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Journal of Nuclear Materials 344 (2005) 79–83

journal of nuclear materials

www.elsevier.com/locate/jnucmat

Thermoelectric properties of uranium filled skutterudites $U_y(Fe_xCo_{4-x})Sb_{12}$

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Abstract

The filled skutterudites of the form $U_yFe_xCo_{4-x}Sb_{12}$ were fabricated and the thermoelectric properties for certain samples studied. For samples containing 100% cobalt, uranium could not be incorporated, or 'filled', into the voids in the skutterudite structure. With substitution of iron for cobalt the void occupancy by uranium increased. Uranium filled samples indicated relatively large Seebeck coefficient and p-type behavior. The thermal conductivity, especially below 500 K, of $U_yFe_xCo_{4-x}Sb_{12}$ was strongly depressed by uranium filling and iron substitution. The dimensionless thermoelectric figure of merits, ZT, were improved by uranium filling and showed a maximum value $ZT = 0.55$ at 800 K for $U_{0.2}FeCo_3Sb_{12}$ of nominal composition.

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1. Introduction

The nuclear fuel cycle discharges a large amount of depleted uranium (99.8% U-238) that is difficult to use for nuclear fuel; however, utilization of the depleted uranium is important in nuclear engineering. Since uranium has 5f-electrons and the largest atomic number in natural resources, uranium compounds exhibit interesting properties. We have been investigated new possibilities for uranium compounds as thermoelectric materials [1–3]. In general a material having a large average atomic number is thought to have enhanced μ_c/κ_{ph} (μ_c: carrier mobility, κ_{ph}: thermal conductivity of phonon) [4] as well as a large thermoelectric figure of merit Z, where $Z = S^2\sigma/\kappa$ (S: Seebeck coefficient, σ: electrical conductivity and κ: thermal conductivity). Since the dimensions of Z are inverse to temperature, it is customary to define the dimensionless figure of merit as ZT, where T is the absolute temperature.

Recently, some of skutterudite compounds have been shown to have high thermoelectric figures of merit and hold out the possibility of fabricating highly efficient thermoelectric generators [5,6]. These compounds are

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doi:10.1016/j.jnucmat.2005.04.020

called ‘filled skutterudite’ and are derived from binary (unfilled) skutterudites of the form AB_3, where A is Co Rh or Ir and B is P, As or Sb. The structure of these compounds has been well determined experimentally [7–9] and consists of a cubic array of metal A atoms containing four-membered square planar rings of pnicogen B atoms (space group *Im3*). Skutterudites have large voids in their lattice structure. This void is thought to be equivalent to the unoccupied site between the AB_6 octahedron as distorted perovskite structure. Since the radius of the rare-earth atom is significantly smaller than the radius of the void, the former ‘rattles’, i.e., exhibits a soft phonon mode. Experimental evidence of such rattling had already been demonstrated in a large X-ray thermal parameter [10–12], characteristic of rare-earth atoms in this structure. Thermal conductivity was more reduced by filling with smaller and heavier rare earth atoms. In this study, we explore the reduction of the thermal conductivity by filling with uranium, which is the much smaller than rare earth atoms and the heaviest in naturally existing atoms, and the thermoelectric properties for uranium filled skutterudite.

2. Experimental

2.1. Sample preparation and phase identification

Polycrystalline samples of $U_yFe_xCo_{4-x}Sb_{12}$ were first synthesized by arc melting the mixture of starting materials, 99.98% pure uranium metal, 99.99% pure iron, 99.98% or 99.999% pure cobalt and 99.999% pure antimony, under purified argon gas with Ti getter. To cover the vaporizing loss of antimony, antimony is added excessively at a few %. The arc-melted ingots were annealed in a vacuum at 973 K for 2 weeks. Then the ingots were pulverized to a powder that was again sintered by the SPS method [13]. In the SPS method, the sample powder was filled into a graphite die and the graphite punches settled. Sintering was done by loading the pulse current (about 1000 A) in the argon atmosphere at 923 K for 20 min under a pressure of 45 MPa. For the electrical conductivity and Seebeck coefficient measurements, samples were rectangular bars of 1.5–2.5 mm thickness, 3 mm width and 20 mm length;, and for thermal diffusivity measurements, disks were 1.0–2.0 mm thickness and 10 mm diameter. The crystal structure was identified by X-ray diffraction analysis and the lattice constants were calculated. Electron-probe microanalysis was performed to determine the composition of the skutterudite phase and check homogeneity of samples.

2.2. Measurements of thermoelectric properties

The Seebeck coefficient and electrical conductivity were measured simultaneously at each temperature. The electrical conductivity was measured by a d.c. 4-probe technique using the platinum wires of each thermocouple as current leads. The current was applied by a regulated d.c. power supply and the voltage and current were measured with digital voltmeters. The Seebeck coefficients were calculated from the least squares regressions of the thermoelectromotive forces as a function of the temperature difference. The thermal diffusivities were measured using a laser flash method over a temperature range from 290 to 1170 K using a TC-7000 (RIGAKU, Japan). The thermal diffusivity measurements of each specimen were carried out three times at each temperature in a vacuum of less than 1×10^{-2} Pa. The thermal diffusivities were estimated from the time dependence of the temperature for the rear sample surface by using a curve fitting method [14]. Heat capacity was measured with a differential scanning calorimeter (DSC-200: Seiko Instruments, Japan) in a range from 350 to 870 K in a purified argon atmosphere.

3. Results and discussion

From X-ray diffraction results, all samples display peaks characteristic of the filled skutterudite structure. In addition, we see that for samples containing higher concentrations of uranium there appear additional small peaks which we attribute to impurity phases of (Co, Fe)Sb_2 and UO_2. The shifting in relative intensity of some peaks, e.g., (2 1 1) peak at $2\theta \approx 24°$, which is strong in $CoSb_3$ but is small in $U_{0.1}FeCo_3Sb_{12}$ is evidence of increasing uranium site occupation, because this peak should be absent when the site is fully occupied. The impurity phases $(Co, Fe)Sb_2$ and UO_2 become more prominent as the uranium concentration increases in these samples, indicating the limited solubility of the uranium filling ions, similar to findings in which solubility limits were reached near 10% for rare earth filling [15,16]. In electron-probe analysis uranium is unevenly distributed. Furthermore O/U ratio was much smaller than 2, which probably indicate uranium metal rather than UO_2 precipitated in the matrix. The peak of UO_2 in XRD pattern should be originated from only surface oxidation of uranium. Table 1 shows the nominal composition, the estimated composition, the lattice constant and the presence of secondary phases in each sample. The lattice constant changes almost linearly as a function of the iron concentration as observed for Ce_yFe_x-$Co_{4-x}Sb_{12}$ [17]. A change of lattice constant for the uranium concentration was not clearly observed for any of the samples. It is not clear whether the solubility limit of uranium in the skutterudite structure is below $y = 0.02$ in $U_yCo_4Sb_{12}$, or the lattice parameter does not change when uranium is filled into the void of skutterudite because of uranium’s small ionic radius. Uranium will be incorporated into the void in the skutt-

Table 1
Nominal overall compositions, lattice constants and presence of secondary phases in $U_yFe_xCo_{4-x}Sb_{12}$ samples

Sample number and nominal composition	Estimated composition of the skutterudite phase $U_yFe_xCo_{4-x}Sb_{12}$	Lattice constant/pm	Secondary phases[a]
1: $CoSb_3$	–	903.51 (10)	None
2: $Fe_{0.5}Co_{3.5}Sb_{12}$	$x = 0.5$	904.74 (10)	None
3: $U_{0.02}Co_4Sb_{12}$	$y < 0.02$	903.49 (15)	$U(UO_2) < 1\%$
4: $U_{0.05}Co_4Sb_{12}$	$y < 0.02$	903.52 (15)	$U(UO_2) \sim 1\%$
5: $U_{0.07}Co_4Sb_{12}$	$y < 0.02$	903.51 (16)	$U(UO_2) \sim 1\%$
6: $U_{0.1}Co_4Sb_{12}$	$y < 0.02$	903.51 (16)	$U(UO_2) \sim 2\%$
7: $U_{0.1}Fe_{0.5}Co_{3.5}Sb_{12}$	$y < 0.05,\ x \approx 0.5$	904.80 (18)	$U(UO_2) \sim 2\%$
8: $U_{0.2}Fe_{0.5}Co_{3.5}Sb_{12}$	$y < 0.05,\ x \approx 0.5$	904.58 (18)	$U(UO_2) \sim 3\%$
9: $U_{0.3}Fe_{0.5}Co_{3.5}Sb_{12}$	$y < 0.05,\ x \approx 0.5$	904.58 (17)	$U(UO_2) \sim 5\%$
10: $U_{0.4}Fe_{0.5}Co_{3.5}Sb_{12}$	$y < 0.08,\ x \approx 0.5$	904.76 (15)	$U(UO_2) \sim 10\%$
11: $U_{0.1}FeCo_3Sb_{12}$	$y < 0.05,\ x \approx 1.0$	903.66 (19)	$(Fe,Co)Sb_2 \sim 5\%$, $U(UO_2) \sim 2\%$
12: $U_{0.2}FeCo_3Sb_{12}$	$y < 0.05,\ x \approx 0.9$	903.72 (19)	$(Fe,Co)Sb_2 \sim 10\%$, $U(UO_2) \sim 4\%$
13: $U_{0.3}FeCo_3Sb_{12}$	$y < 0.05,\ x \approx 1.0$	903.74 (18)	$(Fe,Co)Sb_2 \sim 5\%$, $U(UO_2) \sim 5\%$
14: $U_{0.4}FeCo_3Sb_{12}$	$y < 0.1,\ x \approx 0.9$	903.82 (18)	$(Fe,Co)Sb_2 \sim 10\%$, $U(UO_2) \sim 4\%$
15: $U_{0.2}Fe_2Co_2Sb_{12}$	$y < 0.1,\ x \approx 1.8$	909.30 (20)	$(Fe,Co)Sb_2 \sim 5\%$, $U(UO_2) \sim 5\%$

[a] The ratio of secondary phases is area ratio in the mapping analysis.

erudite structure, but at some point, dependent on the iron content, void filling becomes saturated and any additional uranium above this limit presumably precipitate in the matrix. It is likely that the uranium is incorporated in its ionic radius which is smaller than those of rare earth elements. The difficulty to insert uranium could be depend on its valence (+4) larger than trivalent rare earths.

Thermoelectric properties in the series $U_yFe_xCo_{4-x}Sb_{12}$ are displayed in Figs. 1 and 2 together with $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18]. In Fig. 1, semiconducting behavior is obvious in the electric conductivity of $CoSb_3$. Addition of uranium and iron to semiconducting $CoSb_3$, results in semi-metallic behavior in the conductivity. The electrical conductivity increased with iron content. The effect of uranium filling on electrical conductivity appears to be small, and the effects of secondary phases rather large. Especially in the sample 10, uranium precipitated consecutively around the grain boundary. Therefore the electrical conductivity of sample 4 was larger than those of sample 2 and 3. Fig. 2 shows the Seebeck coefficient of each sample. Seebeck coefficients increased with temperature in the measured temperature range, except those for $CoSb_3$ and $U_{0.05}Co_4Sb_{12}$. This result also indicates that uranium was hardly incorporated into voids of the skutterudite structure without iron substitution for cobalt. There was no obvious propensity for the Seebeck coefficient with chemical substances.

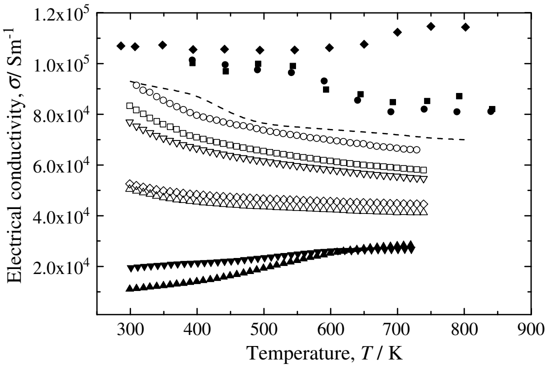

Fig. 1. Electrical conductivity of $U_yFe_xCo_{4-x}Sb_{12}$ for various filling fractions: (▲) sample 1, (▼) sample 4, (○) sample 2, (□) sample 7, (◇) sample 8, (△) sample 9, (▽) sample 10, (●) sample 11, (■) sample 12, (♦) sample 15, (- - -) $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18].

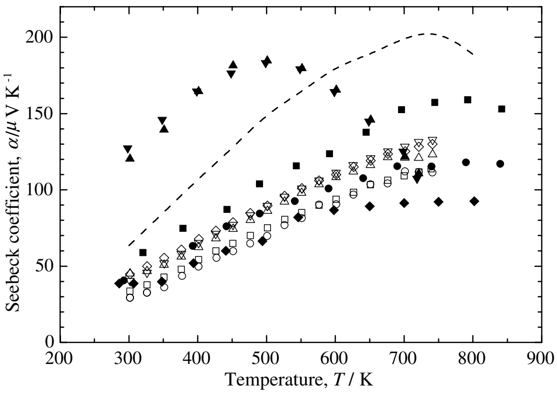

Fig. 2. Seebeck coefficient of $U_yFe_xCo_{4-x}Sb_{12}$ for various filling fractions: (▲) sample 1, (▼) sample 4, (○) sample 2, (□) sample 7, (◇) sample 8, (△) sample 9, (▽) sample 10, (●) sample 11, (■) sample 12, (♦) sample 15, (- - -) $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18].

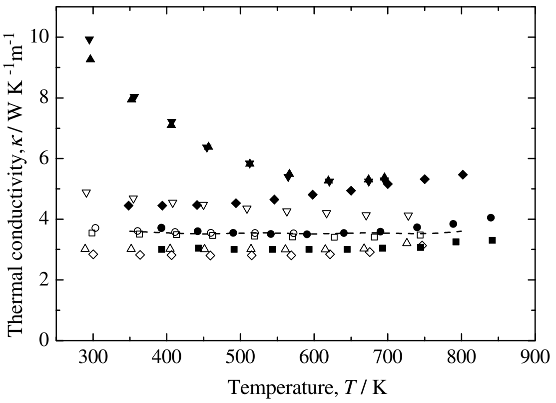

Fig. 3. Thermal conductivity of $U_yFe_xCo_{4-x}Sb_{12}$ for various filling fractions: (▲) sample 1, (▼) sample 4, (○) sample 2, (□) sample 7, (◇) sample 8, (△) sample 9, (▽) sample 10, (●) sample 11, (■) sample 12, (♦) sample 15, (---) $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18].

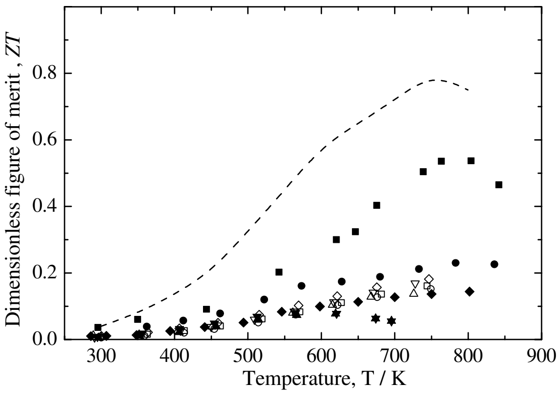

Fig. 4. Thermoelectric figure of merit of $U_yFe_xCo_{4-x}Sb_{12}$ for various filling fractions: (▲) sample 1, (▼) sample 4, (○) sample 2, (□) sample 7, (◇) sample 8, (△) sample 9, (▽) sample 10, (●) sample 11, (■) sample 12, (♦) sample 15, (---) $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18].

The thermal conductivity κ is given by Eq. (1) with the heat capacity C_p, density ρ and thermal diffusivity a

$$\kappa = C_p a \rho. \quad (1)$$

The heat capacity value obtained in this study for $U_yFe_xCo_{4-x}Sb_{12}$ was almost the same with the value calculated by Kopp–Neumann's law using reported elemental data [19]. Therefore the calculated heat capacity value was used to estimate thermal conductivity. Thermal conductivity is shown in Fig. 3. The thermal conductivity values of non-filled $CoSb_3$ and $U_{0.05}Co_4Sb_{12}$ were slightly larger at low temperatures and decreased with temperature. The thermal conductivity of $U_{0.05}Co_4Sb_{12}$ was almost the same as that of $CoSb_3$, which also indicates that uranium was not filled into the voids of the skutterudite structure. The incorporation of uranium with iron substitution reduces the thermal conductivity relative to $CoSb_3$. The weak temperature dependence is characteristic of the scattering due to the rattling uranium atom [20].

Based on the above measurements, the thermoelectric dimensionless figure of merit ZT is shown in Fig. 4. In sample 11, ZT reaches 0.55 at 650 K, which is comparative to that for $Ce_{0.12}Fe_{0.71}Co_{3.29}Sb_{12}$ [18]. The ZT tended to be larger with uranium content and smaller with iron content. Since the iron concentration should be larger to dope more uranium, the optimal iron and uranium concentrations should be able to be determined by further studies.

4. Conclusion

Thermoelectric properties were measured for uranium added (Fe,Co)Sb_3. To fill uranium into the voids of skutterudite structures, a cobalt site should be partially substituted by iron. By uranium filling the dimensionless figure of merit was improved and reached $ZT = 0.55$ in $U_{0.2}FeCo_3Sb_{12}$ of nominal composition at 800 K. The present results proved that the uranium filled skutterudite (Fe,Co)Sb_3 showed a good p-type thermoelectric property.

Acknowledgement

The present work was partially supported by the grant from the 21st century COE program 'Isotope Science and Engineering from Basics to Applications'.

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