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Thermoelectric properties of nanocomposite heavy fermion $CeCu_6$

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ABSTRACT

We report on the thermoelectric performance of the heavy fermion compound $CeCu_6$ nanocomposite samples. Measurements of Seebeck coefficient, electrical resistivity and thermal conductivity are presented over the temperature range $5 < T < 350$ K. The dimensionless figure-of-merit (ZT) was optimized by varying the sample hot-pressing temperature. Thermal conductivity measurements show that the lowest hot pressing temperature (450 °C) produces the lowest thermal conductivity. Electrical resistivity is strongly influenced by hot pressing temperature and drops by a factor of ~3.4 as the hot pressing temperature is lowered from 800 to 450 °C. Seebeck coefficient shows a slight increase over other samples when hot pressed at 800 °C. Our ZT calculations show a broad peak with a maximum value of 0.024 at ~60 K for the sample hot pressed at 800 °C.

1. Introduction

In recent years, solid-state cooling based on the Peltier effect has gained increased attention. Coefficient of performance (Φ) for a Peltier cooler is given as [1,2],

$$\varnothing_{\max} = \frac{T_1\left[(1+ZT)^{1/2} - T_2/T_1\right]}{(T_2 - T_1)[(1+ZT)^{1/2}+1]} \quad (1)$$

where T_1 and T_2 are the temperature of heat source and sink respectively and $T = (T_1 + T_2)/2$. The quantity ZT is dimensionless thermoelectric figure-of-merit and is defined as $ZT = S^2\rho^{-1}\kappa^{-1}T$. Here S is the Seebeck coefficient, ρ is the electrical resistivity, κ is the total thermal conductivity, and T is the absolute temperature. It is essential that high ZT materials and process methods be discovered to build efficient Peltier coolers particularly when operating at low temperatures. Optimizing the ZT of a material has been challenging due to the complex and interrelated quantities: S, ρ and κ. Current state of-the-art materials typically possess a peak ZT in the range of 1–1.8 for different materials [3,4]. Such a system has yet to be discovered for temperatures below 200 K. Correlated electron systems are considered one of the materials which might be useful for Peltier coolers below 77 K. Among the correlated systems, heavy-fermion compounds (HFCs) show promising thermoelectric properties at low temperatures, with a large S and small ρ [5]. In these compounds, below some characteristic temperature T_k a sharp peak of the density of states develops at the Fermi level (E_F) which results in highly enhanced values for both the Sommerfeld (γ) and Seebeck coefficient (S) [6].

Since the discovery by Stewart et al. [7] in 1984, $CeCu_6$ has been one of the widely studied HFCs. A great deal of interest was focused on transport properties of this system in the following years [8–13], owing to the Fermi liquid (FL) behavior at low temperature, similar to that of $CeAl_3$ [14]. Subsequent studies on this compound were focused on non-Fermi liquid (NFL) behavior [15,16] and anomalous thermopower [17–19]. In the recent years this compound has been a platform for studying the quantum critical point (QCP) behavior [20]. Although measurement of its transport properties has long been taken as an approach to investigate quasiparticle excitation, $CeCu_6$ has not been heavily studied as a thermoelectric material. In this work we studied the thermoelectric properties of $CeCu_6$ and applied the technique of mechanical nanostructuring approach to the synthesis of the materials to improve their ZTs.

Nanostructuring has been proven to be very effective at reducing the thermal conductivity without harming the electronic properties [3]. There have been many studies which attempted to employ this technique to increase ZT near or above room temperature. Since the phonon contribution, in general, increases with a decrease in temperature; it is possible that nanostructuring could lead to a reduction in the thermal conductivity of thermoelectric material at low temperatures. In our previous work, we successfully enhanced the ZT of strongly correlated narrow-gap semiconductor $FeSb_2$ using nanostructuring approach [21–23]. This paper

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is a result of our continued investigation of the effectiveness of nanostructuring at improving *ZT* at low temperatures (below 77 K).

2. Experimental

Stoichiometric amounts of Ce (99.9%, Alfa Aesar) and Cu (99.99%, Alfa Aesar) were melted in an argon environment using an arc-melter. To improve chemical homogeneity, the melted sample was flipped over and re-melted three times. The resulting ingot was etched in dilute nitric acid then ball milled for five hours to create a nanopowder of $CeCu_6$. The nanopowder was then hot pressed for two minutes at 450, 600 and 800 °C under a uniaxial pressure of 80 MPa. For simplicity, the samples are given short names. For instance, the name "HP 800" stands for the sample hot-pressed at 800 °C. X-ray diffraction (XRD, Bruker, AXS) was performed on the freshly fractured surface of the samples. Scanning Electron Microscopy (SEM, JEOL 6340F) was used to investigate the grain-size distribution of the samples. The Seebeck coefficient (S), electrical resistivity (ρ), and thermal conductivity (κ) from 5 to 300 K were measured on samples of typical dimensions of $3 \times 3 \times 4$ mm^3. A 2-point method in thermal transport option (TTO) of the Physical Property Measurement System (PPMS) was used to measure the thermoelectric properties. The horizontal rotator option of the PPMS was used to measure Hall coefficient (R_H) of the samples with typical dimensions of $1 \times 2 \times 10$ mm^3.

3. Results and discussion

The X-ray diffraction patterns are shown in Fig. 1 for the ingot and ball milled/hot pressed samples. The peak positions confirm the orthorhombic crystal structure and indicate that the ingot was alloyed in a single phase form. We note the X-ray peaks are broadened only slightly by the ball-milling process, while the crystal structure is retained.

Fig. 2 shows the SEM images of the samples. No voids are seen for ingot and the sample HP 800 °C. The nearly equal values for the densities of the ingot and the sample HP 800 are consistent with the SEM images. The samples hot pressed at 450 and 600 °C show a distinctly different microstructure from the HP 800 sample. Sample porosity increases and surface texture becomes rough at the lower hot pressing temperatures

The electrical resistivity ρ of the samples are shown in Fig. 3 as a function of temperature. All the samples exhibit a similar resistivity profile, typical of single crystal $CeCu_6$. Below 300 K, the resistivity decreases as the temperature is lowered until it reaches a flat minimum. At approximately 75 K, a Kondo-like behavior emerges with a negative value for $\partial\rho/\partial T$. The resistivity then reaches a maximum at around 15 K before declining sharply with decreasing temperature, an indication of coherence development. Electrical resistivity of the 800 °C hot-pressed sample is slightly increased

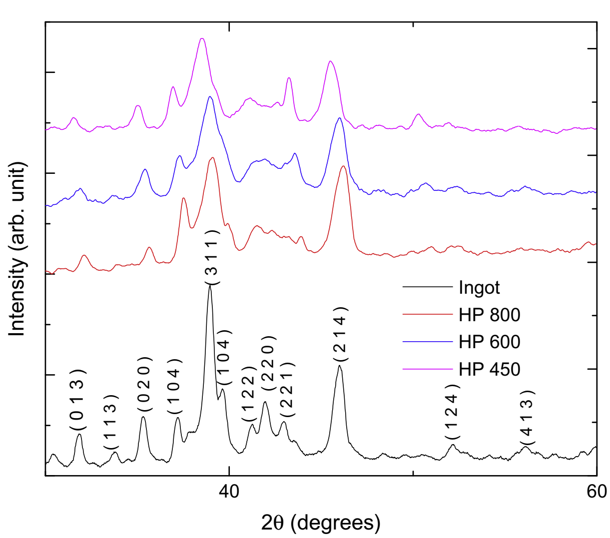

Fig. 1. X-ray diffraction pattern for the arc melted ingot and the three hot pressed samples of $CeCu_6$.

when compared to the ingot; this is expected due to the increased scattering from the nanocomposite grains. A comparison among the hot-pressed samples shows that the electrical properties of $CeCu_6$ are greatly affected by varying HP temperature. With decreasing HP temperature the electrical resistivity increases significantly. When comparing HP 800 and 450 °C samples, we note at 60 K an increase in resistivity by a factor of ~3.4. Such a drastic increase in the electrical resistivity is attributed to the reduced grain size and the increased porosity.

Fig. 4 shows the total thermal conductivity (κ) for the samples as a function of temperature. For comparison the thermal conductivity for polycrystalline samples of $CeCu_6$ was taken from Ref. [24]. The thermal conductivity follows temperature dependence similar to that reported for another HFC $CeCu_4Al$ [25]. The total thermal conductivity decreases as the HP temperature decreases. At 60 K, κ was reduced from ~ 5 W m^{-1} K^{-1} (for ingot) to ~ 2 W m^{-1} K^{-1} (for sample HP 450), a reduction by 60%. In general, $\kappa = \kappa_l + \kappa_e$, where κ_l and κ_e are the lattice and electronic contributions to the total thermal conductivity, respectively. Generally, phonon scattering by grain boundary reduces the phonon contribution (κ_l) whereas macroscale porosity is shown to reduce the electronic contribution (κ_e) [26,27]. The SEM images (Fig. 2) suggest that the reduction of the thermal conductivity with decreasing HP temperature might be attributed to both the contributions from grain boundary scattering and the porosity effect.

In Fig. 5 we present the temperature dependence of the Seebeck coefficient. All the samples exhibit a positive Seebeck coefficient below 300 K with a maximum at $T_{max} \approx 50$ K. This value for T_{max} is in agreement with the previously reported data [18,19]. In the context of heavy-fermions, such a peak in S at higher T ($T > T_K$) is usually attributed to the Kondo scattering on higher multiplets (as opposed ground state doublet) which are split by crystal effect field (CEF). For $T > T_{max}$, S follows an unusual temperature dependence of the form: $S \propto -\ln T$, whereas for $T < T_{max}$, S follows the typical behavior of metals. The Seebeck coefficient decreases as the HP temperature decreases.

We also measured temperature dependent Hall coefficient (R_H) of the samples. Under the assumption of single band (SB) model, the effective carrier density (n) and the Hall mobility (μ_H) were calculated using the formulas, $n = 1/|R_H|e$ and $\mu_H = |R_H|/\rho$, respectively, where $e = 1.6 \times 10^{-19}$ C is the electronic charge. R_H, and μ_H of the samples as a function of temperature are shown in Fig. 6. Our data is consistent with the previous report [28] with R_H staying positive in the whole range of 2–100 K. At high temperature, $R_H \approx 0$ indicates that the electron and hole contributions to R_H cancel the effect of each other. As the temperature decreases, the hole contribution increases leading to a prominent peak at low temperature. This is an indication of coherent state development and is usually observed in heavy fermion metals. The Hall coefficient for the ingot sample (5.26×10^{-4} cm^3 C^{-1} at 50 K) is of the same order as reported in literature [28]. R_H, and μ_H decrease by two orders of magnitude going from the ingot to the hot-pressed samples. This indicates increased carrier concentration in the nanostructured samples when compared to the ingot. The defects induced during ball-milling process might have contributed to such a drastic increase in carrier concentration. When compared among the hot-pressed samples, R_H does not change much. However there is clear trend in mobility data indicating that decrease in hot-pressing temperature decreases the carrier mobility.

The calculated temperature dependent *ZT* is shown in Fig. 7. The *ZT* values reach a peak at around 60 K for all the samples. The peak value of *ZT* for the optimized sample HP 800 is 0.024 at 60 K. Since the ingot and the sample HP 800 have comparable values of power factor at 60 K (Inset of Fig 7), the improved *ZT* is derived from the reduction in thermal conductivity. Here we note that *ZT* greater than 0.1 at cryogenic temperatures (<77 K) has rarely been