Thermal Stability of La$_{0.9}$Fe$_3$CoSb$_{12}$ Skutterudite

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The thermal stability of the La$_{0.9}$Fe$_3$CoSb$_{12}$ skutterudite was examined by varying the aging conditions of temperature, time, and atmosphere (air and vacuum). Thermogravimetry, differential scanning calorimetry and x-ray diffraction analyses revealed that the La$_{0.9}$Fe$_3$CoSb$_{12}$ was significantly oxidized at temperatures above 673 K in air. The Sb-based oxides were preferably formed when aged at high temperatures in air. The thickness of the oxide layers was found to increase with increasing aging temperature and time, while the activation energy for the oxidation of the Fe-Sb-based skutterudite was lower than that of the Co-Sb-based skutterudites. However, when the analysis was performed in a vacuum, the La$_{0.9}$Fe$_3$CoSb$_{12}$ skutterudite was stable, and no oxide layers were observed after aging at 823 K for 100 h. These results suggest that a protective coating for the skutterudite materials or the encapsulated packaging of the skutterudite modules is required for high-temperature applications.

Key words: Thermoelectric, skutterudite, oxidation, thermal stability

INTRODUCTION

Filled skutterudites are the most potential materials for thermoelectric power generation in the intermediate temperature range. Filled skutterudites have the composition RM$_4$X$_{12}$, where R is an alkali-earth or rare-earth element, M is a transition metal such as Fe, Co, Rh, or Ir, and X is composed of a pnictogen element such P, As, or Sb. In contrast to the n-type Co$_4$Sb$_{12}$ with 72 valence electrons, p-type Fe$_4$Sb$_{12}$ is unstable because it has only 68 valence electrons, and thus a deficiency of 4 electrons. However, it can be stabilized to R$^{4+}$[Fe$_4$Sb$_{12}$]$^{4-}$ by filling at the voids in the skutterudite structure with R$^{4+}$ ions. Because most alkali-earth and rare-earth elements are divalent or trivalent, RFe$_4$Sb$_{12}$ should be charge-compensated. Filling of R$_2^+$ or R$_3^+$ and substitution (charge compensation) of Co or Ni for Fe can improve the phase stability and thermoelectric performance by controlling carrier concentration. Recently, Rogl et al. reported a very high dimensionless figure of merit, $ZT = 1.7$, for p-type skutterudites with multiple rare-earth filling and Co/Ni substitutions.

Although the filled skutterudite demonstrated excellent thermoelectric performance, its thermal stability at high operation temperatures is important. CoSb$_3$ starts to oxidize after aging at 673 K in air, and various oxides such as Sb$_2$O$_3$, SbO$_2$, CoSb$_2$O$_4$, and CoSb$_2$O$_6$ are formed with increasing temperature. Formation of these oxides leads to the degradation of thermoelectric properties. Generally, phase stability and resistance to oxidation are the most important factors for evaluating the thermal stability of the filled skutterudites for high-temperature applications. The oxidation resistance can be evaluated by using the activation energy for oxidation, and higher activation energies are better for oxidation resistance. In this study, La-filled and Co-substituted skutterudite (La$_{0.9}$Fe$_3$CoSb$_{12}$) was synthesized, and its thermal stability was evaluated. The phase transformation, oxide formation, oxide layer thickness and atomic redistribution were examined as a function of the following aging variables: temperature, time and atmosphere.
EXPERIMENTAL

La-filled and Co-substituted skutterudite, La$_{0.9}$Fe$_3$CoSb$_{12}$, was synthesized by encapsulated melting and annealing, and sintered by hot pressing. La (purity 99.95%), Fe (purity 99.95%), Co (purity 99.95%) and Sb (purity 99.999%) were melted at 1323 K for 10 h in an encapsulated quartz ampoule that was coated inside with carbon, and then quenched in water. The ingots subjected to encapsulated melting were annealed at 873 K for 24 h for homogenization and transformation to skutterudite phases. These synthesized ingots were ground into fine powders (<75 μm), and then sintered by hot pressing in a graphite die with an internal diameter of 10 mm at 873 K under a pressure of 70 MPa for 1 h in a vacuum.

To evaluate the oxidation and phase transition of the La$_{0.9}$Fe$_3$CoSb$_{12}$, thermogravimeter (TG) and differential scanning calorimeter (DSC) analyses were performed using the TGA-DSC1 system (Star; Mettler Toledo) in static air at a heating rate of 5 K/min. The specimens, with dimensions of 10 mm (diameter) × 2 mm (height), were aged from 573 K for 10–100 h in air or in a vacuum (10$^{-3}$ Torr). After aging, the surface phases of the specimens were analyzed using an X-ray diffractometer (XRD; Bruker D8-Advance) with Cu K$_\alpha$ radiation (40 kV, 30 mA). The diffraction patterns were measured in the 2θ–2θ mode (10°–90° 2θ) with a step size of 0.02°, a scan speed of 3°/min, and a wave length of 0.15405 nm. The aged specimens with disc-shape were cut into halves along the diameter like a half-moon, and scanning electron microscopy (SEM; FEI, Quanta400), in conjunction with energy-dispersive spectroscopy (EDS; Oxford, JSM-5800), was used to observe the microstructure and to analyze atomic redistribution for the cross-sections. The growth kinetics for the oxidation of La$_{0.9}$Fe$_3$CoSb$_{12}$ was also examined.

RESULTS AND DISCUSSION

Figure 1 shows the TG-DSC analysis results for the La$_{0.9}$Fe$_3$CoSb$_{12}$ skutterudite. As demonstrated by the TG curve, La$_{0.9}$Fe$_3$CoSb$_{12}$ became oxidized at temperatures above 673 K. Park et al. reported through XRD analysis that oxidation of In$_{0.25}$Co$_3$FeSb$_{12}$ started at 623 K, and Sklad et al. reported through TG analysis that oxidation of CeFe$_4$Sb$_{12}$ began at 573 K. Direct comparison of the oxidation behavior is difficult, due to the differences in analytical method and chemical composition. In our data, no phase transformations other than oxidation were observed, as shown in the DSC curve in Fig. 1. The positive direction stands for the exothermal reaction in the DSC curve.

Figure 2 presents the XRD patterns for the surfaces of the La$_{0.9}$Fe$_3$CoSb$_{12}$ skutterudites after aging. The skutterudite phase (δ) was found without oxides when the sample was aged at temperatures below 573 K for 10–100 h in air (Fig. 2a, b). Small amounts of Sb$_2$O$_3$ were observed when aged at 673 K for 10 h in air, which increased with the increasing aging time. As shown in Fig. 2d–i, the diffraction peaks of the skutterudite disappeared with increasing aging temperature and time, while the main diffraction peaks observed were those of Sb$_2$O$_3$ and SbO$_2$. However, Sb$_2$O$_3$ was almost completely transformed to SbO$_2$ when aged at 773 K for 100 h in air (Fig. 2j), after which complex oxides such as LaSb$_5$O$_{12}$, FeSb$_2$O$_4$ and FeSb$_2$O$_6$ were also produced (Fig. 2k–n). In the XRD analyses, Fe-based oxides were not detected at aging

![Fig. 1. Plots of TG and DSC for the analysis of hot-pressed La$_{0.9}$Fe$_3$CoSb$_{12}$ skutterudite.](image-url)