Journal of Alloys and Compounds 390 (2005) 51–54

Journal of ALLOYS AND COMPOUNDS

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Electronic structure and thermoelectric properties of the thioantimonate $FePb_4Sb_6S_{14}$

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Received 29 May 2004; received in revised form 24 August 2004; accepted 26 August 2004

Abstract

The title compound was synthesized and its thermoelectric properties investigated. Electronic structure calculations and electrical conductivity measurements show semiconducting behavior. The results of thermopower measurements are presented. The high thermopower motivated us to investigate the effects arising from chemical doping. Cobalt and tin doped variants were synthesized and their physical property measurements show improved electrical conductivity.

Keywords: Thermoelectrics; Chalcogenide; Antimony; Lead; Physical properties

1. Introduction

Thermoelectric materials can convert thermal energy into electricity and can be used for heat pumping or refrigeration. The efficiency of these materials depends on the dimensionless figure-of-merit, ZT, which is defined as $ZT = TS^2\sigma/\kappa$. Therein, T is the absolute temperature, S the Seebeck coefficient, σ the electrical conductivity and κ is the thermal conductivity [1]. Hence, high Seebeck coefficients, high electrical conductivity (thus low electrical resistivity) combined with low thermal conductivity are ideal. Promising materials are small band gap semiconductors composed of heavy elements [2].

Binary lead, bismuth and antimony chalcogenides have been commercially used for a long time. Moreover, some of the most studied materials in thermoelectric research are ternary and higher antimony chalcogenides [3–12]. A major focus in our group is the research on potential thermoelectric materials in transition metal tetrelide, pnictide and chalcogenide systems using both experimental and theoretical approaches [13,14]. Currently, we are investigating ternary and higher lead antimony chalcogenides, for example $FePb_4Sb_6S_{14}$, which might be particularly interesting, since it occurs in nature, with the mineral name jamesonite. One can readily assign the oxidation states of iron, lead, antimony and sulfur to be +2, +2, +3 and –2, respectively. Magnetic susceptibility measurements on $FePb_4Sb_6S_{14}$ showed Curie–Weiss behavior above 150 K, and based on the effective magnetic moment high-spin state for Fe^{2+} was suggested [15,16].

2. Experimental

2.1. Synthesis

All elements were used as purchased from ALFA AESAR with purities between 99.5 and 99.9%. $FePb_4Sb_6S_{14}$ and its corresponding doped variants were synthesized by annealing stoichiometric mixtures of the elements in evacuated quartz tubes at 600 °C. At this temperature, all products were molten, and subsequent slow cooling yielded needle shape crystals.

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doi:10.1016/j.jallcom.2004.08.041

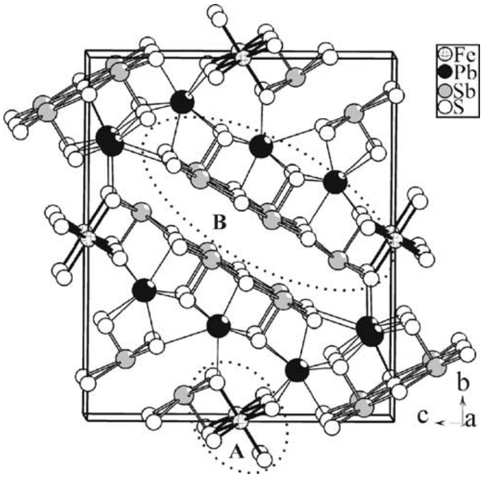

Fig. 1. Crystal structure of $FePb_4Sb_6S_{14}$. (A) One-dimensional chain of edge-sharing FeS_6 distorted octahedra. (B) Ribbon of edge-sharing SbS_5 square pyramids connected to the Pb–S chains.

2.2. Analyses

All samples were investigated by X-ray powder diffraction to check for purity by using an INEL powder diffractometer with a position sensitive detector. EDS analyses (LEO 1530, with integrated EDAX Pegasus 1200) on five selected crystals revealed the presence of iron, lead, antimony and sulfur in the ratio of 3.6:16.8:19.7:59.9 [in atomic percent], which compares well with the anticipated ratio of 4:16:24:56.

2.3. Band structure calculation

We carried out self-consistent tight-binding linear muffin tin orbitals (LMTO) calculations [17,18] using the structural parameters obtained from the refinement of Niizeki and Burger [19]. In this method, the density-functional theory is applied with the local density approximation (LDA) [20]. The integration in *k* space was performed by an improved tetrahedron method [21] on a grid of 488 independent *k* points of the first Brillouin zone, containing two formula units of $FePb_4Sb_6S_{14}$.

2.4. Physical property measurements

Temperature-dependent electrical conductivity measurements were carried out using a four-point method on cold-pressed bars of the dimensions of 6 mm × 1 mm × 1 mm. A self-made device was used to measure the voltage drops ΔV over a distance of 2 mm at a constant current of 0.2 mA under dynamic vacuum between 290 and 165 K.

Seebeck coefficients S of $FePb_4Sb_6S_{14}$ were determined on a cold-pressed bar prepared by exactly the same method. A commercial thermopower measurement apparatus (MMR Technologies) was used to measure S under dynamic vacuum in the temperature range between 300 and 450 K, using constantan as an internal standard to determine the temperature difference. Silver paint (TED PELLA) was used to create the electric contacts.

3. Results and discussion

$FePb_4Sb_6S_{14}$ crystallizes in the monoclinic space group $P2_1/c$. The structure is composed of three different motifs (Fig. 1). One is a ribbon of edge-sharing distorted SbS_5 square pyramids that are connected to the second motif, namely the Pb–S substructure. These two fragments together are reminiscent of the $Pb_4Sb_6S_{13}$ substructure [22]. The third is the chain of one-dimensional edge-sharing distorted FeS_6 octahedra running along the *a*-axis. The geometric distortion of FeS_6 is mainly a result of the Jahn–Teller effect, noting that the magnetic property measurements [15,16] pointed to high spin Fe^{2+}. The experimental powder diffraction pattern was nicely compatible with the simulated pattern from the published crystal structure data.

The band structure and the densities of states are shown in Fig. 2. Partially filled Fe d states are located between −2.4 and −0.6 eV, with a small gap between the "t_{2g}" and "e_g" states (noting that the FeS_6 polyhedron resembles an octahedron, without having O_h symmetry). The six "t_{2g}"-related bands occurring between −2.4 and −1.6 eV (stemming from the two Fe atoms per unit cell) are filled with eight electrons, and the four "e_g"-related bands above the gap comprise four electrons, for a total of six d electrons per Fe atom. In accord

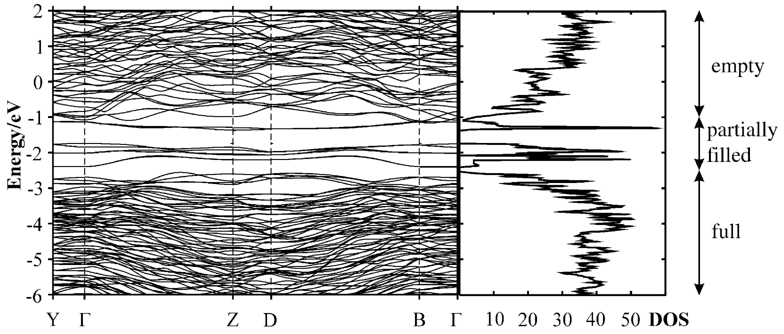

Fig. 2. Band structure (left) and densities of states (right) for $FePb_4Sb_6S_{14}$.