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Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Role of iron in synthetic tetrahedrites revisited

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ARTICLE INFO

Article history:

Received 6 November 2015

Received in revised form

7 December 2015

Accepted 10 December 2015

Available online 12 December 2015

Keywords:

Tetrahedrite

Iron

Crystal structure

Mössbauer spectroscopy

Electron hopping

ABSTRACT

The valence state of iron in $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ tetrahedrites have been revisited by the combination of the crystallographic results, Mössbauer spectroscopy, and magnetization measurements. The crystal structure solution for $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$ (space group $I\bar{4}3m$, $a=10.3253(12)$, $z=2$, $R=0.011$) proved that iron substitutes for copper only in the Cu1 position. At the iron content of $x=0.8, 1.0$, and 1.2 , the presence of two nonequivalent and non-interacting Fe^{3+} cations was inferred from Mössbauer spectra. At higher levels of substitution ($x=1.5$ and 2.0), room-temperature Mössbauer spectra indicate the electron hopping between part of Fe^{3+} and Fe^{2+} centers, whereas the rest of iron atoms exists as valence-localized Fe^{3+} and Fe^{2+} cations. Electron transfer is frozen out at 77 K, where a combination of two Fe^{3+} sites and one high-spin Fe^{2+} site is observed. Paramagnetic effective moments extracted from the magnetic susceptibility data point at the Fe^{3+} state of iron at $x=0.8$, while a mixture of Fe^{2+} and Fe^{3+} is presumed in the samples with higher Fe content.

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1. Introduction

As the efficiency of current state-of-art thermoelectric materials has reached its limit, new ideas for the pursuit of better thermoelectrics are emerging. Thus, the families of semiconductors and semimetals based on complex tellurides, skutterudites, clathrates and various nanostructured materials were intensively investigated, bringing about new and exciting compounds with remarkable thermoelectric properties [1–4]. The unexpected discovery of high thermoelectric efficiency in synthetic and natural tetrahedrites opened a new direction in the search for thermoelectric materials of new generation [5,6]. Tetrahedrites are a family of compounds with a general formula $\text{Cu}_{12-x}\text{M}_x\text{Sb}_4\text{S}_{13}$ ($\text{M}=\text{Fe}, \text{Co}, \text{Ni}, \text{Mn}, \text{Zn}$). They are easy to fabricate, do not contain toxic or rare elements, and their dimensionless thermoelectric figure-of-merit, ZT, reaches a value of 1.13 within the mid-temperature range [7]. Combined, the latter properties make tetrahedrites excellent candidates for creation of thermoelectric materials for automotive power generation [7–9].

Tetrahedrites containing Mn or Fe display the highest figure-of-merit [7], although the valence state of the substituting cation in these materials is different. It was demonstrated that iron is

distinct from the other dopants. Whereas all other substituting 3d metals, including manganese, form the M^{2+} cations, the oxidation state of iron depends on the level of substitution [10]. It is generally believed [8,10,11] that in the $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ series, Fe^{3+} forms until x reaches 1, while Fe^{3+} and Fe^{2+} coexist up to the maximum doping level of $x=2$, at which Fe^{2+} is present exclusively. According to this model, one assumes that the parent compound $\text{Cu}_{12}\text{Sb}_4\text{S}_{13}$, formulated as $(\text{Cu}^+)_{10}(\text{Cu}^{2+})_2(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$, transforms into $(\text{Cu}^+)_{11}(\text{Cu}^{2+})_1(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$ upon substitution of one iron atom for copper with a concomitant change in the oxidation state of one copper atom from +2 to +1. Further substitution of iron for copper leads to a decrease in the number of Fe^{3+} atoms and appearance of Fe^{2+} . For instance, at $x=1.5$ the formula reads as $(\text{Cu}^+)_{10.5}(\text{Fe}^{3+})_{0.5}(\text{Fe}^{2+})_1(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$. Finally, at $x=2$ only Fe^{2+} exists suggesting $(\text{Cu}^+)_{10}(\text{Fe}^{2+})_2(\text{Sb}^{3+})_4(\text{S}^{2-})_{13}$ formulation. The analysis of the literature data on the crystal structure and various properties of pristine and Fe-substituted tetrahedrites [8–16] makes us believe that the above description is unrealistic or, at least, oversimplified. In particular, the cubic unit cell parameter increases linearly with iron content, though Fe^{3+} is smaller than copper for which it substitutes [8,9], and the hyperfine parameters of Mössbauer spectra do not match well with the values expected for high-spin iron tetrahedrally coordinated by sulfur atoms [10,11]. Taking these considerations into account, we have undertaken a comprehensive study of Fe-substituted tetrahedrites by means of X-ray crystallography, Mössbauer

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spectroscopy, and magnetization measurements in order to re-examine the role and the valence state of iron in the $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ compounds.

In this paper, we present the results of the complex study of iron-substituted tetrahedrites $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ as well as discuss the role of iron and the relevance of the proposed distribution of the oxidation states in $\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$. We also put forward new, hitherto unexplained properties of these materials.

2. Experimental

2.1. Starting materials

Elemental Fe (powder, 99%), Sb (pieces, 99.999%), CuO (99.9%), and elemental S were used as starting materials for the synthesis. Copper was obtained by heating CuO under hydrogen flow. Sulfur was gently heated slightly above its melting point under dynamic vacuum for complete water removal. The purity of all reagents was controlled by powder X-ray diffraction.

2.2. Synthesis

$\text{Cu}_{12-x}\text{Fe}_x\text{Sb}_4\text{S}_{13}$ ($x=0, 0.5, 0.8, 0.9, 1.0, 1.1, 1.2, 1.3, 1.5,$ and 2.0) compounds were prepared by a standard ampoule technique generally following the procedure described in the literature [5]. In brief, the mixtures of starting materials were sealed in evacuated quartz ampoules under a vacuum of 2×10^{-2} Torr. Ampoules were heated to 973 K, annealed at this temperature for 3 h, slowly cooled down to 823 K in 30 h, and finally cooled down to room temperature in a switched-off furnace. The reaction products were finely ground in agate mortar and pressed into pellets at a pressure of 80–100 bar at room temperature. These pellets were sealed in evacuated quartz ampoules and annealed at 773 K for 25 h, followed by switching off the furnace and cooling down to room temperature. For each composition, 3–5 samples were synthesized in parallel experiments under the same conditions to ensure reproducibility. The resulting samples were finely ground and used for further investigations.

2.3. X-ray powder diffraction and energy-dispersive X-ray spectroscopy

Phase composition was investigated by a standard X-ray technique using a STADI-P powder diffractometer (Stoe, Cu $K_{\alpha 1}$ radiation, Ge monochromator, $\lambda=1.540598$ Å). The program package STOE WinXPOW was used for data processing. Unit cell parameters for each composition were calculated for 3–5 different synthetic batches and averaged. Elemental composition was determined using a JSM JEOL scanning electron microscope operated at 30 kV and equipped with an EDX detection system INCA x-Sight. Pure elemental Co was used as a standard. The data were collected from 10 points for each sample and then averaged. Uniform distribution of elements across the sample was confirmed by mapping (see Supporting information, Fig. S1).

2.4. Crystal structure investigation

A suitable single crystal was selected from the product of the first annealing step of the composition $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$. Data were collected at 100 K on a Bruker D8 VENTURE with PHOTON 100 CMOS detector system equipped with a Mo-target X-ray tube. A frame width of 0.50° and an exposure time of 15 s/frame were employed for data collection. Data reduction and integration were performed with the Bruker software package SAINT. Data were corrected for absorption effects using the empirical methods

Table 1
Summary of data collection and refinement parameters for $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$.

Composition	$\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$
Crystal system	Cubic
Space group	$I\bar{4}3m$
a , Å	10.3253(12)
V , Å ³	1100.8(4)
Z	1
d_{calc}	5.004
Radiation/wavelength	MoK α /0.71073 Å
Temperature, K	100(2)
Crystal size, mm ³	$0.12 \times 0.09 \times 0.06$
Color	Dark gray
Absorption correction	SADABS
θ range (data collection)	2.79–30.54
Range of h, k, l	–14 \rightarrow $h \rightarrow$ 14 –14 \rightarrow $k \rightarrow$ 14 –14 \rightarrow $l \rightarrow$ 14
R_{int}	0.0744
R/R_w ($I > 2\sigma(I)$)	0.0116/0.0238
Flack parameter x	–0.004(17)
GoF	1.205
Δr_{max} (e/Å ^{–3})	0.563/–0.324

(multi-scan) as implemented in SADABS. The structure was solved and refined using SHELXTL programs. Direct methods were used to solve the crystal structure in the space group $I\bar{4}3m$ (no. 217) in accordance with the literature data [15]. The crystal structure was refined with anisotropic thermal parameters for all atoms, which resulted in $R=0.011$. Data collection and refinement parameters are listed in Table 1, atomic parameters in Table 2, and interatomic distances and bond angles in Table 3. Details of the crystal structure refinement are given and discussed in Section 3.

2.5. Mössbauer spectroscopy

⁵⁷Fe Mössbauer spectra were recorded at 77 and 300 K using a conventional constant-acceleration spectrometer MS-1104Em in the transmission geometry. A radiation source ⁵⁷Co(Rh) was kept at room temperature. All isomer shifts are referred to α -Fe at 298 K. Experimental spectra were processed and analyzed using methods of spectral simulations implemented in the SpectRelax program [17].

2.6. Magnetic properties

Magnetization was measured with the VSM setup of the Physical Property Measurement System (PPMS, Quantum Design) in external magnetic fields of 0.1, 1, 2 and 5 T in the temperature range from 2 to 380 K, using pellets prepared by pressing finely ground polycrystalline samples at a pressure of 80–100 bar at room temperature.

Table 2
Atomic parameters in the crystal structure of $\text{Cu}_{11.0}\text{Fe}_{1.0}\text{Sb}_4\text{S}_{13}$.

Atom	Wyckoff position	x	y	z	U_{eq} , Å ²
Sb	8c	0.231111(13)	x	$-x$	0.01097(7)
Cu1/Fe1 ^a	12d	1/4	1/2	0	0.00972(11)
Cu2	24g	0.01406(18)	x	0.78230(8)	0.0256(5)
S1	24g	0.38412(4)	x	0.86277(5)	0.00853(11)
S2	2a	0	0	0	0.0137(4)

^a The Cu/Fe ratio is fixed at 0.83/0.17. See text for details.

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