Fast and scalable preparation of tetrahedrite for thermoelectrics via glass crystallization

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ABSTRACT

A $Cu_{12}Sb_{3.6}Bi_{0.4}S_{10}Se_3$ glass was prepared by melt spinning and crystallized by heat treatments at selected temperatures, the total preparation procedure taking less than one day. The sample characterization by powder X-ray diffraction, scanning and transmission electron microscopy complemented with EDS indicate the formation of compact materials, with a tetrahedrite relative weight fraction higher than 90% when treated at temperatures close to the crystallization peaks (~200° C). Selenium enters the tetrahedrite structure, while bismuth precipitates in submicron and nanosized spherical shape phases depleted in copper and enriched in antimony, sulfur and selenium (when compared with the matrix composition). The characterization of electrical transport properties (electrical resistivity and Seebeck coefficient) indicate a behavior similar to that obtained by other methods on $Cu_{12}Sb_4S_{13}$, with a maximum power factor of ~400 $\mu W/K^2 m$ at room temperature.

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1. Introduction

Most of the human activity releases heat that is not usefully used. A classical example is the energy produced in an automobile combustion engine, where 60—70% is lost as heat through the exhaust gases, cooling systems and friction [1]. The electrical power plants embody this issue as well, having an efficiency close to 60%, the rest being mainly vanished as waste heat [2]. Thermoelectric systems are devices that can directly convert heat into electricity (via the Seebeck effect) and, vice versa, heating or cooling through the crossing of an electrical current (via the Peltier effect). These systems have a real potential to recover part of the waste heat and are seen as promising components for a more sustainable world. Moreover, they are silent, reliable, and have no moving parts or vibrations. However, actual commercial thermoelectric systems have low efficiencies and are based on modules containing expensive and/or toxic elements, with high materials production costs, making them unsuitable for an extensive use.

The performance of thermoelectric devices depends on the conversion efficiencies of the constituting thermoelectric materials, which are usually small when compared to those of a Carnot engine (<5% [3]). A good measure of a material potential for thermoelectrics is given through its dimensionless figure of merit zT, which is solely determined by the intrinsic physical properties of the material, as according to:

$$zT = \left(\sigma \alpha^2 / \lambda \right) T \tag{1}$$

In this formula σ, α, λ and T represent the electrical conductivity, Seebeck coefficient, total thermal conductivity and absolute temperature, respectively, with $\sigma \alpha^2$ being the power factor. Commercial systems working near room temperature integrate mainly the solid solutions based on Bi_2Te_3, which have $zT_{~300K} \approx 1$. To make thermoelectric devices competitive in large-scale and high-power commercial applications, low-cost materials with at least similar zT (i.e. $zT \geq 1$) in the application temperature range are required.

Since the 1990s new approaches and intensive efforts have been spread out, leading to the identification of new families of materials satisfying the zT ≥ 1 requirement [4].

Several cost analysis of the new thermoelectrics have been made in the last years [5−8]. It was concluded that the price of most of them is high, mainly due to the use of expensive elements as Te and Ge [9], raising the interest in the search of cheap thermoelectric materials, like polymers, oxides or silicides [10−12]. These studies clearly confirm that the production of competitive thermoelectric devices critically depends not only on their efficiency, but also on factors like the material and manufacturing costs [7,8]. Moreover, the simplicity and reproducibility of the materials fabrication, and use of easy scale-up processes, will also play a fundamental role on the production of commercial thermoelectric devices [7].

Tetrahedrites are world spread Cu sulfosalt minerals, with $Cu_{10}M_2Sb_4S_{13}$ (M = Cu, Mn, Fe, Co, Ni, Zn) general formula. They crystallize in the cubic $Cu_{12}Sb_4S_{13}$-type structure, with the I-43m space group and $a \cong 10.39$ Å cell parameter [13,14], being environment friendly materials mainly formed by the non-expensive elements copper and sulfur [15]. In its unit cell there are 58 atoms, with sulfur lying in the 2a and 24 g positions, copper being in the 12d and 12e sites and antimony occupying the 8c site. Copper substitutions for other M d-metals seem to preferably go into the Cu(12d) position, with a maximum occupation of 16.67% [16].

Recently, mineral-based and synthetic tetrahedrite materials were considered as promising thermoelectric materials [17−24], with zT reaching 1 at T ~ 575 °C, or even higher values when optimally co-doped [25]. The materials alloyed with manganese, nickel and zinc show the highest performances, which reflects a proper tuning of the Fermi level and an intrinsic low lattice thermal conductivity that results from the low-energy vibration of Cu(12e) perpendicular to the CuS_3 triangle plane [18]. Recent studies indicate that such rattling is originated from the asymmetric chemical environment of the copper atoms [26,27]. Substitutions on the Sb sites by Te atoms, proved also to be an interesting path to tune the electrical properties [28]. However, tetrahedrite melts incongruently, making the material obtained from the melt multiphasic [29,30]. Moreover, a complex decomposition occurs when elements other than copper, antimony and sulfur exist [31,32]. The impurity phases can have detrimental effects on the transport properties and on the chemical and thermal stability. As a consequence, the preparation of appropriate tetrahedrite samples usually requires long-term annealing procedures in order to proper perform the desired solid state reactions. At an industrial scale, this would imply long times and high costs.

Melt-spinning is a method of rapid cooling of liquids that has been routinely used in industrial productions, like in the manufacture of polymer filaments or in the preparation of NdFeB magnets [33]. In this last case, continuous ribbons of rare earth-boron alloys are directly prepared from high temperatures, the obtained ribbons being after used for the production of the magnets. Melt-spinning is a well-established method, characterized by its reproducibility, quickness and simplicity of procedures.

In this paper, a novel approach for the preparation of tetrahedrite materials, which can be later densified and shaped as module legs, is presented. Starting from $Cu_{12}Sb_{3.6}Bi_{0.4}S_{10}Se_3$ glassy ribbons prepared by melt-spinning, is shown that their controlled annealing leads to well-crystallized tetrahedrite samples with a low amount of secondary phases, making this approach a fast and scalable preparation method of tetrahedrite materials. Se and Bi were introduced as vitrifying and nucleating agents [34,35], respectively, as the first results on 12Cu:4Sb:13S melt-spunned samples showed a crystallized, multiphase material. Preliminary transport property measurements performed near room temperature point to power factor values (of the synthesized samples) similar to those achieved in materials prepared by conventional methods.

2. Experimental

A polycrystalline bulk charge with 12Cu:3.6Sb:0.4Bi:10S:3Se nominal composition was prepared by reacting the elements (Cu, ≥99.999%, Sigma−Aldrich; Sb, 99.999%, Ventron; Bi, 99.997%, Alfa Aesar; S, 99.9%, Alfa Aeser; Se, 99.99+%, Sigma−Aldrich) inside a quartz tube sealed under vacuum. The temperature of the elemental mixture was raised to 950 °C with a heating speed of 3 °C/min, kept at that temperature for 60 min and removed from the furnace with no extra procedure (~6 h of total process time). The charge was then broken into smaller pieces and put inside a quartz tube with a 0.5 mm diameter nozzle, which was transferred to the melt spinning system. The material was subsequently melted under the protection of an argon atmosphere, and ejected, with an extra pressure of 1 bar of argon, onto a copper roller rotating with a linear speed of 12 ms^{-1}, resulting in ~0.25 mm thickness millimeter-size flakes.

The melt-spun material was studied by differential scanning calorimetry (DSC) from room temperature up to 600 °C, under argon atmosphere with a flux of 50 cm^3/min, a heating rate of 10 °C/min and a sample weigh of ~5−35 mg, using a TA Instruments Q100 calorimeter.

DSC results were used to select the heat-treatment temperatures. Melt-spunned flakes were introduced into quartz tubes, which were sealed under vacuum and put inside furnaces preheated at the desired temperatures. The tubes remained there for 60 min, before being quenched in cold water, except in the case of the annealing at 220 °C, where a second sample was also treated for 120 min.

The heat treated samples were hand-ground and the powders transferred onto a low-noise X-ray diffraction sample holder. X-ray diffraction measurements were performed using a PANalytical X'Pert Pro powder diffractometer (Cu Kα-radiation) with Bragg−-Brentano geometry. Step-scanning mode X-ray diffraction patterns were taken in the 15−60° 2θ region with the θ/2θ configuration, a step of 0.01° and a counting time per step of 15 s. The theoretical powder patterns were calculated with the help of the Powder-Cell package [36]. The lattice parameters and unit cell volumes were obtained by least-squares fitting using the UnitCell program [37]. Rietveld refinements were made using the FullProf [38] software, with Pseudo-Voigt profile shape function and manually introduced background. Due to the minor amounts of the other phases, only the tetrahedrite and skinnerite (Cu_3SbS_3) structures were considered in the refinements. The copper positions were always considered totally filled, whereas the antimony position was also fixed as totally occupied, but only in the final refinements of tetrahedrite-based phases, as in the previous ones it converged to unity. No constraints were made for the sulfur occupations. All thermal displacement parameters were fixed.

Each of the most intense individual peaks of the tetrahedrite-type structure phases was analyzed and fitted by a Gaussian curve using the least squares procedure. The instrumental broadening was subtracted from the integral breadth to correct the instrumental effects and the resulting final values were used on a Williamson-Hall analysis of the average crystallite size and strain peaks broadening [39].

The heat treated materials were studied using both scanning and transmission electron microscopy (SEM and TEM, respectively). The SEM observations were made on polished surfaces of ribbon pieces mounted vertically inside epoxy resin, using a Jeol JSM-7001F field emission gun scattering electron microscope equipped for energy-dispersive spectroscopy (EDS) with a light element