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Petr Levinský, Jean-Baptiste Vaney, Christophe Candolfi, Anne Dauscher, Bertrand Lenoir, et al.. Electrical, Thermal, and Magnetic Characterization of Natural Tetrahedrites–Tennantites of Different Origin. *Journal of Electronic Materials*, 2016, 45 (3), pp.1351-1357. 10.1007/s11664-015-4032-x . hal-01299681

HAL Id: hal-01299681

<https://hal.science/hal-01299681>

Submitted on 6 Mar 2023

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Electrical, Thermal and Magnetic Characterization of Natural Tetrahedrites-Tennantites of Various Origins

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ABSTRACT

Naturally occurring sulfosalt minerals from the tetrahedrite-tennantite series $((\text{Cu,Fe,Zn,Ag,Hg})_{12}(\text{Sb,As})_4\text{S}_{13})$ are studied with respect to their potential use as a basic component in manufacturing of moderate temperature applications thermoelectric devices. Herein, four specimens coming from various ores in Europe and America are exhaustively characterized from the chemical, crystallographic, thermoelectric and magnetic point of view. Our study unveils that these natural tetrahedrites behave in general as low-to-moderately doped p-type semiconductors with low mobility. Their carrier charge transport is thus located at the edge between hopping and itinerant mechanisms. The magnetic study, probing the behaviour of constituent iron species, reveals that insignificant part of iron occurs as ferromagnetic impurities, while the dominant iron species occur as Fe^{2+} ions with antiferromagnetic interactions. The maximum value of ZT observed amounts to 0.13 at 700 K; this value is impaired primarily because of high electrical resistivity.

Key words: Thermoelectric properties, natural minerals, sulfosalts, tetrahedrite-tennantite series, spark plasma sintering (SPS), magnetism

Introduction

Materials that show poor ability to conduct heat are focusing attention due to their potential use as thermal barriers or in thermoelectric modules for either electrical generation or cooling. In the latter area of research, several families of semiconductors have been identified over the last years, all of them demonstrating very low thermal conductivity values whose temperature dependence mimics that of amorphous alloys. Among others, these include Zintl phases [1-2], Mo-based cluster compounds [3-5], chalcogenide-based compounds [6-8] or cage-like structures such as clathrates [9-10]. Combined with semiconducting-like properties, the extremely low thermal conductivity enables achieving high dimensionless thermoelectric figures of merit ZT defined as $ZT=S^2/(\rho\kappa)T$ where T is the absolute temperature, S is the Seebeck coefficient or thermopower, ρ is the electrical resistivity and κ is the total thermal conductivity, which is the sum of a lattice contribution κ_l and an electronic contribution κ_e .

Naturally occurring sulfosalt minerals belonging to the tetrahedrite-tennantite series $\text{Cu}_{10}\text{TM}_2(\text{Sb,As})_4\text{S}_{13}$ (TM = transition metal) represent another family of compounds behaving like the above-mentioned classes of materials with κ values of the order of $0.5 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ above 300 K. These compounds have been recently proposed for direct use in manufacturing thermoelectric devices working at moderate temperatures [11-12]. Their high thermoelectric potential relies on abundant occurrence of raw sulfosalt minerals and, simultaneously, on their extremely low lattice thermal conductivity, which originates from the peculiar environment of some of the Cu atoms giving rise to strong anharmonicity of the associated lattice vibrations [13-14]. While their chemistry and crystal structure have been studied extensively for many decades [15-18], their thermoelectric properties are still not yet well explored and understood.

In the present manuscript, we present a detailed study of four minerals coming from Europe, North and South America. These specimens differ by their Sb/As ratios (thus covering wide range of the tetrahedrite-tennantite solid solutions) and, simultaneously, by various concentrations of TM ions substituting for Cu species. Due to fractures, poor mechanical strength and slight fluctuation of chemical composition of raw minerals, they had to be ground and re-sintered using spark plasma sintering (SPS) method prior to the physical studies. This way, highly dense materials (density >94%) were obtained and characterized by means of x-ray diffraction, scanning electron microscopy, electron probe microanalysis and high-temperature thermoelectric properties measurements. Due to significant and highly variable iron concentration, whose magnetic nature can significantly influence the carrier transport, the thermoelectric characteristics were complemented by magnetic

measurements. Our results corroborate both the chemically determined Fe concentration and shed light on the nature of magnetic interactions.

Experimental

Four samples of natural minerals from the tetrahedrite-tennantite series were obtained from a private collection. They originated from mines located in Peru, Mexico, Slovakia (Rudňany) and France (Saint-Sylvestre mine in the Vosges mountains). Energy dispersive X-ray (EDX) spectroscopy was used to identify the elemental composition of the studied minerals using a FEI Quanta 650 FEG scanning electron microscope equipped with a Bruker XFlash silicon drift detector. Quantitative chemical analysis was performed by electron probe microanalysis (EPMA) on mirror-polished graphite-coated samples using a Cameca SX 100 microprobe. Crystal structure and phase purity were investigated by powder X-ray diffraction (XRD) carried out with a Bruker D8 Advance X ray diffractometer using Cu $K_{\alpha 1}$ radiation.

Mortar-ground minerals were sintered using the SPS Dr. Sinter 515S apparatus. Due to the different nature of the minerals, the process parameters had to be optimized for each composition to obtain dense materials, which were further used for thermoelectric and magnetic characterizations. The obtained pellets, 10 mm in diameter and roughly 4 mm in height, were further cut into several pieces to fit to the dimensions required for the various characterization techniques. We note that for each origin of the mineral, all characterizations were performed on samples coming from a single pellet. Measurements of the Seebeck coefficient and the electrical resistivity were performed simultaneously between 300 and 780 K with a four-point method using a ZEM-3 (Ulvac-Riko) apparatus. The thermal diffusivity α was determined in the same temperature range with a laser flash Netzsch LFA 427 equipment. Thermal conductivity κ was calculated from the relation $\kappa = \alpha c_p \rho$, where c_p is the specific heat and ρ is the density. The specific heat was evaluated using the Dulong-Petit relation; density was considered temperature independent. Magnetic susceptibility and magnetization measurements were performed using a Quantum Design MPMS XL SQUID magnetometer.

Results and discussion

Primarily, the selected minerals were polished and EDX spectroscopy was used to identify all elements present in the samples: these are Cu, Ag, Zn, Fe, Hg, Sb, As, S representative of the tetrahedrite and tennantite minerals, as well as Si and O which form inclusions of both SiO_2 and pure Si (this observation is based on local analyses of inclusions). No other element was detected considering the estimated sensitivity of ca 0.1 at %. EPMA was then used to determine the chemical compositions more precisely. The results, normalized to 29 atoms per formula unit, are summarized in Table 1 together with some magnetic characteristics.

Simple optical inspection of the polished cross section revealed that all minerals exhibited significant cracks, both macroscopic (see Fig. 1) and microscopic. This fact, among all, prevented direct thermoelectric characterization, both due to the influence of interfaces and the fact that the minerals tended to crack and fall apart when heated. It was therefore necessary to obtain samples in a shape more appropriate for transport properties measurements. We thus selected small pieces of respective minerals and mechanically cleaned and sanded them to maximize the removal of surface layers of parasitic inclusions of foreign minerals (pyrite, chalcopyrite, quartz ...) sometimes present. The products were then ground in an agate mortar into fine powders and sintered by spark plasma sintering (SPS).

To produce dense crack-free samples (with relative densities higher than 94%), the sintering procedure had to be optimised for each sample. For all samples, we applied 80 MPa of pressure and a heating rate of 100 K/min up to the sintering temperature which was maintained for roughly 90 seconds. Table 2 lists the final density of the samples as well as the optimal sintering temperatures, which were different for each sample and had to be optimised experimentally to produce single-phase samples without additional decomposition and/or formation of secondary phases. The single-phase character of the sintered specimens was verified by comparing powder XRD patterns collected before and after the sintering process. As an example, we show in Fig. 2 the powder XRD patterns for the “Slovakian” sample. All diffraction peaks could be indexed to the tetrahedrite crystal structure – with the exception of the main diffraction peak of quartz (see inset of Fig. 2). This “benign” (~0.5%) impurity was already present in powder appointed for sintering.

In Figure 3, we show back-scattered electron images obtained on sintered samples. Small inclusions of Si, SiO₂, FeS₂ (pyrite) and ZnS (sphalerite) are present in the parent tetrahedrite phase. As these parasitic phases tend to grow on the surface of the minerals or the cracks protruding into the minerals’ interior, it is obviously utmost impossible to completely avoid their presence without the use of advanced techniques. However, they do not constitute more than 0.5% of the sample mass for the case of Si and SiO₂ and 0.1% for other minerals.

Considering that iron is an important substituent which can essentially influence the physical properties [19], we probed the magnetic properties of the samples. Measurements of the magnetization M as a function of applied magnetic field H showed paramagnetic behaviour for all samples down to 2 K. In most cases, the paramagnetic response was superimposed with ferromagnetic (FM) signal; namely for the samples of French, Mexican and Slovakian origin. In Figure 4a, we show, after the subtraction of the paramagnetic contribution using a standard linear $M(H)$ dependence, this ferromagnetic response. Supposing that most likely this FM behaviour is caused by iron impurities located outside of the tetrahedrite structure and taking into account the

saturation moment of metallic iron (221 emu.g^{-1} [20]), the observed ferromagnetic moment corresponds to concentration of $\sim 10^{-4}$ atoms which form metallic iron inclusions per tetrahedrite-tennantite formula unit (see Table 1). Let us note, however, that this amount is smaller than the experimental uncertainty of the Fe content determined by EPMA.

Figure 4b shows the paramagnetic susceptibility χ of the samples, corrected for the FM contribution. This paramagnetic response can be understood supposing the Curie-Weiss behaviour with paramagnetic contribution originating mainly from tetrahedrally coordinated Fe^{2+} ions in the tetrahedrite structure [21]. As Fe ions are in the high spin d^6 configuration possessing a magnetic moment of $4 \mu_B$ (Bohr magneton), their concentrations, extracted from the fitted Curie's constants, can be evaluated and are listed in Table 1. Most importantly we note that such iron concentrations agree well with those determined by EPMA. Furthermore, the negative values of the obtained Weiss constants (Θ_C) indicate that dominating interactions between iron atoms are unambiguously antiferromagnetic. It explains why the charge carriers, tentatively associated with Fe substitution, should be highly localized [19].

Thermoelectric properties measured at 300 and 673 K are summarized in Table 3. The temperature dependences of respective characteristics are displayed in Figure 5.

The largest variation between samples is seen for the electrical resistivity ρ which varies by one order of magnitude between the most and the least resistive ones. Electrical resistivity has thus the largest impact on the figure of merit ZT . The semiconducting character of the samples is revealed by an activated temperature dependence of the electrical resistivity which decreases with increasing temperatures fairly exponentially, as is typical for lightly-doped semiconductors. This is in contrast with the temperature variation of the Seebeck coefficient whose absolute values increase with increasing temperature. This is a feature seen in metals or highly-doped semiconductors. In this context, only the Peruvian sample containing significantly less iron than the other samples, shows a fairly constant value of S . On the other hand, the most metallic behaviour is seen for the Slovakian sample (note that this is the only one containing Hg atoms) whose Seebeck coefficient is characteristic of metallic behaviour.

Tetrahedrites are known for their extremely low lattice thermal conductivity [11-12]. All of our samples with thermal conductivities varying between $0.35\text{-}0.55 \text{ W.m}^{-1}\text{.K}^{-1}$ in the temperature range investigated corroborate this fact. Electronic part of thermal conductivity can be neglected as, using the Wiedemann-Franz law, it represents at most $\sim 0.01 \text{ W.m}^{-1}\text{.K}^{-1}$ even for the most conducting sample. Once again, we point out the Hg containing sample whose thermal conductivity: (i) is lower than that measured in other samples and (ii) shows

little change with temperature as opposed to other samples where it decreases with temperature. Finally, let us conclude that we have not noticed any obvious trends based on the chemical composition of the samples.

The maximum value of ZT that we have observed amounts to 0.13 at ~ 700 K for both the Slovakian and Mexican samples. While this value is very low from an application point of view (due to non-optimized doping), we note that it was obtained for samples without any important modification, apart from simple grinding and re-sintering.

Conclusions

Four natural sulfosalt minerals from the tetrahedrite-tennantite series coming from Europe and North and South America were investigated with respect to their potential use as a basic component in thermoelectric devices operating at moderate temperatures. Structural and chemical analyses as well as thermoelectric and magnetic measurements were conducted on SPS densified samples. The magnetic studies showed that iron contained in the samples is found in two forms: minute amount exists in the form of ferromagnetic impurities, while the dominant part constitutes antiferromagnetically coupled Fe^{2+} ions in the tetrahedrite structure. Transport measurements unveiled that natural tetrahedrites behave as lightly-doped p -type semiconductors with extremely low lattice thermal conductivity. Highest ZT observed in these samples amounts to 0.13 at 700 K. Such low value is caused primarily by high electrical resistivity; this is the limiting factor that should be reduced for further prospects in thermoelectricity.

Acknowledgements

This work was performed with the financial support of the Grant Agency of the Czech Republic (Projects No. GA13-17538S and 14-36566G) and the French Ministry of Foreign Affairs.

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Fig. 1 Cross section of a tetrahedrite mineral of Peruvian origin showing large cracks

Fig. 2 Powder X ray diffraction pattern of the Slovakian sample before (bottom) and after (top) sintering. Note the unchanged phase composition and unit cell parameter. Inset shows the main (and only visible) diffraction peak from quartz impurities

Fig. 3 Back-scattered electron images of polished surfaces of sintered samples: (a) France, (b) Peru, (c) Mexico, and (d) Slovakia. Major phase represents tetrahedrite/tennantite (even grey colour). Darker spots represent FeS₂ (pyrite) for (a) and (d) and FeS₂ or ZnS for (b), respectively. Black spots represent Si inclusions for (a) and (b) and quartz for (d)

Fig. 4 Extracted ferromagnetic behaviour (a) and paramagnetic susceptibility (b) of the studied samples. Points represent measured data, lines fits with Curie-Weiss law ($\chi = \chi_0 + C/(T-\theta_C)$, where χ_0 is the temperature independent part of the total susceptibility χ and C and θ_C represent Curie and Weiss constants, respectively)

Fig. 5 Temperature dependence of the thermoelectric properties of the studied samples

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Table 1 Chemical compositions of the studied minerals determined by EPMA, classified by decreasing ratios of Sb/As (tetrahedrite to tennantite compositions). In the right part, the iron content (in a form of ferromagnetic inclusions and paramagnetic Fe^{2+} species) determined using magnetic measurements together with Weiss constant (whose negative value is indicative of antiferromagnetic interactions) is also shown for comparison. Values are normalized to give 29 atoms per tetrahedrite formula unit.

Table 2 Material parameters of the samples sintered with SPS.

Table 3 Summary of thermoelectric properties of the studied samples measured at temperatures T of 300 and 673 K.

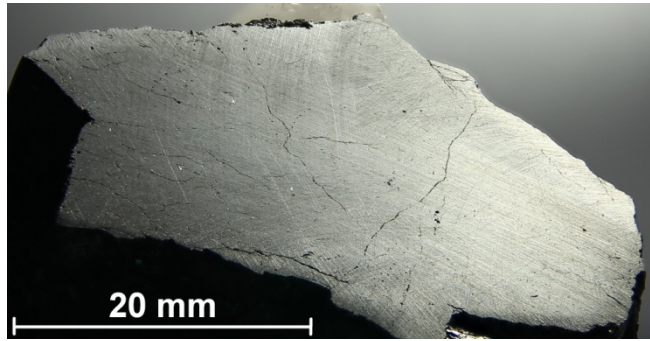


Fig 1

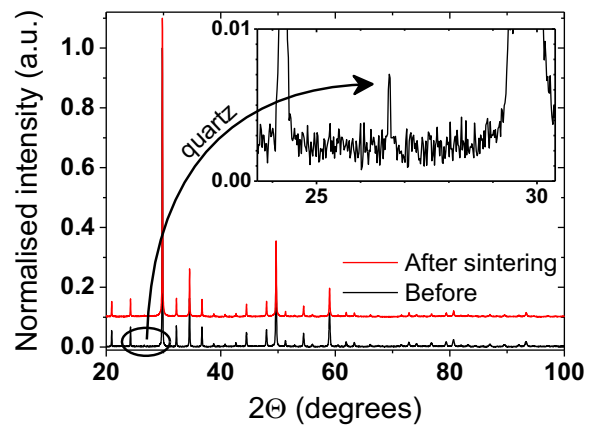


Fig 2

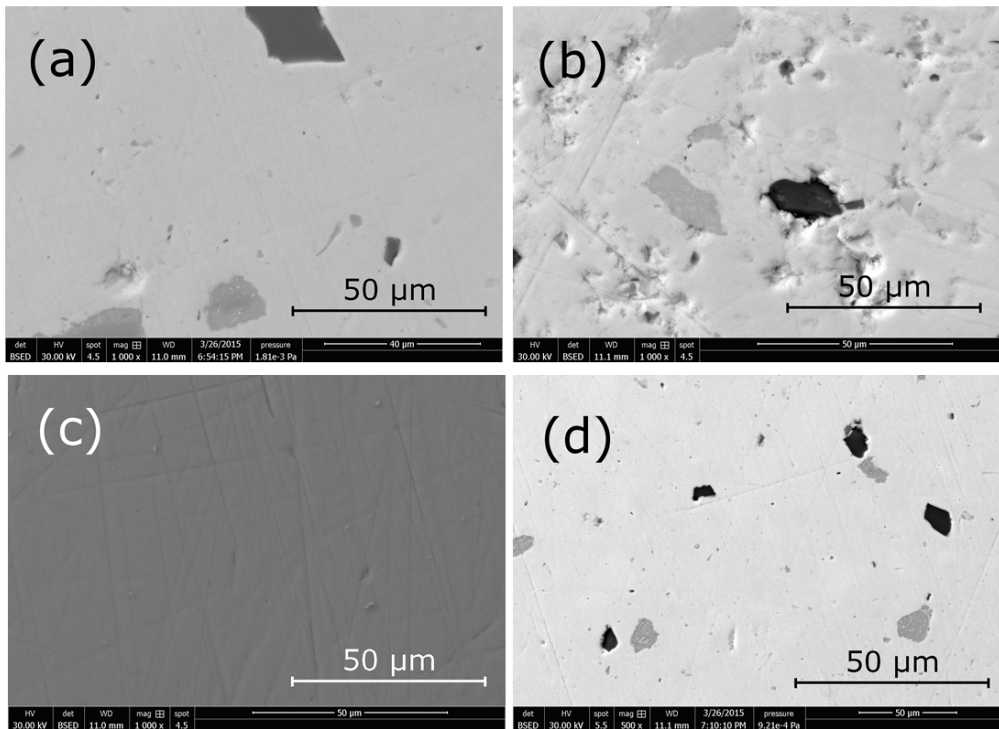


Fig 3

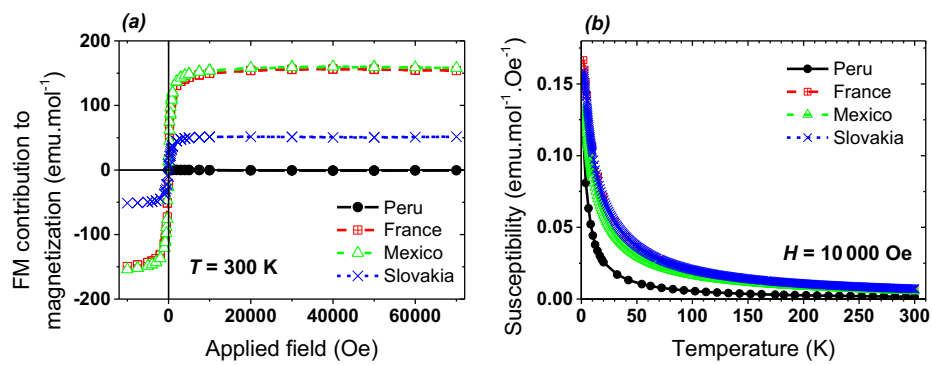


Fig 4

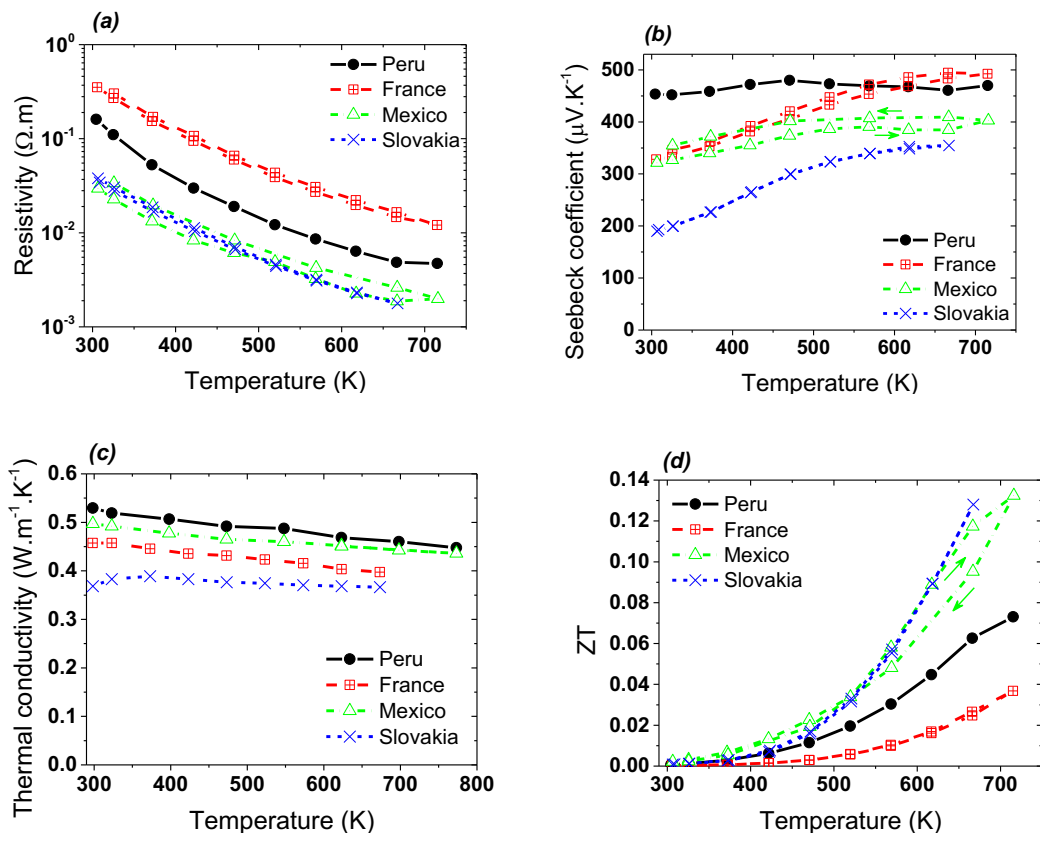


Fig 5