



## Thermoelectric properties of CeAl<sub>3</sub> prepared by hot-press method



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### ABSTRACT

We present data on the heavy fermion compound CeAl<sub>3</sub> as a potential *p*-type thermoelectric material at cryogenic temperatures. Samples of CeAl<sub>3</sub> were synthesized by arc-melting, ball milling and hot pressing the nano-powder at different temperatures. Thermal conductivity ( $\kappa$ ), Seebeck coefficient ( $S$ ), electrical resistivity ( $\rho$ ) and Hall coefficient ( $R_H$ ) of the samples were measured at temperatures ranging from 5 to 330 K. The thermoelectric properties of this compound are highly dependent on the hot-pressing (HP) temperature. The thermal conductivity increases with increase in HP temperature which is compensated by increased power factor ( $S^2\rho^{-1}$ ). As a result the samples with higher HP temperatures exhibit higher  $ZT$  values. The highest  $ZT$  value of 0.016 at 55 K was observed for the sample hot-pressed at 800 °C. The Hall coefficient data reflects an increase in carrier concentration and a decrease in carrier mobility with decreasing hot pressing temperature.

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### 1. Introduction

Thermoelectricity is the reversible conversion between thermal and electrical energy. For a given material, the efficiency of this process is quantified by the dimensionless figure of merit,  $ZT = \frac{S^2}{\rho\kappa} T$  where  $S$  is the Seebeck coefficient,  $\rho$  is the electrical resistivity,  $\kappa$  is the thermal conductivity, and  $T$  is the absolute temperature [1]. Thermoelectric materials currently available for high temperature applications typically exhibit a  $ZT \approx 2$  at their peak operating temperature. A material as this efficient below ambient temperature has not yet been observed. There are several materials which possess promising thermoelectric properties at cryogenic temperatures [2]. One class of materials that we feel has been overlooked is a class of materials called Heavy Fermion Compounds (HFCs). While many materials included in this category have been the subject of extensive study [3–9], as correlated electron materials and quantum behavior, they have not yet been thoroughly investigated as thermoelectric materials. Many materials that belong to this class are known to exhibit unique correlated electron properties at low temperatures which make them potential candidates for thermoelectric cooling applications.

Measurement of thermoelectric properties usually offers an excellent approach to investigate quasiparticle excitation in heavy fermion materials [10,11]. Many HFCs have been shown to exhibit

large Seebeck coefficient values at low temperatures [12,13]. Among them, many Ce-based compounds have been reported to exhibit two well separated maxima (minima) in the temperature dependent Seebeck coefficient [14–16]. Usually, the low-T extremum occurs around the characteristic temperature  $T_K$  and is attributed to the Kondo scattering on the ground state doublet. The high temperature peak ( $T > T_K$ ) on the other hand, results from Kondo scattering on higher multiplets which are split by crystal electric field (CEF) effects [12]. In addition to large Seebeck coefficients, many compounds of this class exhibit relatively high electrical conductivity values which make them promising thermoelectric materials.

In this work, we studied the thermoelectric properties of the heavy fermion compound CeAl<sub>3</sub>. Since the first study by Andres et al. [17] in 1975, CeAl<sub>3</sub> has been the subject of extensive research. This compound exhibits an extremely large Sommerfeld coefficient  $\gamma = 1620$  mJ/(K<sup>2</sup>·mol) and  $A = 35$   $\mu\Omega$  cm/K<sup>2</sup> where  $A$  is associated with the Fermi liquid relation of the electrical resistivity  $\rho = \rho_0 + AT^2$  [17]. Originally, CeAl<sub>3</sub> was considered to be a heavy fermion without any magnetic ordering. Later, it was revealed by  $\mu$ SR and NMR experiments [18,19] that CeAl<sub>3</sub> orders antiferromagnetically below  $T_N = 1.2$  K. Initially, many researchers paid attention to its electrical transport properties [20,21] and their pressure dependence [16]. Later Ott et al. [22] reported the thermal conductivity in the temperature range of 0.06–50 K thereby demonstrating the validity of Wiedemann–Franz law in heavy electron systems. We focus on determining  $ZT$  of CeAl<sub>3</sub> as a potential material for Peltier cooling applications.

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In general, an increase in  $ZT$  can be achieved through either power factor ( $S^2\rho^{-1}$ ) enhancement or thermal conductivity reduction or by both. For strongly correlated systems like HFCs, the electronic transport properties ( $S$  and  $\rho$ ) are usually found to be very sensitive to the carrier density. Therefore it is plausible to assert that the power factor of these systems can be effectively optimized by tuning carrier density. In an earlier study on another strongly correlated system,  $\text{FeSb}_2$ , we showed that mechanical nanostructuring (ball-milling of ingot into powder and hot pressing of the powder into bulk pellets) not only reduces the thermal conductivity but also induces modification of the electronic band structure which in turn changes the carrier density [23]. In this study we employ the technique of nanostructuring in  $\text{CeAl}_3$  and investigate the effects of varying hot-pressing (HP) temperature on its thermoelectric properties.

## 2. Experimental

Stoichiometric amounts of Ce (99.9%) and Al (99.99%) were mixed and arc melted together on a water-cooled copper hearth in an argon atmosphere. To attain chemical homogeneity, the melted sample was flipped on the hearth plate and re-melted twice. Nanopowders of  $\text{CeAl}_3$  were prepared by ball milling the ingot for 5 h. The nanopowder was then hot pressed for 2 min at 400, 600 and 800 °C while a uniaxial pressure of 80 MPa was applied. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed on the fresh fracture surfaces of the samples. The Seebeck Coefficient ( $S$ ), electrical resistivity ( $\rho$ ), and thermal conductivity ( $\kappa$ ) from 5 to 330 K were measured simultaneously on a sample of typical dimensions of  $2 \times 2 \times 8 \text{ mm}^3$ . The four-point method of thermal transport option (TTO) of the Physical Property Measurement System (PPMS) was used. The horizontal rotator option of PPMS was used to measure Hall coefficient ( $R_H$ ) on a sample with typical dimensions of  $1 \times 2 \times 10 \text{ mm}^3$ .

## 3. Results and discussion

Fig. 1(a) shows the X-ray diffraction patterns for the samples. Some impurity phases associated with  $\text{CeAl}_2$ , Ce, and Al can be seen

for the ingot. However, these impurity phases disappear in the X-ray diffraction patterns for the hot-pressed samples at 800 °C and the peaks can be indexed to the hexagonal  $\text{Ni}_3\text{Sn}$ -type crystal structure. The samples become more homogeneous and show an enhanced single phase behavior after the ball-milling and hot-pressing process. The SEM images of the freshly fractured surface of the four samples are presented in Fig. 1(b). Clearly, texture of the hot-pressed samples differs drastically from that of the ingot sample with porosity increasing with decreasing pressing temperature. As the hot-pressing temperature decreases, the grains tend to agglomerate. Approximate grain-size in the hot-pressed samples is in the order of  $\sim 1 \mu\text{m}$ .

The results on the temperature dependence of the total thermal conductivity are shown in Fig. 2. The temperature dependence for all the samples are typical of heavy fermion systems and closely resemble the dependence reported for other HFCs such as  $\text{CeB}_6$  [24] and  $\text{CeCu}_4\text{Al}$  [25]. The thermal conductivity values for the ingot sample are consistent with the values for the polycrystalline sample reported by Ott et al. [22]. Within the 5–330 K range, the thermal conductivity decreases significantly as the HP temperature decreases. As a reference, at 55 K,  $\kappa = 2.5 \text{ W m}^{-1} \text{ K}^{-1}$  and  $0.4 \text{ W m}^{-1} \text{ K}^{-1}$  for the samples HP 800 and HP 400 respectively, this represents a reduction in the thermal conductivity by  $\sim 85\%$ . In ball-milled and then hot-pressed samples, such a decrease in thermal conductivity is mainly attributed to the increased scattering of phonons off the grain boundaries.

In general, the total thermal conductivity is the sum of two independent contributions from the lattice and the carriers. The relationship is described by the following equation:  $k = k_{\text{carrier}} + k_{\text{lattice}}$  where  $k$  is the total effective thermal conductivity of the system, and  $k_{\text{carrier}}$  and  $k_{\text{lattice}}$  are the carrier and lattice contributions respectively. A rough estimation of  $k_{\text{carrier}}$  can be made using the Wiedemann-Franz law,  $k_{\text{carrier}} = L_0\rho^{-1}T$  where  $L_0 = 2.45 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$  is the Lorenz number,  $\rho$  is the electrical resistivity, and  $T$  is the temperature in K. The  $k_{\text{carrier}}$  for all the samples was calculated using the experimentally determined values of  $\rho$ . In Fig 3, we show the temperature dependence of  $k_{\text{lattice}}$  ( $= k - k_{\text{carrier}}$ ) in a log-log plot in the 6–50 K temperature range. At 55 K, 65% of the total thermal conductivity of the sample HP 800 comes from the lattice contribution. For the HP 600 and HP 400 samples, these

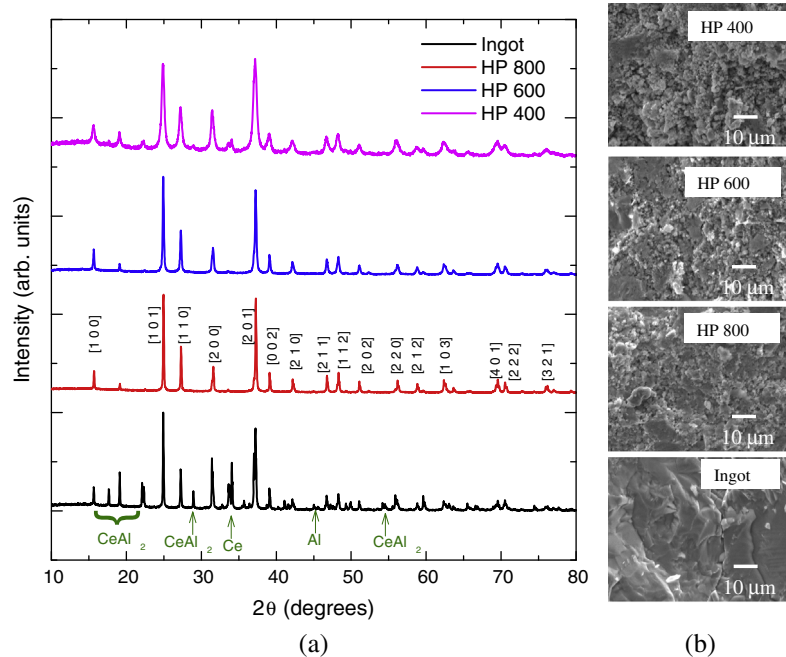


Fig. 1. X-ray diffraction pattern (a) and the SEM images (b) of the samples.

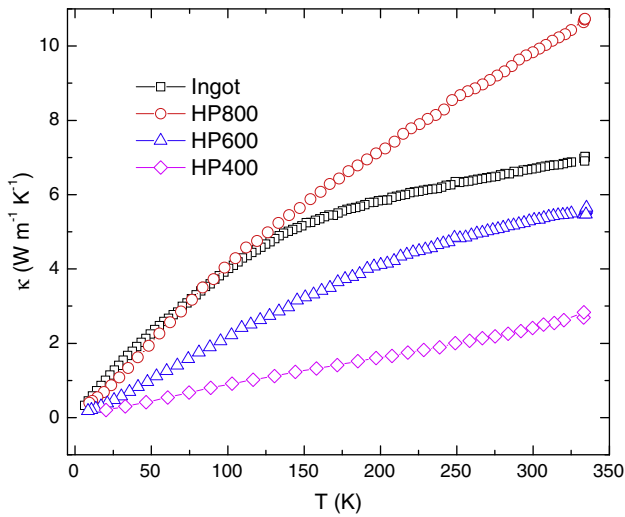


Fig. 2. Thermal conductivity of the samples as a function of temperature.

contributions are 74% and 78%, respectively. Fitting data to the power law,  $k = \beta T^\alpha$ , shows the almost linear dependence of  $\kappa$  on  $T$  with the  $\alpha$  values ranging from 0.83 to 1.11. Such a linear dependence is consistent with previous reports and is related to the fact that relevant phonon wavelengths are comparable to or larger than the electronic mean free paths [22].

The experimental data on the electrical resistivity is shown in Fig. 4.  $\rho(T)$  curves for all the samples follow the classic shape for a strongly correlated HF metal, with a coherence peak at  $\sim 35$  K. While the coherence peak has been consistently reported to occur at around 35 K, the resistivity values for our samples hot pressed at 400 and 600 °C are considerably larger than previously reported values for their single crystal counterparts. This is expected due to the increased porosity and number of defects in the hot-pressed samples. Among the hot-pressed samples, the electrical resistivity varies significantly with HP temperature. At 35 K, the resistivity increases by a factor of 1.9 from the HP 800 sample to the HP 600 sample, and from HP 600 to HP 400, it increases by a factor of 2.6. A similar behavior in resistivity at lower HP temperature was observed in the HFC CeCu<sub>6</sub> [26].

Fig. 5 shows the Seebeck coefficient as a function of temperature. For all the samples, the Seebeck coefficient is positive in the temper-

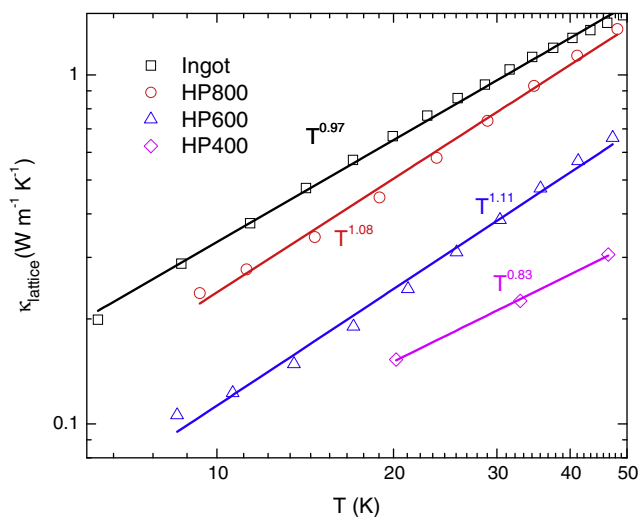


Fig. 3. Lattice thermal conductivity as a function of temperature in the range of 6–50 K.

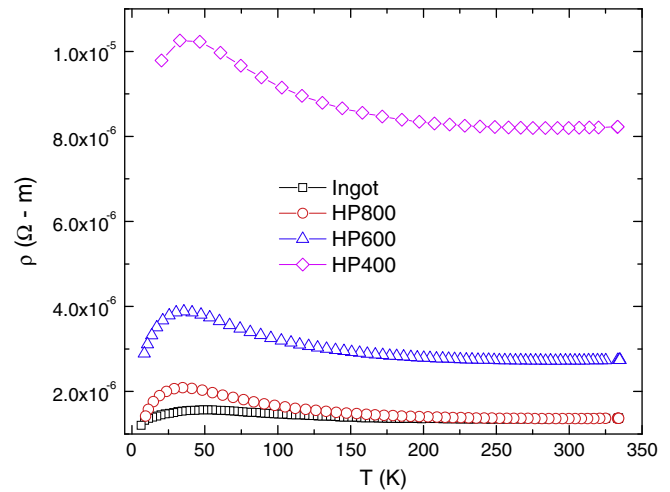


Fig. 4. Electrical resistivity of the samples as a function of temperature.

ature range of 5–330 K, implying that the majority charge carriers are holes (p-type). The peak in Seebeck coefficient, which is thought to result from Kondo scattering of higher energy multiplets, occurs at  $\sim 55$  K. The negative peak due to the Kondo scattering of ground state doublet has been shown to occur at 3.5 K for CeAl<sub>3</sub> [16] which is out of the temperature range of this experiment. Above 55 K, a logarithmic dependence  $S \propto -(\ln T)$  is followed. This trend is consistent with the data previously reported and is usually associated with the formation of heavy charge carriers (also called the spin polarons) as a result of the density of states (DOS) renormalization in the vicinity of the Fermi energy [11]. The maximum value of  $S = 36 \mu\text{V K}^{-1}$  was observed for the HP 800 sample. The peaks are suppressed as hot-pressing temperature decreases.

In Fig. 6, we plot the power factor ( $PF = S^2 \rho^{-1}$ ) as a function of temperature. The HP 800 sample produces the highest value of  $PF$  ( $6.6 \mu\text{W K}^{-2} \text{cm}^{-1}$ ) at 55 K that is less than the value of  $15 \mu\text{W K}^{-2} \text{cm}^{-1}$  at 50 K reported by Mahan et al. [27]. The smaller  $PF$  value in our samples is due to decreased Seebeck coefficient and increased resistivity. As the HP temperature decreases,  $PF$  decreases dramatically.

The original goal of nanostructuring was to increase the power factor ( $PF$ ) by employing quantum confinement of carriers [28,29],

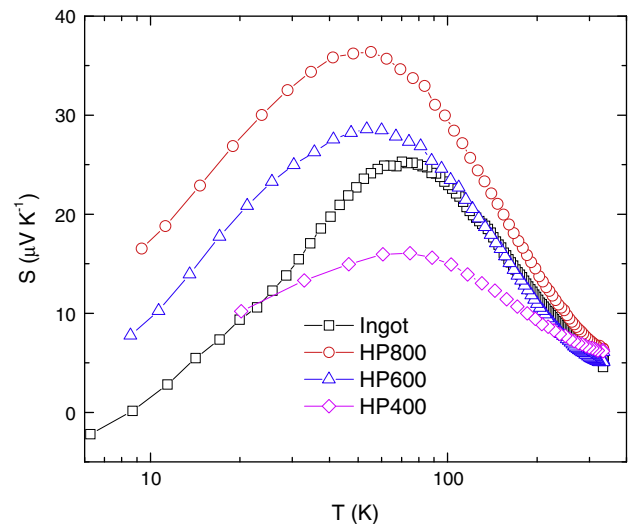


Fig. 5. Seebeck coefficient of the samples as a function of temperature.

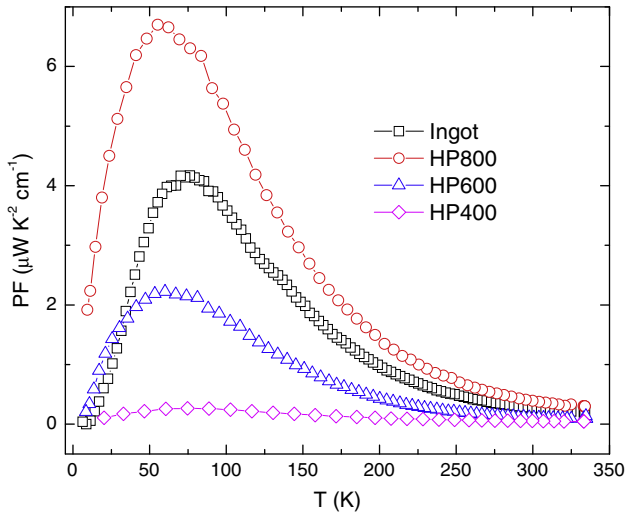


Fig. 6. Power factor of the samples as a function of temperature.

but the experiments [30–32] have shown that the main reason for the  $ZT$  improvement was the reduction of thermal conductivity. Therefore in the recent years, research on nanostructured thermoelectric materials have mainly focused on reducing the thermal conductivity while producing only minimal adverse effects on the Seebeck coefficient and electrical conductivity. In case of  $CeAl_3$ , although reducing the HP temperature decreases thermal conductivity of  $CeAl_3$ , it also lowers the Seebeck Coefficient and electrical conductivity, which ultimately results in a decrease in  $ZT$  with decreasing HP temperature (see Fig. 7). The highest  $ZT$  reported is 0.016 at 55 K in the HP 800 sample. Since at 55 K the ingot and the sample HP 800 have nearly the same thermal conductivity value, the improved  $ZT$  value for the latter comes from the improved Seebeck coefficient.

Fig. 8 shows the temperature dependence of the Hall coefficient ( $R_H$ ). A magnetic field of 9 T was applied during Hall measurements. Our data is consistent with previous reports [33,34] with  $R_H$  staying positive in the whole range of 5–330 K. At high temperatures,  $R_H$  is small indicating that the electron and hole contributions to  $R_H$  cancel each other. As the temperature decreases, the hole-contribution increases leading to a well-defined peak at

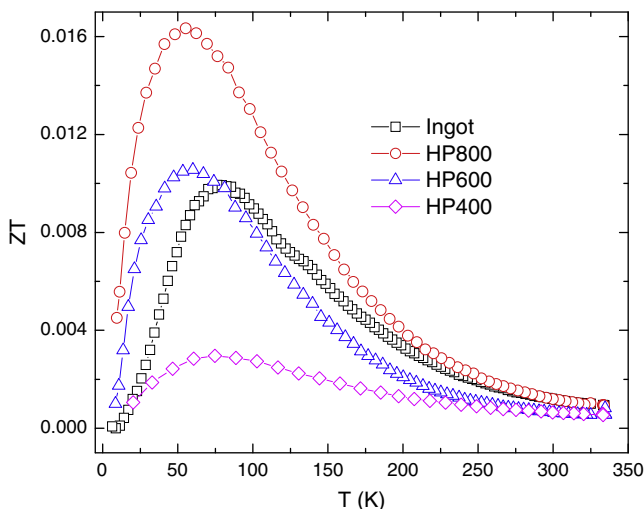


Fig. 7. Thermoelectric figure-of-merit ( $ZT$ ) of the samples as a function of temperature.

$T \approx 10$  K. A rapid increase in the Hall coefficient above the residual value at low temperatures is typical feature of heavy fermion metals and is associated with the development of skew scattering by fluctuation about the coherent state [21]. The Hall coefficient of the ingot sample remains significantly smaller than that of the hot-pressed samples throughout the temperature range of the experiment. Under one band model, the Hall coefficient ( $R_H$ ) and the carrier density ( $n$ ) are related as,  $R_H = 1/ne$ , where  $n$  is the carrier density and  $e$  is the electronic charge. Carrier density calculated based on this simplified model as a function of temperature is shown in the inset of Fig. 8. The carrier density decreases in hot-pressed samples when compared with carrier density of the ingot sample. Among the hot-pressed samples, amplitude of  $R_H$  (or  $n$ ) decreases (or increases) with decrease in HP temperature. In general, increases in carrier concentration decrease the absolute value of the Seebeck coefficient [35]. Therefore the decrease in  $S$  with decreasing HP temperature in our samples can be attributed, in part, to the increase in carrier density.

A rough calculation of effective mass ( $m^*$ ) can be done using the relation  $s = \frac{8\pi^2 k_B^2 T}{3eh^2} m^* (\frac{\pi}{3n})^{2/3}$ . Here  $k_B = 1.38 \times 10^{-23} \text{ J K}^{-1}$  is the Boltzmann constant,  $h = 1.05 \times 10^{-34} \text{ J s}$  is the reduced Planck constant,  $T$  is the absolute temperature and  $n$  is the carrier density. Using experimentally determined Hall coefficient (Fig. 8) and the Seebeck coefficient (Fig. 5), calculations give  $m^* \approx 33 m_o$ ,  $25 m_o$  and  $23 m_o$  ( $m_o$  is bare mass of electron) for samples HP 800, 600 and 400 respectively at 20 K (shown in inset of Fig. 9). These values are slightly less than previously reported values ( $\approx 45 m_o$ ) in reference [11]. Hall mobility ( $\mu_H$ ) for the samples were calculated under the assumption of one band model using relation  $\mu_H = R_H/\rho$ . Fig. 9 shows the temperature dependence of the Hall mobility, these results were derived from resistivity measurement shown in Fig. 3. Quantitatively, the Hall mobility values are of the same order as reported earlier [36]. Despite lower carrier concentration and enhanced effective mass, the sample HP 800 has significantly small resistivity compared to the resistivity of samples HP 600 and HP 400. This is due possibly to the decreased defect concentration at higher pressing temperature.

In conclusion, samples of the heavy fermion compound  $CeAl_3$  have been successfully synthesized by ball-milling of arc-melted ingot followed by hot-pressing. The thermoelectric properties of the samples have been measured and it has been shown that the temperature dependences of the properties are typical of the heavy fermion metal. The results show that variation of hot-pressing

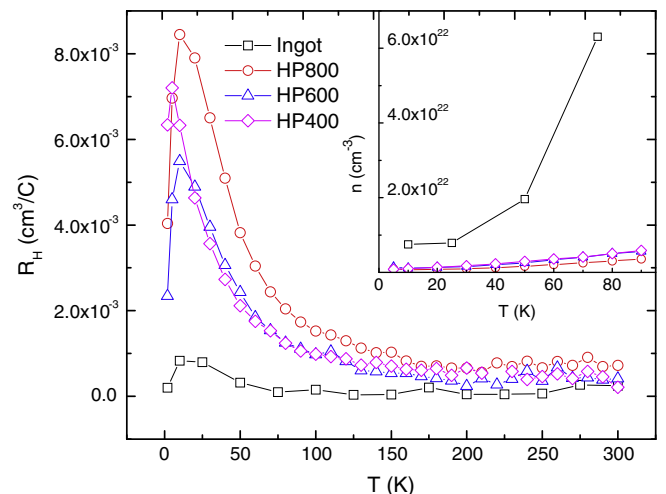
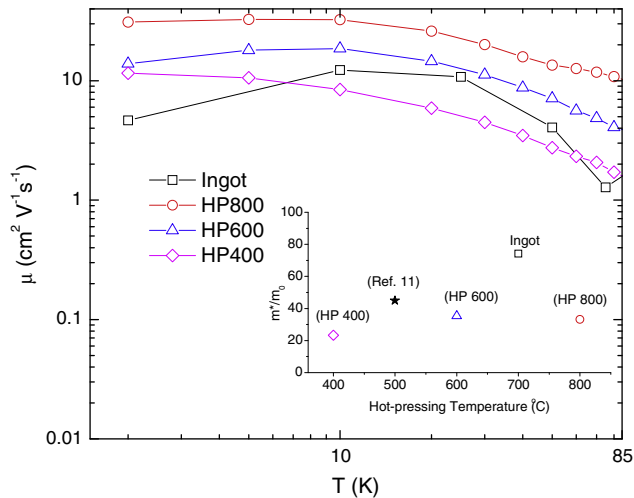


Fig. 8. Hall coefficient of the samples as a function of temperature. Inset shows temperature dependent carrier concentration.



**Fig. 9.** Hall mobility of the samples as a function of temperature. Inset shows the effective mass to bare mass ratio at 20 K for the samples.

temperature results in significant changes in the thermal and the electronic transport properties. Mechanical nanostructuring was shown to be effective at decreasing the thermal conductivity of the system. The highest  $ZT$  value measured was 0.016 at 55 K in the sample that was hot-pressed at 800 °C. The results from the Hall coefficient measurements provide evidence for the differences in the carrier density and mobility among the samples. Further optimization of the thermoelectric properties of the heavy fermion compound  $\text{CeAl}_3$  may also be achievable by doping.

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