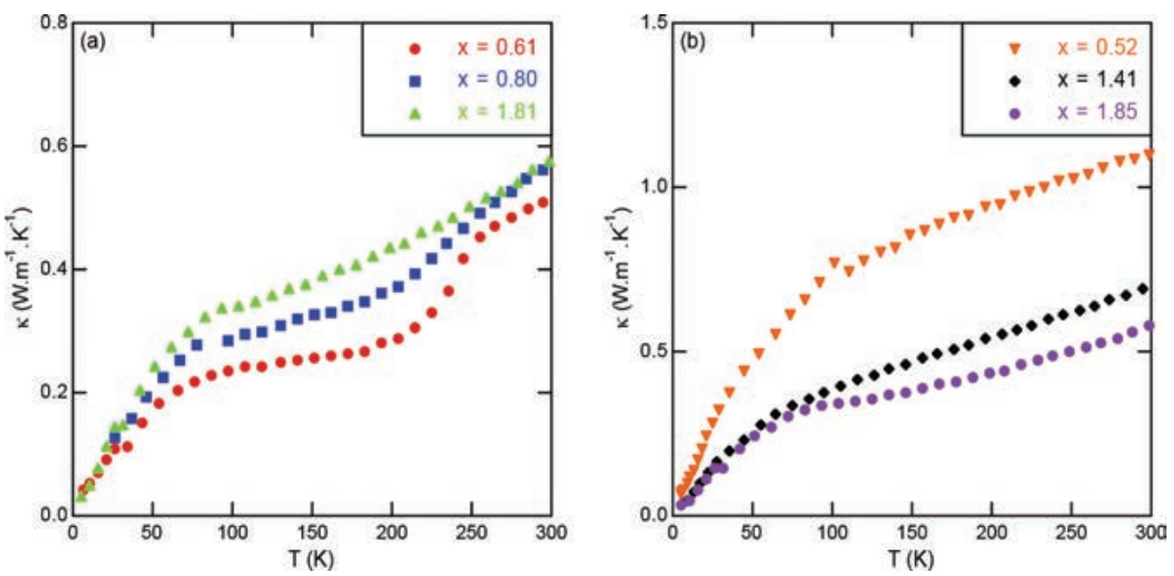


Figure 5. Temperature dependence of the total thermal conductivity for the samples prepared from precursors (a) and from reaction of elemental powders (b). For the first series, the exsolution process results in a significant drop in the thermal conductivity values near 250 K (panel a). Reprinted (adapted) with permission from Bouyrie et al. [42]. Copyright 2015 by the American Chemical Society.

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The possibility to substitute on the S site has only been recently considered by Lu et al. [43] who reported a detailed study on the $Cu_{12}Sb_4S_{13-x}Se_x$ tetrahedrites. Although a maximum *ZT* value of 0.9 was achieved for $x = 1$, these authors have shown that the presence of selenium tends to result in phase separation yielding samples with rather poor chemical homogeneity.

While all these studies focused on the influence of a single isovalent or aliovalent substitution on the thermoelectric properties, only few works have been devoted so far to double substitutions. Lu et al. [40] have extended their investigations to double-substituted tetrahedrites with Ni and Zn substituting for Cu. These authors have shown that this combination of elements results in higher thermoelectric performances with a peak *ZT* value of 1 at 700 K. Of note, this increase was mainly due to increased thermopower values while maintaining the electrical resistivity to relatively low values. These results suggest that judicious combinations of elements substituting for Cu can lead to improved thermoelectric properties. Following these ideas, Bouyrie et al. [41, 44] have investigated double substitutions on both the Cu and Sb sites with Co and Te, respectively. The presence of Co and Te did not result in enhanced thermoelectric performances with respect to the single-substituted compounds with a maximum *ZT* value of 0.8 at 673 K achieved in $Cu_{11.47}Co_{0.82}Sb_{3.78}Te_{0.41}S_{13}$.

4. Thermal properties

In addition to being one of the key ingredients that leads to high *ZT* values, the extremely low lattice thermal conductivity of tetrahedrites is a remarkable property on its own. Both the values measured and the temperature dependence of the lattice thermal conductivity are reminiscent to those observed in amorphous systems (**Figure 6**) [45].

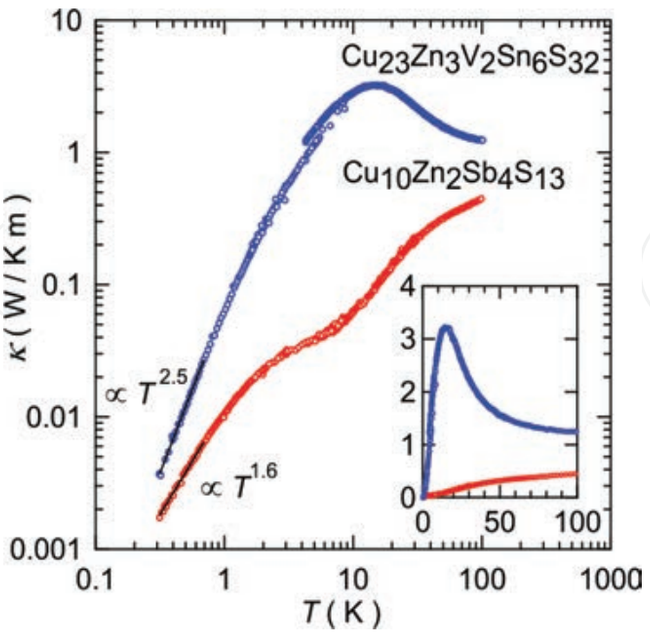


Figure 6. Temperature dependence of the total thermal conductivity of the tetrahedrite $Cu_{10}Zn_2Sb_4S_{13}$ and of the colusite $Cu_{23}Zn_3V_2Sn_6S_{32}$. The temperature dependence observed in the tetrahedrite below 1 K is similar to that observed in glassy SiO_2. Copyright 2015 by the Physical Society of Japan (Suekuni et al. [45]).

The large and anisotropic thermal displacement parameters of the Cu2 atoms had been thought to play a major role in disrupting efficiently the heat-carrying acoustic waves. A detailed study of the lattice dynamics of tetrahedrites has been undertaken recently using a combination of inelastic neutron scattering on poly- and single-crystalline tetrahedrites [46]. The conventional temperature dependence of the lattice thermal conductivity in the Cu-deficient tetrahedrite $Cu_{10}Te_4S_{13}$ offered an interesting experimental platform to unveil the microscopic mechanisms responsible for the low, glass-like thermal conductivity of tetrahedrites (**Figure 7**).

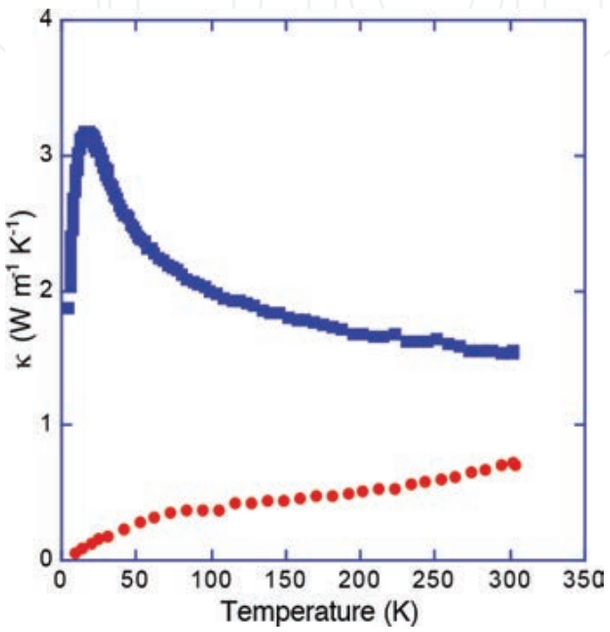


Figure 7. Temperature dependence of the total thermal conductivity of the tetrahedrites $Cu_{12}Sb_2Te_2S_{13}$ (red filled circles) and $Cu_{10}Te_4S_{13}$ (blue filled squares). Adapted from Ref. [46] with permission from the PCCP Owner Societies.

Bouyrie et al. [46] carried out a comparison study between this compound and the tetrahedrite $Cu_{12}Sb_2Te_2S_{13}$ that behaves as a glassy system. Despite adopting the same crystal structure, the contrast between the thermal transports in these compounds suggests that distinct microscopic mechanisms are at play.

A first important difference between these two compounds was found in the temperature dependence of the ADPs of the Cu2 atoms investigated by laboratory X-ray diffraction on single crystals. The ADPs inferred in $Cu_{10}Te_4S_{13}$ were nearly three times smaller than those observed in $Cu_{12}Sb_2Te_2S_{13}$ providing a first experimental hint of the direct link between the thermal vibrations of the Cu2 atoms and the lattice thermal conductivity. Further decisive evidences were delivered by inelastic neutron scattering and Raman spectroscopy performed on polycrystalline samples of $Cu_{10}Te_4S_{13}$ and $Cu_{12}Sb_2Te_2S_{13}$ between 2 and 500 K. The results showed the presence of an excess of vibrational density of states at low energies in $Cu_{12}Sb_2Te_2S_{13}$, which is clearly absent in the isostructural compound $Cu_{10}Te_4S_{13}$ (**Figure 8**). This finding is consistent with recent INS measurements performed by May et al. [28] on the ternary compound $Cu_{12}Sb_4S_{13}$. The temperature dependence of this low-energy excess of vibrational states further indicates that this excess can be unambiguously attributed to the thermal vibrations of the

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Cu2 atoms. Upon cooling, this excess experiences a strong renormalization of its characteristic energy, which shifts significantly toward lower energies. This dependence, at odds with a conventional quasi-harmonic behavior, indicates a strongly anharmonic character of this excess.

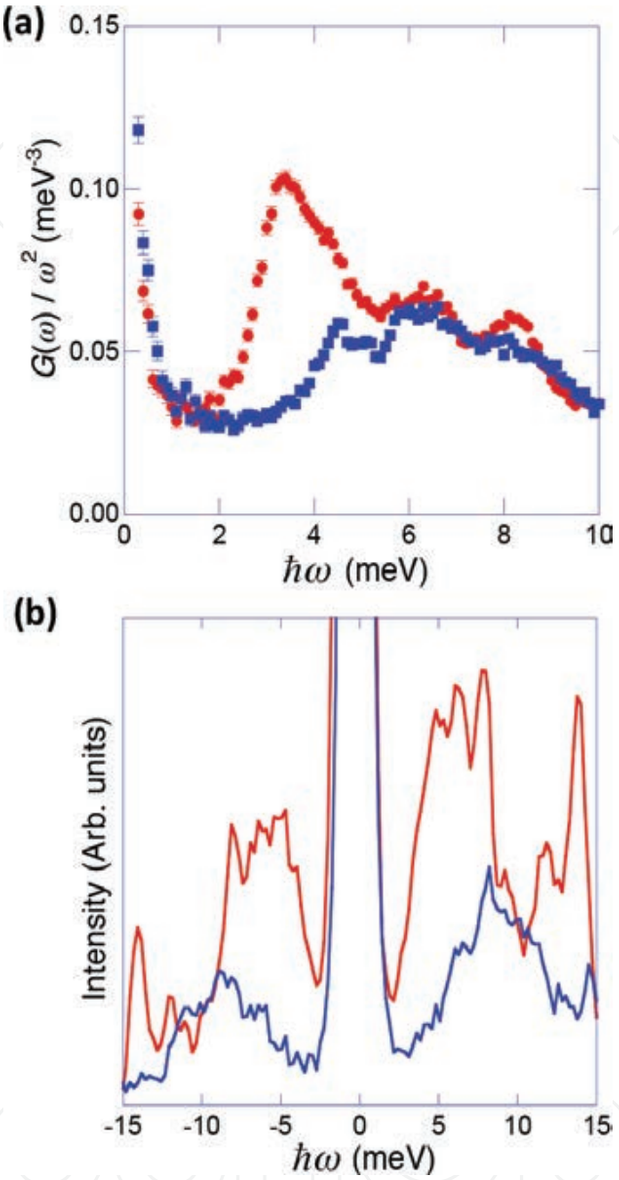


Figure 8. (a) Generalized phonon density of states measured at room temperature on the tetrahedrites $Cu_{12}Sb_2Te_2S_{13}$ (red filled circles) and $Cu_{10}Te_4S_{13}$ (blue filled squares). A clear excess at low energies is present in $Cu_{12}Sb_2Te_2S_{13}$. (b) Raman spectra of $Cu_{12}Sb_2Te_2S_{13}$ (red) and $Cu_{10}Te_4S_{13}$ (blue) measured at the Stokes and anti-Stokes line. Reproduced from Ref. [46] with permission from the PCCP Owner Societies.

INS measurements performed on natural, single-crystalline specimen further shed light on the role played by this excess on the lattice thermal conductivity [46]. These experiments enable to directly probe the dispersion of transverse acoustic phonons and the optical branch associated with the thermal vibrations of the Cu2 atoms. The low-energy optical branch strongly limits the phase space over which the acoustic phonon branch disperses (**Figure 9**). This strong limitation is accompanied by a drastic suppression of their intensity. The presence of this

low-energy optical mode has two main consequences: (i) the suppression of the acoustic phonon states that are the main heat carriers and (ii) the presence of a novel channel of Umklapp processes that remain active even at low temperatures. The first of these two consequences naturally explains the very low lattice thermal conductivity values measured in tetrahedrites, while the second consequence explains the absence of an Umklapp peak at low temperatures in $Cu_{12}Sb_2Te_2S_{13}$ suppressed by active Umklapp processes. The lack of this excess in $Cu_{10}Te_4S_{13}$ is thus at the origin of its higher lattice thermal conductivity values and the presence of the Umklapp peak centered at 25 K.

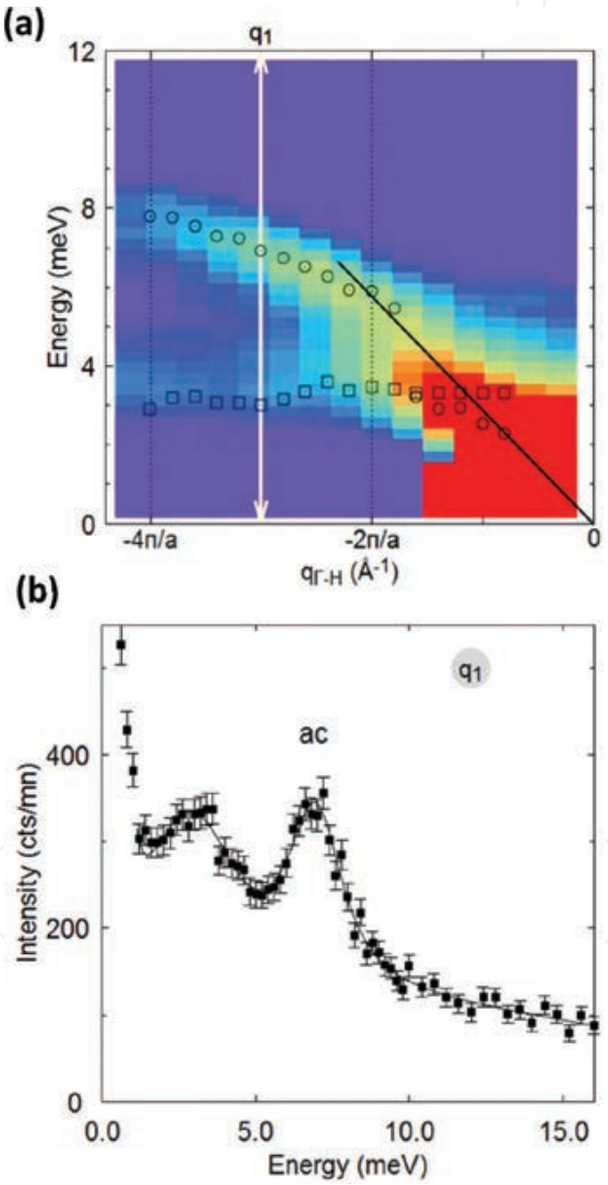


Figure 9. (a) Mapping of the transverse acoustic phonon propagating along the (011) direction and polarized along the (100) direction measured in a natural specimen. (b) Raw data of constant energy scan performed at the constant wave vector q_1 = 0.91 Å^{-1}. The black solid line corresponds to the fit of the measured scattering profile using damped harmonic oscillator for acoustic phonons (ac) and Gaussian functions for the low-lying optical excitations. Reproduced from Ref. [46] with permission from the PCCP Owner Societies.

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The origin of the strong anharmonicity has been attributed to the active 5*s* lone pair electrons of the Sb atoms located at either side of the Cu2 atoms. Electronic band structure calculations have suggested that the lone pair electrons are inactive in $Cu_{10}Te_4S_{13}$. A study of Wei et al. [47] based on a combination of theoretical calculations with synchrotron X-ray diffraction has further corroborated that the strong anharmonic potential felt by the Cu2 is linked to the lone pair electrons of the Sb atoms.

5. Scaling up tetrahedrite synthesis

Owing to their interesting thermoelectric properties, tetrahedrites hold promise to be used as *p*-type legs in thermoelectric generators. Yet, any widespread thermoelectric application would require fast, easily scalable, and cost-efficient synthetic methods to produce these materials in high yield. Several studies have dealt with these issues and focused either on the direct use of natural ore to decrease the cost and the time of preparation or on different synthetic routes faster than conventional powder metallurgy techniques. In this regard, James et al. [48] have recently developed a solvothermal route to produce synthetic tetrahedrites without using long-chain ligands that usually leads to a strong increase in the electrical resistivity due to difficulties in separating them from the targeted compound. Upon optimizing their process, these authors successfully synthesized phase-pure tetrahedrites within only one day at moderate temperatures (around 150°C). Of note, this fast synthesis process was not at the expense of the thermoelectric performances since the tetrahedrites prepared by solvothermal and solid-state synthesis methods showed similar *ZT* values.

Barbier et al. [49] have investigated another processing technique based on a combination of high-energy ball milling of stoichiometric mixtures of elemental powders and spark plasma sintering. This study, performed on the composition $Cu_{10.4}Ni_{1.6}Sb_4S_{13}$, has demonstrated that pure, highly dense samples of this tetrahedrite can be synthesized over a reduced period of time (estimated to eight times shorter by the authors) with respect to conventional solid-state synthesis. Similarly to the study of James et al. [48], the thermoelectric performances were not adversely affected and were comparable to those prepared by conventional methods in prior studies with a peak *ZT* value of 0.8 at 700 K.

Besides these two direct processes, Gonçalves et al. [50] used a different approach to synthesize within less than one day a tetrahedrite phase. This approach relies on the preparation of a glass of composition $Cu_{12}Sb_{3.6}Bi_{0.4}S_{10}Se_3$ by melt-spinning, i.e., fast quenching of the melt on a fast-rotating copper wheel, and subjected to controlled heat treatments to crystallize the targeted tetrahedrite phase. Within this strategy, both Se and Bi were introduced as vitrifying and nucleation agents to produce a homogeneous glassy sample. The authors further showed that annealing treatments at temperatures close to the crystallization peaks (around 200°C) leads to the crystallization of a tetrahedrite phase. Analysis of the chemical composition revealed the presence of Se partially substituting S, while Bi could not be detected within the experimental uncertainty of the instruments used. Thermopower and electrical resistivity measurements resulted in room-temperature power factors that are close to those measured in the ternary $Cu_{12}Sb_4S_{13}$ tetrahedrite (~400 $\mu W\ m^{-1}\ K^{-2}$). Further investigations on the thermal

conductivity of these samples will be essential in determining whether high thermoelectric performances can be equally achieved by this technique.

Finally, a radically different approach has been used by Lu et al. [31] who synthesized "composite" tetrahedrites from a mixture of synthetic and natural samples. Achieving high *ZT* values in such composite system would significantly reduce the time and cost required to synthesize synthetic specimens. While tetrahedrite minerals exhibit too high electrical resistivity to be viable thermoelectric materials, mixing ore with a fraction of synthetic tetrahedrite exhibiting metallic-like properties were shown to result in maximum *ZT* values of 1.0 at 700 K. The authors used two ores of composition $Cu_{10.5}Fe_{1.5}As_{3.6}Sb_{0.4}S_{13}$ and $Cu_{9.7}Zn_{1.9}Fe_{0.4}As_4S_{13}$, i.e., two As-rich tetrahedrites which are then named tennantites. These ores were mixed with the ternary tetrahedrite $Cu_{12}Sb_4S_{13}$ that behaves as a metal by ball milling. Remarkably, the powder X-ray diffraction pattern collected after ball-milling showed only one single tetrahedrite phase. This process thus provides an interesting and time-efficient way of producing single-phased tetrahedrite displaying high thermoelectric performances. Further investigations aiming at determining the influence on the chemical composition of the mineral on the thermoelectric properties will be interesting to undertake. In this regard, a preliminary study carried out on minerals from various geographical origins has shown that all of them show semiconducting-like properties despite differences in their chemical composition [51].

6. Conclusion

Progress in synthesizing tetrahedrites in laboratory environment and in understanding their transport properties have significantly advanced over the last 4 years, thanks to both experimental and theoretical efforts. Tetrahedrites possess transport properties not only interesting for thermoelectric applications but also for fundamental reasons. Subtle differences in their chemical compositions have a sizeable influence on their transport properties thereby adding another degree of freedom to study the interplay between their crystallographic, chemical, and transport properties. This is one of the main reasons why these materials have attracted attention in thermoelectricity yielding several *p*-type materials with *ZT* values ranging between 0.7 and 1.0 at 700 K. These high values originate from a favorable combination of semiconducting-like electronic properties and extremely low lattice thermal conductivity. The electronic properties can be tuned by substituting on the three possible sites, all of them resulting in either a control of the hole concentration or a favorable modification of the electronic band structure. Spectroscopic tools used to investigate the lattice dynamics of these materials have unveiled the presence of strong anharmonicity whose exact origin seems to be tied to the lone pair electrons revolving around the Sb atoms.

On the application side, several studies have successfully speed up the synthetic procedures used to obtain phase-pure tetrahedrites. Combined with the possibility to mix synthetic tetrahedrites with natural ores, these techniques may lead to the production in high yield of low-cost efficient tetrahedrites for thermoelectric applications. Despite proved to be feasible, these "composite" tetrahedrites have so far received little attention and future research will lead to an improved knowledge of their transport properties and of the influence on the chemical composition of the ore on the thermoelectric properties of the composite.

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