Attrition-enhanced nanocomposite synthesis of indium-filled, iron-substituted skutterudite antimonides thermoelectric nanocomposites

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ABSTRACT

Nanostructuring has been the foremost approach to the manufacture of high-performance thermoelectric materials for nearly a decade. It is often achieved by harnessing the thermodynamic instability of metastable compositions to produce nano-sized precipitates, long heat-treatments, however, are often required. This study explores the efficacy of a novel nanostructuring technique, attrition-enhanced nanocomposite synthesis, in maximum indium-filled, iron-substituted cobalt antimonide skutterudites. This technique exploits both the open cage-like skutterudite crystal structure *and* the intrinsic metastability of the indium interstitial in the indium-filled cobalt antimonide skutterudites. $\text{In}_{0.3}\text{Fe}_{0.8}\text{Co}_{3.2}\text{Sb}_{12}$ was synthesized and subjected to varying duration of mechanical attrition (via ball milling) exhibited a degree of indium precipitation coincident with the duration of mechanical attrition. Indium readily diffused through the skutterudite crystal structure and rapidly precipitated forming 20-50 nm-sized indium-based inclusions, generating the genuine prospect of producing high-performance nanostructured thermoelectric materials from a cost-effective and easily scalable technique.

1. INTRODUCTON

The prospect of catastrophic social and economic consequences triggered by global climate change has stimulated unprecedented demand for a host of diverse, clean, and sustainable energy technologies.¹ This demand may be satiated in part by high-efficiency thermoelectric materials.² Consequently, decades of research have focused on enhancing their efficiency. Thermoelectric efficiency is typically reported as a dimensionless figure-of-merit (zT) at a specified temperature (T) (Eq. 1):

$$zT = \frac{\sigma S^2}{\kappa_T} T \quad \text{Eq. 1}$$

$$\text{where } \kappa_T = \kappa_L + \kappa_e \quad \text{Eq. 1a}$$

The zT is dependent on the electrical conductivity (σ), Seebeck coefficient (S), and lattice (κ_L) and electronic (κ_e) thermal conductivities of the material. Enhanced power-factors (σS^2) are often observed in moderately to heavily doped semiconductors which can possess both optimum charge carrier concentration and charge carrier mobility while maintaining a relatively high Seebeck coefficient.^{3,4}

Therefore, much research has focused on maintaining high-power factors while reducing lattice thermal conductivity in optimally doped semiconductors.^{5,6} Two techniques have proven

successful: 1) The substitution of loosely bonded atoms into large open cage-like crystal structures, as in the clathrates and skutterudites; and 2) the incorporation of nano-sized features within polycrystalline matrices, as in lead antimony silver telluride (LAST).^{5,7-13}

The large icosahedral voids within the open cage-like skutterudite crystal structure (Fig. 1) can be filled with a wide-array of disparate elements. These interstitials are loosely bound and reduce the lattice thermal conductivity considerably while also enhancing the electrical conductivity by contributing supplemental charge carriers.^{7,8,14} The zT of skutterudites, therefore, can be enhanced strongly by icosahedral void-site filling.

No technique, however, has been more effective at increasing the zT of bulk thermoelectric materials than nanostructuring.^{10,11,15-17} Nanostructured thermoelectrics – typically consisting of a polycrystalline matrix imbedded with nano-sized inclusions – are often synthesized from supersaturated (metastable) compositions.¹⁷ The metastable compositions are synthesized by cooling rapidly in order to prevent precipitation of the thermodynamically stable phases, and then heat treated (often for many days) to precipitate nano-sized inclusions.^{10,18,19} Ideally, the size of the inclusions is on the order of the matrix-phonon path length – which are strongly scattered by the nano-sized obstructions – and larger than the charge-carrier path length in order to avoid deleterious effects on the electronic transport.²⁰ Therefore, the controlled precipitation of the nanoinclusions to manage size, distribution, and morphology in general, is of paramount importance.

Attrition-enhanced nanocomposite synthesis (AENS) combines both approaches by embedding nano-sized inclusions into a polycrystalline matrix of interstitially filled open cage-like skutterudites.²¹ The primary requisite of the technique is that the interstitial filler is metastable, as in the $\text{Ga}_x\text{Co}_4\text{Sb}_{12}$ and $\text{In}_x\text{Co}_4\text{Sb}_{12}$ compositions.²¹⁻²⁴ These compositions are then subjected to heavy attrition via mechanical milling where they are reduced to heavily deformed fine-grained powders containing dislocations and other defects. The sample powders are sintered, and heat-treated to precipitate the metastable fillers from the icosahedral void-sites. In our previous work, we theorized that the combination of the open cage-like crystal structure, high dislocation and other defect concentrations, and minimized interstitial diffusion path lengths indeed enhance the diffusion kinetics and distribution of the precipitated interstitial – thus enabling the wide-spread dissemination of nano-sized phonon-scattering precipitates.²¹ The technique, however, has not been fully optimized.

This research reports a refined AENS procedure that employs both spark-plasma sintering and rapid heat treatment to achieve large reductions in the lattice thermal conductivity of indium-filled and cobalt-site-doped $\text{In}_{0.1}\text{Pd}_{0.15}\text{Co}_{3.85}\text{Sb}_{12}$ compositions. The sample was divided and subjected to various durations of ball milling, and rapidly densified using plasma-assisted sintering (SPS). It is found that a subsequent heat treatment dramatically reduces the lattice thermal conductivity in both samples – ostensibly due to the precipitation of indium from the skutterudite icosahedral void-sites – and that this reduction is coincident with the duration of ball milling.

2. EXPERIMENTAL

A large 20-gram batch of void-site-filled and cobalt-site-doped $\text{In}_{0.3}\text{Fe}_{0.8}\text{Co}_{3.2}\text{Sb}_{12}$ was synthesized from elemental indium (Aldrich, 100 mesh, 99.99 %), iron (Alfa Aesar, 200 mesh, 99+%), cobalt (Aldrich, < 2 μm , 99.8 %), and antimony (Alfa Aesar, 100 mesh, 99.5 %) under an atmosphere of antimony vapor and a 95%:5% $\text{N}_2\text{:H}_2$ gas mixture according to the procedure developed by He et al.²⁵ The batch was divided into four samples and mechanically milled in a

Fritzch Pulverisette 357 planetary ball mill for different durations (0, 10, 20, and 40 hours) at 400 rpm with silicon nitride bowls and grinding balls according to the procedure developed by us.²¹ The milled powder was loaded into 20-mm graphite dies and sintered using an FCT System GmbH SE607 spark-plasma sintering furnace: The samples were purged with argon and heated to 600 °C under vacuum with a heating ramp rate of 400 °C/min, sintered in AC mode using 10^3 A current with 10^4 N of applied force, and the sample chamber was back-filled with argon and rapidly cooled to room temperature at approximately 40 °C/min.

Each sintered pellet was cut into two disc-shaped samples. One set of samples was used for immediate analysis, and the other set was loaded into a tube furnace and reheated to 600 °C under a 95%:5% N₂:H₂ gas mixture at a rate of 40 °C/min, held for 20 minutes, and rapidly cooled by removing from the furnace.

Powder X-ray diffraction (XRD) data were collected on as-synthesized, milled and sintered, and heat-treated samples 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 °step⁻¹ and 0.1 sec step⁻¹ from 10 to 120 °2θ.

The diffraction data were analyzed using the Le Bail technique as implemented in the Fullprof program.^{26,27} Peak shape was described by a Pseudo-Voigt function with additional asymmetric parameters for low-angle domain peaks (below 40 °2θ), and the background level was fitted with a linear interpolation between a set of 40 to 60 given points with refineable heights.

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 N₂ using a Netzsch LFA 457 Micro Flash, and a Mettler Toledo 821e Differential Scanning Calorimeter, respectively. Total thermal conductivity was determined from the relation $\kappa_T = c_p \alpha d$, where d is the sample bulk density.

3. DISCUSSION

3.1 X-ray diffraction and microstructural data

X-ray diffraction data of as-synthesized and sintered, and 40-hour-milled and sintered samples are shown (Fig. 2). X-ray diffraction data reveal the indium-filled, palladium-doped skutterudite structures form. A small Sb impurity is observed in the as-synthesized In_{0.3}Fe_{0.8}Co_{3.2}Sb₁₂ sample, and is attributed to the excess antimony vapor employed during synthesis.

Lattice parameter data derived from LeBail refinements of as-synthesized and sintered, milled and sintered, and heat-treated samples are shown (Table 1). A significant lattice-parameter contraction is not observed in the sample following sintering or heat treatment as observed in our previous work on the In_{0.1}Co₄Sb₁₂ skutterudites treated to a similar nano-structuring procedure.²¹ Since palladium expands the cobalt antimonide skutterudite lattice a significant contraction due to the precipitation of indium from the icosahedral void sites is not expected. In fact a slight increase in lattice parameter is observed with the duration of ball milling and is attributed to the mechanical alloying of unreacted starting material.

Figure 1: XRD data of the as-synthesized and sintered (a), and 40-hour ball-milled and sintered $\text{In}_{0.3}\text{Fe}_{0.8}\text{Co}_{3.2}\text{Sb}_{12}$ samples. A small FeSb_2 is observed in the as-synthesized and sintered sample (a) and a small Sb impurity is observed in both (black arrows).

Figure 2: SEM data of the 40-hour ball-milled and sintered $\text{In}_{0.3}\text{Fe}_{0.8}\text{Co}_{3.2}\text{Sb}_{12}$ sample polished surface. The sample was replete with 20 - 30 nm inclusions, their composition was determined to be indium rich from EDS.

3.2 Electronic property data

The electrical conductivity data of the $\text{In}_{0.1}\text{Pd}_{0.15}\text{Co}_{3.85}\text{Sb}_{12}$ samples are shown (Fig. 4). All compositions are degenerate. A strong trend with the duration of milling in the as-sintered samples is not observed. It is possible that with greater mechanical milling, alloying of unreacted and undetected starting material may affect the observed electrical conductivity.

A clear correlation between the duration of milling and the observed drop in electrical conductivity in the sintered and heat-treated samples is evident. The magnitude of the drop trends with the duration of milling. As reported previously, precipitation of the void-site filler is strongly enhanced by mechanical milling.²¹

The Seebeck coefficient data of the sintered, and sintered and heat-treated samples are shown (Fig. 5). There is little variation in Seebeck coefficients. Moreover, aside from the 40-hour-milled sample, the Seebeck coefficients do not change appreciably following heat

treatment. The drop in Seebeck coefficient in the heat treated 40-hour-milled sample is attributed to the drop in charge-carrier concentration concomitant with precipitation of indium from the icosahedral void-site. The lack of a clearly definitive trend following heat treatment is likely due to the combined effects of partial indium precipitation, alloying of unreacted starting material, and nano-sized charge-filtering inclusions.

3.3 Thermal conductivity

The total and lattice thermal conductivity data of the samples are shown (Fig. 6). Little variation in thermal conductivity is observed prior to heat treatment. However, following heat treatment a dramatic decrease in total and lattice thermal conductivity is observed in the 20- and 40-hour-milled samples.

The dramatic drop is likely due to the precipitation of well-dispersed nano-sized phonon scattering precipitates (Sec. 3.1, Figure 3). It is probable that the 40-hour-milled sample possesses a higher concentration of more thoroughly dispersed inclusions as compared to the 20-hour samples, though more TEM is needed to confirm this assertion.

Figure 3

4. CONCLUSION

Indium-filled and n-type cobalt-site doped antimonide skutterudites were subjected to attrition-enhanced nanocomposite synthesis (AENS) combined with spark-plasma sintering and a

rapid heat-treatment. A substantial reduction in thermal conductivity was observed in the 20- and 40-hour milled $\text{In}_{0.1}\text{Pd}_{0.15}\text{Co}_{3.85}\text{Sb}_{12}$ sample following heat-treatment.

It is evident that AENS combined with rapid sintering, cooling, and heat-treatment can synthesize extremely low thermal conductivity nanocomposites. This procedure can be employed to synthesize nanocomposites from multiple-filled skutterudites where one of the filler elements is metastable – following this technique exceptional ZT's may be realized.

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