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Rapid communication

Synthetic $Cu_{0.507(5)}Pb_{8.73(9)}Sb_{8.15(8)}I_{1.6}S_{20.0(2)}$ nanowires

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Abstract

Nanowires of an iodine containing Pb–Sb-sulfosalt have been synthesized by chemical vapor transport. Their structure was studied using high-resolution transmission electron microscopy and X-ray powder diffraction. The lattice parameters show values equal to $a = 4.9801(4)$ nm, $b = 0.41132(8)$ nm (with two-fold superstructure), $c = 2.1989(1)$ nm and $\beta = 99.918(6)^\circ$. These parameters and the results of a multislice simulation are in good agreement with the mineral pillaite, $Cu_{0.10}Pb_{9.16}Sb_{9.84}S_{22.94}Cl_{1.06}O_{0.5}$ (space group $C2/m$, $a = 4.949(1)$ nm, $b = 0.41259(8)$ nm, $c = 2.1828(4)$ nm, and $\beta = 99.62(3)^\circ$). Microprobe and EDX analyses yielded a chemical composition of $Cu_{0.507(5)}Pb_{8.73(9)}Sb_{8.15(8)}I_{1.6}S_{20.0(2)}$ which is close to natural pillaite but contains no oxygen and iodine instead of chlorine. The structure of the investigated material is based on chains of M–S polyhedra (M = Pb or Sb) typical for the architecture of sulfosalts implying iodine atoms in trigonal prismatic coordination with Pb atoms from the M–S polyhedra of neighboring chains. The [010] superstructure of the specimen was found to be unstable under electron beam irradiation with a rapid decrease of the b lattice parameter from 0.8 to 0.4 nm within 5 min.

Keywords: Sulfides; Nanowires; Synthesis; Structure; Transmission electron microscopy; XRD

1. Introduction

Sulfosalts form a class of complex sulfides with the general formula of $A_mB_nX_p$, where A stands for metallic elements like Pb, Ag and Cu, B represents formally trivalent, semi-metallic elements as As, Sb and Bi and X can be S and Se. In some cases sulfosalts can contain minor amounts of Cl and O. The structures of sulfosalts consist of infinite layers or rods of M–S polyhedra on the basis of the archetype structures of SnS and PbS [1]. Owing to relatively strong bonds in the chain direction, these compounds tend to grow as thin needles parallel to this direction, observed, e.g., for the minerals boulangerite [2] and jamesonite [3–5] which occur as micro needles. The stability conditions of these intermediate PbS–Sb_2S_3 phases are given in literature [6] and some data on physical properties of iodine containing Pb–Sb–S-materials are reported [7,8]. It is highly expected that the chain-like structure of the sulfosalts may enhance the possibility for producing these materials in the nanowire-shape by relatively simple, template-free methods, such as chemical vapor transport (CVT), resublimation or rapid crystallization from the melt. Sulfosalt nanowires and nanorods bear potentialities for applications in electronics, as their structures and semiconducting properties are derived from archetypes such as CuS, Sb_2S_3 and PbS which have band gaps between 1.2 and 1.7 eV [9–14]. It is important to note that superstructures possibly responsible for the electronic effects have been observed in natural and synthetic Pb–Sb-sulfosalts [5,15–17]. Recently, we reported that nanowires of Pb–Sb-sulfides with diameters of ca. 100 nm could be synthesized from the melt [18]. Scanning electron microscopy (SEM) gave evidence that this material solely occurs as bundles of

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parallel-intergrown individual nanowires. Using these facts and because natural halogen-bearing sulfosalts such as pillaite [19], pellouxite [20], dadsonite [22] and ardaite [23] as well as the halogen-free mineral boulangerite [21] reveal needle-like morphology, we tried to apply the CVT procedure with iodine as transport agent to grow different Pb–Sb-sulfosalts in the form of nanowires. In this paper an XRD-study as well as HRTEM analysis along with computer simulation of HRTEM images were used to examine the structural arrangement of the ternary sulfosalt and to provide a structural model of this compound.

2. Experimental

CVT synthesis was performed in 10 mm diameter and 75 mm long silica tubes with I_2 as transport agent (0.3 mg I_2/mL) in a two-zone furnace with a temperature gradient ranging from 456 to 380 °C. Initially it was intended to recrystallize different Pb–Sb-sulfosalts in the form of nanowires or nanorods using CVT. Therefore in one experiment natural jamesonite, $FePb_4Sb_6S_{14}$, from Wolfsberg (Harz, Germany) was used as starting material. Since the source was a massive piece of intergrown needles, there was no risk of mixing the starting material with the products, which were separately growing needles.

After 10 days the ampoules were cooled down at the precursor side by water to condensate I_2 and to avoid contamination of the transported products and grown needles, respectively.

The XRD-data were collected using Cu $K\alpha$-radiation ($\lambda = 1.541874$ Å) on a XRD3000-diffractometer (Seifert) in a range of $2\theta = 12$–$90°$ with a step size of 0.02° and a counting time of 20 s. The device operates in Bragg-Brentano-Geometry with a secondary monochromator (graphite (002)) and a scintillation detector. For the profile calculation and the determination of the lattice parameters, the program FULLPROF [26] was used.

Study of the specimens' morphology has been carried out with the use of Zeiss DSM 640 scanning electron microscope (SEM) operating at 15 kV/20 μA. The chemical composition of the samples was determined by electron probe microanalysis using Cameca SX 100 (15 kV/20 nA, standards: synthetic PbS, Sb_2S_3 or InSb) and by energy-dispersive X-ray analysis in a transmission electron microscope. HRTEM examinations were carried out in a Philips CM200 transmission electron microscope operated at 200 kV. For HRTEM analysis the specimen was placed between GaAs-wafers used as dummy materials and cut across and along the wires length followed by mechanical polishing and etching by Ar^+ ions using an acceleration voltage of 4 kV, a beam current of 0.5 mA and beam incident angle of 13°. HRTEM image simulations were performed using MacTempas program based on the multislice algorithm [24].

3. Results

The SEM image of the synthesized specimen (Fig. 1) shows bundles consisting of several wires with sizes of 300 nm in diameter and up to 80 μm in length, respectively. In a TEM bright field image of such bundle in a cross section (projection in [010]-direction), individual nanowires with diameters down to 200 nm become visible (Fig. 2). Microprobe and EDX analyses on the CVT-grown material yielded a formula of $Cu_{0.507(5)}Pb_{8.73(9)}Sb_{8.15(8)}I_{1.6}S_{20.0(2)}$. This unbalanced formula may be explained by the following facts. On the one hand the measurement of iodine has high uncertainties due to overlaps of the lines in the measured spectra and on the other hand an evaporation of iodine from the material during specimen irradiation within the microprobe is possible. Therefore, one can expect that the iodine content is higher than measured. Compared to natural pillaite, the CVT material contains no oxygen, iodine instead of chlorine and has one formula unit Sb_2S_3 less than the mineral. This suggests that the structures of the iodine containing material and natural pillaite are very similar but not exactly the same and reflects the chemical variability of sulfosalts. Furthermore, this result was unexpected since a natural jamesonite was the starting material in the CVT experiment. A reinvestigation of the initial material by electron microprobe analysis revealed that the mineral sample from Wolfsberg (Harz, Germany) consists mainly of jamesonite with a composition of $Fe_{0.873(8)}Pb_{4.01(4)}Sb_{6.12(6)}S_{13.8(2)}$ and minor amounts of a further copper-containing phase with a composition

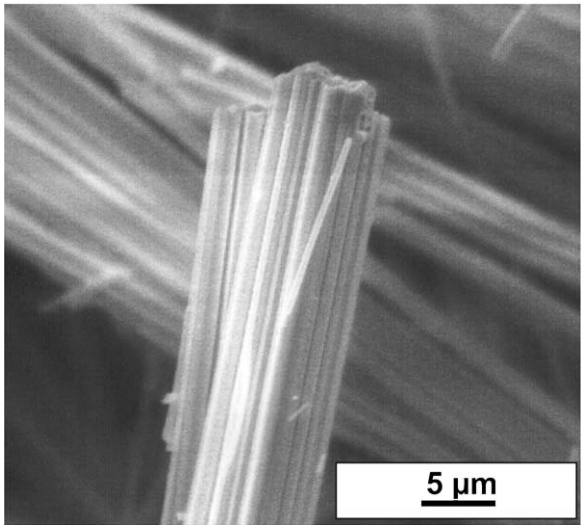

Fig. 1. SEM micrograph of a bundle of CVT-grown $Cu_{0.507(5)}Pb_{8.73(9)}Sb_{8.15(8)}I_{1.6}S_{20.0(2)}$.