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Crystal structure and high temperature transport properties of Yb-filled *p*-type skutterudites $Yb_xCo_{2.5}Fe_{1.5}Sb_{12}$

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ABSTRACT

Partially Yb-filled Fe substituted polycrystalline *p*-type skutterudites with nominal compositions $Yb_xCo_{2.5}Fe_{1.5}Sb_{12}$, with varying filler concentrations *x*, were synthesized by reacting the constituent elements and subsequent solid state annealing, followed by densification by hot-pressing. The compositions and filling fractions were confirmed with a combination of Rietveld refinement and elemental analysis. Their thermoelectric properties were evaluated from 300 to 800 K. The Seebeck coefficients for the specimens increase with increasing temperature and plateau at around 750 K. The thermal conductivity decreases with increasing Yb filling fraction, and bipolar conduction becomes evident and increases at elevated temperatures. A maximum *ZT* value of 0.8 was obtained at 750 K for $Yb_{0.47}Co_{2.6}Fe_{1.4}Sb_{12}$. The thermoelectric properties and potential for further optimization are discussed in light of our results.

1. Introduction

A very active area of research is the direct conversion of waste heat to electrical energy. This technology requires materials with specific properties [1–3]. A good thermoelectric material will have a high value for the dimensionless thermoelectric figure-of-merit, ZT ($=S^2T/\rho\kappa$, where S is the Seebeck coefficient, ρ the electrical resistivity, κ the thermal conductivity, and T the absolute temperature), in the temperature range of interest. In general a material should possess a relatively large S (negative for *n*-type and positive for *p*-type) to maximize ZT while ρ and κ should be low to minimize Joule heating and thermal losses. The three material properties that define ZT can be varied by doping; however, they are not independent of each other [2,4].

Skutterudites are among the more promising thermoelectric materials for thermoelectric waste heat recovery at intermediate temperatures because of their excellent thermoelectric and mechanical properties [4–7]. One reason for this is their crystal structure (Fig. 1a). Two relatively large voids per *cubic unit cell* can accommodate rare-earth, alkali-earth, or alkali metal atoms [6,7]. The dynamic disorder from the void fillers results in significant reduction in the lattice thermal conductivity, κ_L, as compared to unfilled compositions [8–10].

To date *n*-type skutterudites have been more extensively studied, resulting in relatively high ZT values for single to triply filled compositions [6,7,11]. However, since both *p*- and *n*-type materials are essential for thermoelectric applications, *p*-type skutterudites have recently been the focus [12–23], although Sales et al. initially reported a high ZT for *p*-type $LaFe_3CoSb_{12}$ at elevated temperatures [24]. Nevertheless optimizing the thermoelectric properties of *p*-type skutterudite compounds is challenging due to a small hole effective mass, as compared to the much larger electron effective mass in *n*-type compounds [6,7,25]. Although Fe substitution for Co strongly affects the transport properties and filling fraction [15,22], Fe is readily incorporated into the lattice in order to generate *p*-type filled skutterudites. Thus, far several studies have shown that κ can be reduced at a certain Fe content and filling fractions [11,14,17,20,22]. In this work, we report on the high temperature transport properties of Yb filled and Fe substituted $CoSb_3$ compounds with nominal compositions of $Yb_xCo_{2.5}Fe_{1.5}Sb_{12}$. Along with refinements in synthesis and structural analyses, the thermoelectric properties of these materials are discussed.

2. Experimental

All compounds were prepared by direct reaction of the elements. Yb chunks (99.9%, Ames Labs), Co powder (99.998%, Alfa Aesar), Fe powder (99.998%, Alfa Aesar), and crushed Sb lumps (99.5%, Alfa Aesar) were loaded into silica ampoules in stoichiometric ratios $Yb_xCo_{2.5}Fe_{1.5}Sb_{12}$ (where $x=0.4$, 0.6, and 0.8) inside a N_2-filled glove box to minimize exposure of the reactants to air. The ampoules were sealed in quartz tubes, heated to 1223 K

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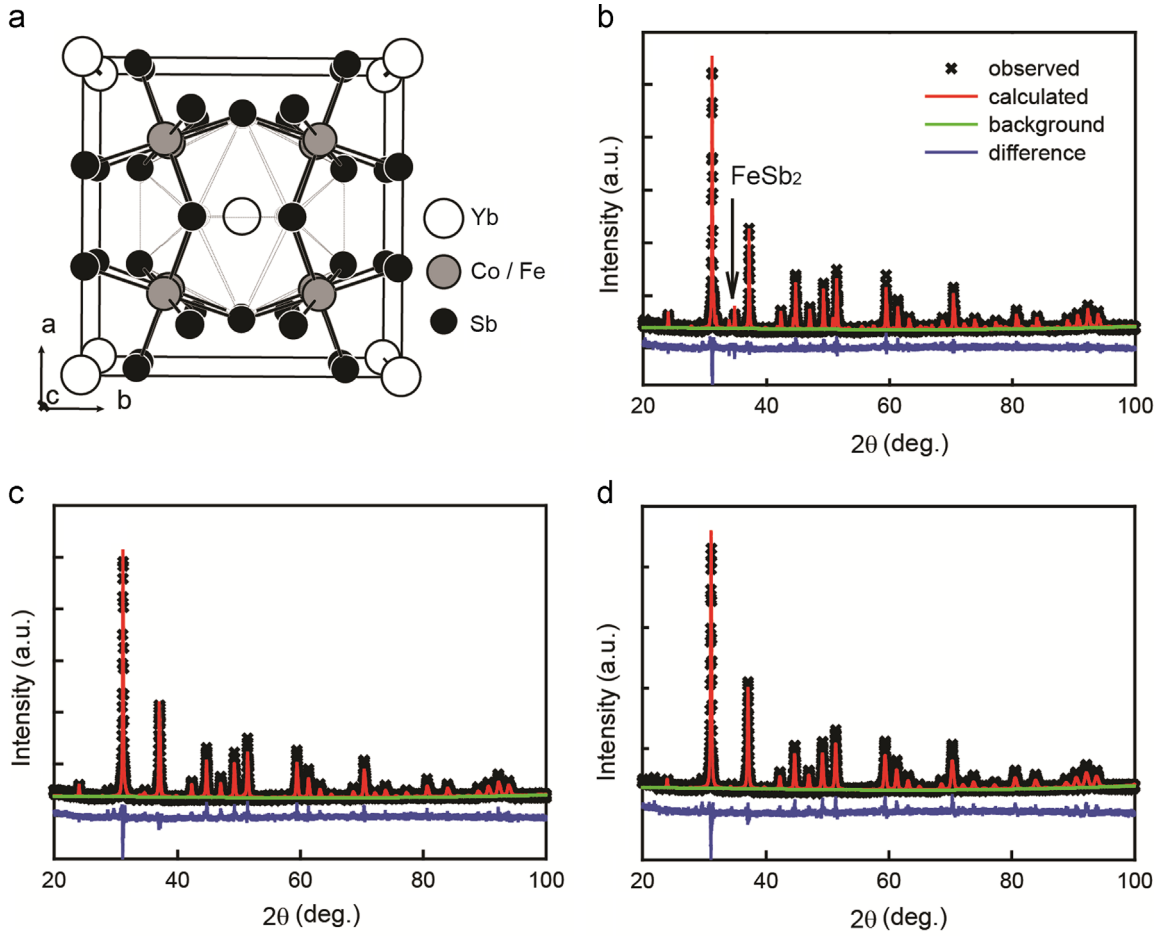

Fig. 1. (a) Crystal structure of $Yb_xCo_{2.5}Fe_{1.5}Sb_{12}$. Co/Fe atoms on the 8*c* crystallographic site are surrounded by six Sb stoms in an octahedral geometry. These octahedra share corners. The linked octahedra produce a vacancy site, at the center of the 8 Oh clusters, which Yb atoms occupy. Powder XRD data for (b) $Yb_{0.22}Co_{2.4}Fe_{1.6}Sb_{12}$, (c) $Yb_{0.38}Co_{2.5}Fe_{1.5}Sb_{12}$, and (d) $Yb_{0.47}Co_{2.6}Fe_{1.4}Sb_{12}$ including profile fit, profile difference, and profile residuals from Rietveld refinement.

and subsequently held at this temperature for 48 h. While at 1223 K the tubes were gently shaken to promote homogeneity of the melts. The furnace was turned off and the reaction tubes were quenched in air to room temperature. The products were then ground into fine powders, cold pressed into pellets and annealed at 923 K for one week. Additional grinding and annealing were performed in order to further promote homogeneity of the products. After appropriate annealing the products were then ground into fine powders (sieved to 325 mesh) inside the glove box and loaded into graphite dies for hot pressing. Densification was accomplished by hot pressing at 873 K and 150 MPa for 2 h under N_2 flow. The density of the hot-pressed pellets was determined by the measurement of their dimensions and weight after polishing the surfaces of the pellets. These measurements indicated that high density polycrystalline skutterudites ($>96\%$ of theoretical density) were obtained.

X-ray diffraction (XRD) and electron probe analyses were used to examine the purity and chemical composition of the specimens. Powder XRD data were collected with a Bruker D8 Focus diffractometer in Bragg-Brentano geometry using Cu$K_{\alpha,\beta}$ radiation and a graphite monochromator, and examined by the Rietveld method using the GSAS suite of programs [26]. Energy dispersive X-ray analysis (EDX) of the hot-pressed pellets was accomplished with an Oxford INCA X-Sight 7582M equipped scanning electron microscope (JEOL JSM-6390LV). The average atomic ratios were calculated from at least twelve data sets obtained from random positions of the hot pressed pellet for each specimen.

High temperature κ values were determined using the equation $\kappa = D \cdot d \cdot C_p$ where D is the measured density, d is measured thermal diffusivity, and C_p is the heat capacity. Thermal diffusivity measurements employed the laser flash method in a flowing Ar environment with a NETZSCH LFA 457 system. The uncertainty in the thermal diffusivity measurements was ~5–10%. Heat capacity C_p ($\approx C_v$) measurements (NETZSCH DSC 404C) were carried out and resulted in κ values that are similar to values estimated with the Dulong–Petit limit ($C_p = 3nR$, where n is the number of atoms per formula unit and R is the ideal gas constant). High temperatures S and ρ were measured on parallelepipeds, cut from the hot pressed pellets, with an ULVAC ZEM-2 system (experimental uncertainty of 5–10% for S and ρ at elevated temperatures). The thermoelectric measurements were performed perpendicular to the pressing axis, whereas the laser flash diffusivity measurements were carried out on the entire pellet parallel to the pressing axis. This is typically not a concern in these cubic materials with large grains.

3. Results and discussion

Powder XRD data were collected from 20° to 100° with a 0.02° step width. The details of the refinement results and data collection are given in Table 1. For all specimens the space group $Im\bar{3}$ (#204) was applied to refine the crystal structure. The initial atomic positions used were from the data on $Ba_{0.6}Fe_{1.6}Co_{2.4}Sb_{12}$