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Structure and transport behavior of In-filled cobalt rhodium antimonide skutterudites

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ABSTRACT

The effect of indium icosahedral void-site filling on the transport properties of cobalt and rhodium antimonide solid solutions is investigated. $Co_{4-x}Rh_xSb_{12}$ and indium-filled $In_{0.1}Co_{4-x}Rh_xSb_{12}$ solid solutions were synthesized. Partial rhodium substitution produces a distinct clustering-induced lattice strain that is partly relieved upon indium substitution into the skutterudite icosahedral void-sites. Indium lowers the thermal conductivity of all samples near room temperature. A distinct increase in thermal conductivity is observed in all indium-filled rhodium substituted samples at elevated temperatures and is attributed to bipolar thermal conductivity. In addition, the indium-filled samples were subjected to a 6-day heat treatment at 673 K. Void-site filled indium was found to be metastable at this temperature, and was found to partially precipitate during the 6-day heat treatment; thereby presenting concerns over the long-term stability of thermoelectric devices based on indium-filled skutterudites.

1. Introduction

Thermoelectric materials are the subject of intense research. The prospect of potentially catastrophic social and economic consequences triggered by global climate change has stimulated unprecedented demand for a host of diverse, clean, and sustainable energy technologies. This demand may be satiated in part by high-efficiency thermoelectric materials [1].

Skutterudites are a particularly promising class of thermoelectric materials as they can be tuned to possess some of the highest thermoelectric efficiencies observed in single-phase materials [2,3]. Skutterudites possess an open cage-like crystal structure with two large icosahedral void-sites per unit cell (Fig. 1). The void-sites can be filled with an array of disparate elements ranging from the electropositive alkalis and rare-earths, to poor metals such as indium, lead, and tin [4]. Thermoelectric efficiency – correlated to a dimensionless, temperature dependent (T) thermoelectric figure of merit (zT) – is enhanced by reducing the total thermal conductivity (κ_T), increasing the electrical conductivity (σ), or increasing the Seebeck coefficient (S) of the material (Eq. (1))

$$zT = T(\sigma S^2)/\kappa_T \quad (1)$$

The skutterudite zT is strongly enhanced by void-site filling. The filling atoms dramatically suppress thermal conductivity while concurrently contributing charge carriers to the total electrical conductivity. Moreover, the Seebeck coefficient, which is inversely related to the carrier concentration, generally remains reasonably large in filled skutterudites. Consequently, a sizable increase in zT is often exhibited in filled skutterudites compared to unfilled skutterudites [2,5–10]. However, in addition to icosahedral void-site filling, transition metal- and pnicogen-site alloying has also proven to be an effective strategy for suppressing thermal conductivity in skutterudites [11–15].

Researchers have studied the individual effects of cobalt and rhodium alloying [15,16] and indium icosahedral void-site filling [6,7,17,18] on the thermoelectric properties of antimonide skutterudites – both of which suppress lattice thermal conductivity – their combined effect, however, has not yet been investigated. Moreover, although high zT's have been reported for indium-filled skutterudites, their thermodynamic stability is suspected [19,20]. This study, therefore, examines the collective influence of both indium filling *and* rhodium-cobalt alloying on the thermoelectric properties of skutterudite antimonides, and investigates the possible metastability of the indium void-site filler.

2. Experimental

$Co_{4-x}Rh_xSb_{12}$ and indium-filled $In_{0.1}Co_{4-x}Rh_xSb_{12}$ compositions (with $x=0$, 1, 2, 3, 4) were synthesized from elemental

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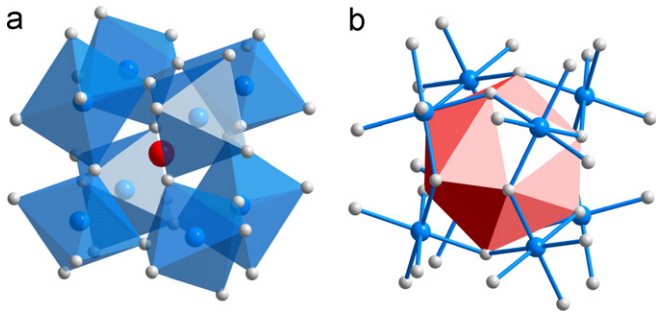

Fig. 1. The body-centered cubic indium-filled skutterudite crystal structure: (a) Indium (red) is shown at the center of the icosahedral-void site, surrounded by titled $(Co/Rh)Sb_6$ octahedra (blue and gray, respectively). (b) The icosahedral void constructed from 12 Sb-atoms from the tilted octahedra is shown in red. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

indium (Aldrich, 100 mesh, 99.99%), cobalt (Aldrich, <2 um, 99.8%), rhodium (Aldrich, 100 mesh, 99.5%), and antimony (Alfa Aesar, 100 mesh, 99.5%) in excess antimony vapor via a procedure developed by He et al. [6]. The as-synthesized powder was briefly ground in an agate mortar and hot pressed according to the sintering procedure published by Eilertsen et al. [18].

X-ray diffraction (XRD) data were collected on ground post-sintered sample powders using a Rigaku Ultima IV Multipurpose X-ray Diffraction System. The samples were loaded onto an oriented Si single-crystal sample holder (MTI Corporation) with nearly zero background to maximize the possibility of detecting impurity phases. Diffraction patterns were collected with a fixed-time scan rate of $0.01^\circ step^{-1}$ and 0.1 s $step^{-1}$ from 10 to $120^\circ 2\theta$.

The diffraction data were analyzed using the Le Bail technique [21] as implemented in the Fullprof program [22]. Peak shape was described by a Pseudo-Voigt function with additional asymmetric parameters for low-angle domain peaks (below $40^\circ 2\theta$), and the background level was fitted with a linear interpolation between a set of 40–60 given points with refineable heights.

The room temperature coefficient of thermal expansion (CTE) was determined from a linear fit of lattice parameter expansion data obtained from 308 to 873 K [23]. The principal thermoelectric properties were measured from 300 to 650 K. Electrical conductivity and Seebeck coefficient data were collected using an Ulvac-Riko ZEM 3 under static helium atmosphere. Thermal diffusivity (α) and specific heat (C_p) data were collected under flowing N_2 using a Netzsch LFA 457 Micro Flash, and a Mettler Toledo 821e Differential Scanning Calorimeter, respectively. Total thermal conductivity was determined from the relation $\kappa_T = c_p \times \alpha \times d$, where d is the sample bulk density.

Following thermoelectric measurements, the indium-filled samples were loaded into a tube furnace and reheated to 673 K for 6-days, under a flowing N_2/H_2 95:5 gas mixture to prevent oxidation. The samples were furnace-cooled. X-ray diffraction data was collected as above.

3. Results and discussion

3.1. Crystal structure

X-ray diffraction data reveal all compositions are single phase and crystallize in the body-centered cubic *Im*-3 skutterudite crystal structure (Fig. 2). The lattice parameter expansion observed upon Rh-substitution follows Vegard's relationship (Fig. 3a). Further expansion of the lattice is observed upon indium void-site filling. The percent lattice parameter expansion for indium-filled compositions is shown (Fig. 3a).

From main X-ray diffraction peaks, mean crystallite size (l) and strain (ε) were separated by constructing Halder–Wagner plots for each composition (Eq. (2)) [24–27]

$$\beta^2/(\tan^2\theta) = K\lambda/l \times (\beta/\tan\theta \sin\theta) + 16\varepsilon^2 \quad (2)$$

where a linear plot of the above relation between integral breadths (β), shape factor (K), wavelength (λ), and diffraction angle (θ) yields a slope and y-intercept from which the crystallite size and strain is determined, respectively. Although the data is not corrected for instrumental broadening, a qualitative comparison of crystallite size and strain is presented (Fig. 4, Table 1). It is evident that the unfilled $x=0$–4 compositions possess similar crystallite sizes, but a significant strain is observed in the alloyed ($x=1$–3) compositions (Fig. 4a). However, the strain is largely relieved upon indium void-site substitution (Fig. 4b).

The observed strain is likely due to clustering. Although the alloyed ($x=1$–3) compositions are single-phase, clustering of cobalt- and rhodium-rich regions likely produces strain that is absent in the end-members. The clustering is likely a precursor to the phase segregation predicted by Shi et al. [16], where the miscibility gap in the rhodium-substituted cobalt antimonide skutterudites is largely due to the large size difference between cobalt and rhodium. The cluster-induced strain is partially relieved upon indium substitution, however. As the percent lattice parameter expansion with indium filling decreases with rhodium content (Fig. 3a), indium-filled cobalt-containing compositions can expand further to accommodate larger rhodium atoms. Therefore, the indium-filled solid solutions are more thermodynamically stable – with respect to cobalt and rhodium substitution – than the unfilled solid solutions.

Lattice parameter expansion from 308 to 873 K and room temperature CTE data for all compositions are shown (Fig. 3b and c). Lattice parameter expansion is generally linear for all samples throughout the temperature range. The CTE decreases as rhodium content increases, consistent with a noteworthy increase in the covalent character of the Rh–Sb bonds. Slight differences are observed in the CTE data between unfilled- and the corresponding indium-filled compositions.

3.2. Electrical properties

The electronic conductivity of all samples from 300 to 650 K are shown (Fig. 5). All unfilled $Co_{4-x}Rh_xSb_{12}$ compositions (Fig. 5a) are semiconducting. The conductivity increases steadily with rhodium content as the highly covalent Rh–Sb bonding creates highly mobile charge carriers [28]. However, the cobalt-rich indium-filled samples ($x=0$, 1) are metallic (Fig. 5b). While with increasing rhodium content, the indium-filled samples become increasingly semiconducting consistent with the reported behavior of other filled Rh_4Sb_{12} skutterudites [12,18]. The semiconducting behavior is likely retained in the rhodium-rich samples as the charge carrier concentration donated by indium is small. As the void-site radius is much larger in the rhodium-rich compositions less orbital overlap between indium and the surrounding antimony cage is possible [18].

A comparison of the Seebeck coefficient data of both unfilled and filled samples supports the same conclusion (Fig. 5c and d). All unfilled compositions, except Co_4Sb_{12}, exhibit p-type conductivity. All indium-filled compositions are n-type near room temperature. However, all compositions, except $In_{0.1}Co_4Sb_{12}$, exhibit diminishing Seebeck coefficients at elevated temperatures. In fact compositions $x=3$ and 4 become p-type, and begin to approach the Seebeck coefficients of their unfilled counterparts. It is apparent that with increasing rhodium content the electronic effects of void-site filled indium are increasingly diminished.