

Thermoelectric properties of Co substituted synthetic tetrahedrite



R. Chetty^a, A. Bali^a, M.H. Naik^b, G. Rogl^{c,d}, P. Rogl^{c,d}, M. Jain^b, S. Suwas^e, R. C. Mallik^{a,*}

^aThermoelectric Materials and Devices Laboratory, Department of Physics, Indian Institute of Science, Bangalore 560012, India

^bDepartment of Physics, Indian Institute of Science, Bangalore 560012, India

^cInstitute of Materials Chemistry and Research, University of Vienna, Währingerstrasse 42, A-1090 Wien, Austria

^dChristian Doppler Laboratory for Thermoelectricity, Vienna University of Technology, Vienna A-1090, Austria

^eDepartment of Materials Engineering, Indian Institute of Science, Bangalore 560012, India

ARTICLE INFO

Article history:

Received 28 February 2015

Revised 13 August 2015

Accepted 16 August 2015

Available online 31 August 2015

Keywords:

Tetrahedrite

X-ray diffraction (XRD)

Scanning electron microscopy (SEM)

Transport properties

Elastic properties

ABSTRACT

Transition metal atom (Co) substituted synthetic tetrahedrite compounds $\text{Cu}_{12-x}\text{Co}_x\text{Sb}_4\text{S}_{13}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) were prepared by solid state synthesis. X-Ray Diffraction (XRD) patterns revealed tetrahedrite as the main phase, whereas for the compounds with $x = 0, 0.5$ a trace of impurity phase Cu_3SbS_4 was observed. The surface morphology showed a large grain size with low porosity, which indicated appropriate compaction for the hot pressed samples. The phase purity, as monitored by Electron Probe Micro Analysis (EPMA) is in good agreement with the XRD data. The elemental composition for all the compounds almost matched with the nominal composition. The X-ray Photoelectron Spectroscopy (XPS) data showed that Cu existed in both +1 and +2 states, while Sb exhibited +3 oxidation states. Elastic modulus and hardness showed a systematic variation with increasing Co content. The electrical resistivity and Seebeck coefficient increased with increase in the doping content due to the decrease in the number of carriers caused by the substitution of Co^{2+} on the Cu^{1+} site. The positive Seebeck coefficient for all samples indicates that the dominant carriers are holes. A combined effect of resistivity and Seebeck coefficient leads to the maximum power factor of $1.76 \text{ mW m}^{-1} \text{ K}^{-2}$ at 673 K for $\text{Cu}_{11.5}\text{Co}_{0.5}\text{Sb}_4\text{S}_{13}$. This could be due to the optimization in the carrier concentration by the partial substitution of Co^{2+} on both the Cu^{1+} as well as Cu^{2+} site at the same doping levels, which is also supported by the XPS data. The total thermal conductivity systematically decreased with increase of doping content as it is mainly influenced by the decrease of carrier thermal conductivity. The maximum thermoelectric figure of merit $zT = 0.98$ was obtained at 673 K for $\text{Cu}_{11.5}\text{Co}_{0.5}\text{Sb}_4\text{S}_{13}$.

© 2015 Acta Materialia Inc. Published by Elsevier Ltd. All rights reserved.

1. Introduction

Thermoelectric (TE) materials are finding interest due to their potential application for solid state thermoelectric generators and coolers by converting heat energy to electrical energy, and vice-versa. Recently, there is a large focus on finding low cost and environmental friendly TE materials. The conversion efficiency of TE materials depends on the parameters of the dimensionless figure of merit, defined by $zT = (\alpha^2/\rho\lambda_T)T$, where α , ρ , T and λ_T represent the Seebeck coefficient, electrical resistivity, absolute temperature and total thermal conductivity, respectively. The latter is composed of the carrier (λ_C) and the lattice contribution (λ_L). Recently, there is a lot of interest in studying the thermoelectric properties of tetrahedrites ($\text{Cu}_{10}\text{Tr}_2\text{Sb}_4\text{S}_{13}$, Tr = Mn, Fe, Co, Ni, Cu, Zn) because of their natural abundance on earth and because they consist of environmentally friendly elements copper and sulfur [1–3]. Apart

from this, these materials have beneficial features to behave as good thermoelectric materials such as (i) complex crystal structure with a large number of atoms per unit cell, which is helpful to provide low thermal conductivity, (ii) the existence of a high band degeneracy due to the high symmetric (cubic) crystal structure which is useful for improving the power factor [1]. The crystal structure of the tetrahedrites is a derivative of the sphalerite structure [4,5]. $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$ is the parent compound of the tetrahedrite minerals containing 58 atoms per cubic unit cell with the space group $\bar{1}43m$. It was reported that natural mineral tetrahedrite compounds can incorporate transition metal atoms [6,7]. Thermoelectric properties, studied for the first time for synthetic transition metal substituted end member tetrahedrites $\text{Cu}_{10}\text{Tr}_2\text{Sb}_4\text{S}_{13}$ (Tr = Mn, Fe, Co, Ni, Cu, and Zn), yielded a maximum zT of 0.15 at 340 K for the Ni substituted tetrahedrite, as result of a large Seebeck coefficient and a low thermal conductivity [1]. Later Lu et al. [2] investigated high temperature thermoelectric properties (between 373 K and 673 K) of synthetic tetrahedrites by varying the Zn and Fe concentration and reached a $zT \sim 1$ at 723 K for

* Corresponding author.

E-mail address: rcmallik@physics.iisc.ernet.in (R.C. Mallik).

$\text{Cu}_{12-x}(\text{Zn}, \text{Fe})_x\text{Sb}_4\text{S}_{13}$ ($x = 1.0$ for Zn and $x = 0.5$ for Fe) whereas a $zT > 0.8$ was shown for a broader range of x values. Suekuni et al. [3] studied structural and TE properties of $\text{Cu}_{12-x}\text{Ni}_x\text{Sb}_4\text{S}_{13}$ and achieved a maximum zT of 0.7 at 665 K for $\text{Cu}_{10.5}\text{Ni}_{1.5}\text{Sb}_4\text{S}_{13}$. Also, natural earth abundant tetrahedrite minerals can be used as TE materials and a maximum zT was reached near unity at 723 K [8,9]. A new approach of doping by Te on the Sb site achieved the maximum zT of 0.92 at 723 K for synthetic $\text{Cu}_{12}\text{Sb}_3\text{Te}_1\text{S}_{13}$ [10]. Chetty et al. reported the adverse effect of Mn doping on thermoelectric properties and showed the maximum zT of 0.76 at 623 K for the parent compound [11]. Barbier et al. [12] studied phase purity, structural and thermal stability of undoped and Ni doped tetrahedrite compounds and a maximum $zT = 0.8$ at 700 K for $\text{Cu}_{10.4}\text{Ni}_{1.6}\text{Sb}_4\text{S}_{13}$ was obtained. Lu et al. [13] reported an effect of co-doping for the Ni doped tetrahedrite by addition of Zn, which lead to the increment of $zT = 1.03$ at 723 K for $\text{Cu}_{10.5}\text{Ni}_{1.0}\text{Zn}_{0.5}\text{Sb}_4\text{S}_{13}$. Recently, Lai et al. [14] reported that a possible mechanism for the existence of intrinsic low thermal conductivity for tetrahedrite compounds is due to the local bonding asymmetry created by the Sb lone pairs of electrons, which lead to the out of plane anharmonic vibration of low energy modes; this explanation was derived via high-resolution synchrotron XRD and density functional theory calculations. Also, Bouyrie et al. [15] reported the origin of low thermal conductivity in tetrahedrite compounds using the lattice dynamics from the Inelastic neutron scattering (INS) and Raman scattering data.

The previous reports on the thermoelectric properties of tetrahedrites as a function of varying amounts of transition metals (e.g., Mn, Fe, Ni, Zn) [2,3,11] motivated us to focus on Co. Thus, in the present work, the Co content in $\text{Cu}_{12-x}\text{Co}_x\text{Sb}_4\text{S}_{13}$ is varied to optimize the power factor and decrease the total thermal conductivity. This is expected because substituting Co^{2+} on the Cu^{1+} site causes a reduction of the carrier concentration, which leads to an increase of the electrical resistivity and the Seebeck coefficient and as a consequence to an optimization of the power factor in a combined effect. Also the total thermal conductivity decreases with doping due to the suppression of the carrier thermal conductivity. It is expected that both the power factor and thermal conductivity can be tuned by Co substitution on the Cu site and will lead to an improvement of the thermoelectric figure of merit. Although the performance of a thermoelectric material is evaluated by the figure of merit (zT), it is important to know about the mechanical properties of these materials. A good combination of figure of merit and mechanical response will render the material suitable for the fabrication of desirable devices.

In the present work, a systematic study of structural and phase characterization in addition to thermoelectric properties of Co substituted tetrahedrites is presented. Two very important mechanical properties, the hardness and the elastic modulus, have been measured in addition of the thermoelectric properties. The knowledge of elastic properties such as Young's modulus will enable this material to manufacture thermal shock resistant devices.

2. Experimental details

$\text{Cu}_{12-x}\text{Co}_x\text{Sb}_4\text{S}_{13}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$) compounds were prepared by a melting, pulverization, compaction and annealing sequence following a procedure described in the literature [3]. The starting materials Cu, Co, Sb, and S with high purity (5N) were weighed in stoichiometric ratio into a quartz ampoule and sealed under vacuum ($\sim 10^{-4}$ mbar). The quartz ampoules were slowly heated to 973 K, held at that temperature for 3 h and then cooled to 823 K for 30 h. Then the furnace was switched off to cool down to room temperature. The resulting materials were ground into powder and shaped into pellets by cold pressing. These cold

pressed pellets were sintered at 773 K for 30 h in evacuated quartz tubes. The sintered samples were re-ground, loaded into graphite dies with a diameter of 14 mm, and then hot pressed under a pressure of ~ 30 MPa at the temperature 823 K under a dynamic vacuum for 2 h. The relative densities of the hot-pressed samples were determined using Archimedes' principle (measured densities) reaching $>95\%$ for all samples. Cylindrical samples were cut into discs with 6.0 mm diameter and 0.5 mm thickness for thermal conductivity measurements, and into cuboids ($\sim 11.0 \times \sim 3.0 \times \sim 3.0$) mm for Seebeck coefficient and electrical resistivity measurements, respectively.

X-ray diffraction (XRD) patterns of all samples were collected on a Rigaku Smart Lab X-ray diffractometer using $\text{Cu K}\alpha$ radiation after hot pressing. Rietveld refinement was carried out for the crystallographic phase identification using the Fullprof software [16]. Microstructural features of the hot-pressed samples were examined by an Environmental Scanning Electron Microscope (Quanta 200, ESEM) and Electron Probe Micro Analysis (EPMA). A JEOL JXA-8530F Electron Probe Micro Analyzer was used for this. X-ray Photoelectron Spectroscopy (XPS) was carried out on AXIS ULTRA using $\text{Al K}\alpha$ as the excitation source.

A nanoindenter TI 900 TriboIndenter, Hysitron was used in the present investigation for the determination of hardness and elastic modulus. The indentations were performed using the maximum load of 8 mN and dwell time of 2 s. Four indentations were performed per sample in order to obtain the hardness and moduli.

Electrical resistivities and Seebeck coefficients were measured between 323 K and 673 K with a LINSEIS (LSR-3) system. Thermal conductivity, $\lambda_T = Dd_s C_p$ (where D ($\text{mm}^2 \text{s}^{-1}$) is the thermal diffusivity, d_s (in cm^{-3}) is the density of sample and C_p ($\text{Jg}^{-1} \text{K}^{-1}$) is the specific of heat of the sample) was obtained from an ANTER Flashline 3000 unit in the temperature range between 423 K and 673 K, measuring the thermal diffusivity and specific heat. The measurement errors for the electrical resistivity, the Seebeck coefficient and the thermal conductivity are 10%, 7% and 10% respectively.

3. Results and discussion

3.1. X-ray diffraction

X-ray diffraction patterns of all powder samples are displayed in Fig. 1. All peaks are indexed with the cubic tetrahedrite phase

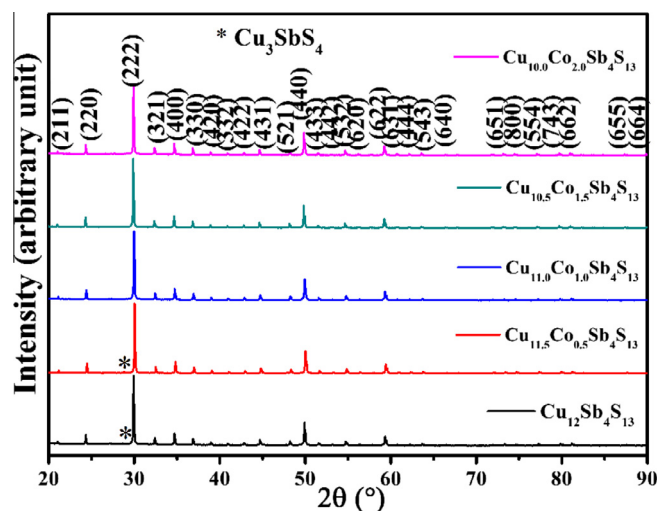


Fig. 1. X-ray diffraction patterns of powder samples for the compounds $\text{Cu}_{12-x}\text{Co}_x\text{Sb}_4\text{S}_{13}$ ($x = 0, 0.5, 1.0, 1.5, 2.0$).

Download English Version:

<https://daneshyari.com/en/article/7879460>

Download Persian Version:

<https://daneshyari.com/article/7879460>

[Daneshyari.com](https://daneshyari.com)