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Simple and efficient synthesis of nanograin structured single phase filled skutterudite for high thermoelectric performance

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ABSTRACT

Filled skutterudites are promising mid-to-high temperature range thermoelectric materials for power generation, however, a traditional melt-solidification process followed by annealing (TMA) and powder metallurgical sintering requires a long processing time more than 10 days to ensure the structural and compositional homogeniety of materials with a high thermoelectric conversion efficiency *zT*. To address this, we herein report a simple and efficient synthesis of high-performance n- and p-type filled skutterudites that successfully produces a complete single phase from single to multiple filled materials in a day. The nanograin (~440 nm) structured bulks are prepared from the combined process of temperature-regulated melt spinning (MS) using ingots and short-time spark plasma sintering (SPS). The controlled phase evolution and transformation by adjusting rapid solidification and densification conditions are demonstrated by a comprehensive analysis including structure refinement and atomic-scale observation, verifying the desired occupancy and random distribution of filling elements, respectively. The maximum *zT* values of filled skutterudites fabricated here were 1.48 ± 0.17 at 800 K for n-type $In_{0.12}Yb_{0.20}Co_{4.00}Sb_{11.84}$ and 1.15 ± 0.13 at 750 K for p-type $Ce_{0.91}Fe_{3.40}Co_{0.59}Sb_{12.14}$, which are comparable to the highest *zT* values reported for filled skutterudites fabricated by TMA-based processes. Superior reproducibility achieved in shortened processing time enables the present synthetic process to be utilized for commercial manufacturing process that can be readily applied to massive production of bulk filled skutterudites for high-performance thermoelectric power generators.

1. Introduction

Filled skutterudites with a chemical composition $R_xT_4Pn_{12}$ (R = rare earth, actinide, alkaline-earth, or alkali metal, T = transition metal, Pn = pnictogen atom) are compounds with cubic lattice in which R atoms (fillers or rattlers) fill in voids (nanosized cages) at the body-centered position [1]. Among them, filled skutterudite $CoSb_3$- and $FeSb_3$-based alloys are potential thermoelectric materials especially for mid-to-high temperature power generation applications such as automotive thermoelectric generators (ATEGs) due to their high thermoelectric figure of merit, zT ($= S^2\sigma T/\kappa_{tot}$, where S is Seebeck coefficient, σ is electrical conductivity, and κ_{tot} is total thermal conductivity at a given absolute temperature T), originated from extremely low lattice thermal conductivity (κ_{lat}) due to the rattling effect of fillers [2–4]. It has been regarded that the rattling effect by multiple fillers can be more effective for the further reduction of κ_{lat} due to the resonant phonon scattering [4–6].

Traditional melt-solidification (MS) processes generally produce large grain structured ingots with a complex phase formation behavior, in which the Co-Sb and Fe-Sb binary systems with a

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peritectic phase transformations solidify into various secondary phases including constituent elements and binary alloys such as $CoSb_2$ (or $FeSb_2$), RSb, and RSb_2 [7–11]. It is thus generally accepted that the long-time annealing process is indispensable to ensure homogeneity in composition and structure, especially for multiple filled skutterudites [4,8,9]. Indeed, a very high zT value of 1.7 at 850 K in n-type $CoSb_3$-based multiple filled skutterudites was obtained by melt-solidification and subsequent 7 days annealing at 750 °C [4]. In these considerations, the long-time melt-solidification-based fabrication process has been regarded as one of the main obstacles for cost-effective practical thermoelectric device applications.

In search for a simple and efficient method with shortened processing time, several approaches using ingots fabricated by traditional melt-solidification (TMA) processes have been developed [10–12], in which key aims are to reduce the grain size to nanoscale and to obtain a homogenous dispersion of various nanoscale secondary phases by pulverizing ingots. This can trigger the transformation to the filled skutterudite compounds during the sintering through the reaction between Co (or Fe), $CoSb_2$ (or $FeSb_2$), Sb, and R-Sb binary alloys. Although the high-energy ball milling of ingots followed by hot pressing produced Ce and Nd double filled p-type $Ce_{0.45}Nd_{0.45}Fe_{3.5}Co_{0.5}Sb_{12}$ in 2 days, the nanoinclusions of secondary phases have been inevitable [13], making difficult to precisely control the thermoelectric performance and ensure the performance reliability. Another route is the rapid solidification process such as gas atomization and MS followed by spark plasma sintering (SPS) [10,11,14]. Indeed, the n-type $Yb_{0.3}Co_4Sb_{12}$ and p-type $CeFe_4Sb_{12}$ filled skutterudites were prepared without long-time annealing process. However, these materials are not single phase compounds but composites with nanoinclusions, implying that the reproducibility and high temperature stability issues might be aroused along with thermoelectric performance degradation due to the non-stoichiometric contents of constituent atoms [10,11].

For a more simple and efficient synthesis of high-performance single phase filled skutterudites that is always more favorable for a cost-effective large-scale industrial production. Thus we focused on the clarification of phase transformation behavior at every step of process based on the quantitative analysis that allows the reproducibility of reliable and high-performance materials. We conceived that the compositional and dimensional control of melt spun ribbons with the homogeneous distribution of secondary phases is an essential prerequisite to accelerate the evolution of single phase filled skutterudites. This conceptual strategy would be well implemented by the control of melting and consolidating conditions in non-equilibrium rapid solidification followed by pressure induced sintering process.

In the present study, we demonstrate for the first time that the complete single phase of both n- and p-type single, double, and multiple filled skutterudites are fabricated in a day by temperature-regulated MS followed by SPS process. We intentionally set the melting temperature of MS process at ~1250 °C, which is slightly higher than solidus temperature (~1050 °C) of skutterudites, to suppress the formation of undesired secondary phases in melt-spun ribbons. From the manipulation of phase formation behavior, we can trace the transformation history from precursor powders with various secondary phases to complete single phase bulk filled skutterudites. Notably, this approach is feasible for both n- and p-type nanograined filled skutterudites and yields the high zT values of 1.48 ± 0.17 at 800 K for n-type $In_{0.12}Yb_{0.20}Co_{4.00}Sb_{11.84}$ and 1.15 ± 0.13 at 750 K for p-type $Ce_{0.91}Fe_{3.40}Co_{0.59}Sb_{12.14}$, which are comparable to the highest values ever reported filled skutterudites. It is noted that the present simple and efficient synthesis of filled skutterudites is verified by the comprehensive qualitative analysis confirming the actual contents of fillers from structural refinement and chemical composition analysis, and by the direct observation of atomic structure confirming the random distribution of fillers. Finally, the high-performance of nanograined filled skutterudites is attributed to the enhanced power factor ($S^2\sigma$) and reduced κ_{lat}.

2. Methods

2.1. Synthesis

High purity Co (99.9%, ingot, Kojundo Chemical), Fe (99.99%, grains, Kojundo Chemical), Sb (99.999%, shot, CLCDM), Ce (99.9%, grains, RND Korea), Yb (99.99%, grains, RND Korea), and In (99.99%, shot, RND Korea) were commercially obtained and used as received. The mixtures of raw materials with the appropriate ratio were loaded into a vacuum-sealed (~10^{-5} torr) quartz tube, and the contents were melted in a box furnace for 12 h at 1150 °C then water quenched. The acquired ingots were pulverized into powders, and ribbons were prepared from the powders by using MS at intentionally controlled melting temperatures (~1250 ± 40 °C) to manipulate the phase formation behavior. The powders (~6 g) were loaded into a graphite tube with a 0.35 mm nozzle and held under Ar atmosphere (30 kPa). After that, they were melted by a temperature monitoring induction system, and were injected under a pressure of 40 kPa Ar onto a Cu wheel (~300 K) rotating with linear speed of 50 m s^{-1}. In the present study, we obtained ~6 g melt spun ribbons from the compacted powders of ~8.5 g (yield ~70%) by optimization of MS processing variables. The obtained melt-spun ribbons were ground into powders and then sintered by SPS at 687 °C for 10 min under 80 MPa and at 587 °C for 10 min 40 MPa for n- and p-type materials, respectively. Highly dense (relative density > 96%) disk-shaped pellets with 20 mm in diameter and 8 mm in thickness were obtained. The ingot for TMA-SPS N0 sample was prepared by a typical melt-solidification and annealing at 740 °C for 336 h. The ingot was pulverized and densified at 687 °C for 10 min under 80 MPa using SPS [15].

2.2. Characterizations

Phase formation behavior of the melt-spun ribbons and SPSed bulks were investigated by X-ray diffraction (XRD) using a Smartlab (9 kW, Rigaku, Japan) with Cu Kα radiation (λ = 1.5418 Å). The actual compositions of the compacted samples were obtained by Field emission electro probe micro analyzer (FE-EPMA, JXA-8500F, 15 kV, JEOL) and also calculated from Rietveld refinement. The microstructures of the melt-spun ribbons and SPSed bulks were investigated using scanning electron microscope (SEM, JSM-7600F, JEOL) and electron backscatter diffraction (EBSD). Atomic structure of fillers into 2a site was confirmed by scanning transmission electron microscope (STEM, JEM-AEM 200F, 200 keV, JEOL).

2.3. Measurements

The σ and S were measured using a bar-type sample (16 mm × 3 mm × 3 mm) from 300 to 800 K with a ZEM-3 (Ulvac, Japan) in a He atmosphere. The thermal conductivity ($\kappa = \rho_s \times C_p \times \alpha$) was calculated from the separate measurements. Sample density (ρ_s) was measured by the Archimedes principle (AlfaMiracle, MD-300S). Temperature dependences of heat capacity (C_p) and thermal diffusivity (α) were collected using a DSC (NETZSCH, DSC 200 F3) and a laser flash method (Ulvac, TC-1200RH), respectively. The data of Hall effects were measured at a magnetic field of 2 T by a home-made equipment based on the van der Pauw method [16]. All measured TE transport properties,