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High temperature electrical transport properties of the $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ filled skutterudites

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Abstract. Polycrystalline samples of the filled skutterudites $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ were prepared by direct melting and hot pressing. The samples were characterized using x-ray powder diffraction and differential thermal analysis. It was found that both compounds melt incongruently at peritectic temperatures of 1023 ± 5 K for $EuFe_4Sb_{12}$ and 975 ± 5 K for $YbFe_4Sb_{12}$. At room temperature these materials possess a positive Seebeck coefficient of 65–67 μV K^{-1} and high carrier concentration in the range 5.6×10^{21}–3.6×10^{21} cm^{-3}. The electrical transport properties were measured over the temperature range 100–860 K. For both compounds the electrical resistivity and Seebeck coefficient gradually increase with increasing temperature and for $YbFe_4Sb_{12}$ exhibit a maximum at 760–800 K. The estimated ZT value of $YbFe_4Sb_{12}$ is 0.4 at 670 K.

1. Introduction

Filled skutterudite compounds have recently received considerable attention because of their potential for achieving high thermoelectric efficiency at elevated temperature [1–3]. The composition of filled skutterudites can be represented by the formula LnA_4B_{12} (Ln = rare earth; A = Fe, Ru, Os; B = P, As, Sb). These compounds possess the cubic $LnFe_4P_{12}$-type crystal structure (space group $Im\bar{3}$) with the unit cell containing eight AB_3 groups. There are also two large cages in the unit cell which are filled with rare earth atoms. The radius of the rare earth atom is usually smaller than the radius of the cage of the As- and Sb-based filled skutterudites. Due to the weak bonding of the rare earth atom with 12 nearest pnictogen neighbours (group B^V), filling atoms are able to interact with a wide spectrum of low frequency phonons which results in a substantially lower lattice thermal conductivity value of filled skutterudites than that of unfilled binary skutterudites [3–6]. As a result of low thermal conductivity and the good overall electrical transport properties of antimony-based filled skutterudites, the dimensionless figure of merit (ZT) of $CeFe_4Sb_{12}$ exceeds unity at temperatures over 800 K [2].

Several antimonide ternary compounds $LnFe_4Sb_{12}$ filled with various rare earth elements (Ln = La, Ce, Pr, Nd, Sm, Eu, Yb) have been synthesized [2, 4, 7–14]. Among known ternary filled skutterudites only Eu- and Yb-based compounds contain heavy lanthanide atoms [8–12]. Atoms of other heavy lanthanides Gd–Tm and Lu cannot be accommodated in the cages of the skutterudite structure because the small metallic radii of their ions in the oxidation state of 3+ prevent adequate bonding to the host lattice [13]. However, in contrast to the other heavy

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lanthanides, Eu and Yb exhibit the oxidation state of 2+ in some compounds and their large ion radii stabilize the skutterudite structure.

There is limited information in the literature on the thermoelectric properties of Eu- and Yb-based iron antimonides. The transport properties of $YbFe_4Sb_{12}$ have been measured over the temperature range 4–300 K [6, 11]. However, there is no information on the thermoelectric properties of $EuFe_4Sb_{12}$ or $YbFe_4Sb_{12}$ above room temperature. For filled iron antimonide skutterudites the peritectic decomposition of the compounds has been suggested [3]; however, the phase diagram for the ternary systems is unknown. In this paper we report the preparation of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ and determination of their peritectic temperature and present the results of measurements of the Seebeck coefficient and electrical resistivity over the temperature range 100–870 K.

2. Experiment

Filled skutterudites were synthesized by melting stoichiometric quantities of iron (99.99%), antimony (99.999%) and lanthanide (99.9%) in carbon-coated quartz tubes. The elements were handled in pure argon atmosphere in an oxygen- and moisture-free glove box. The ampoules were slowly heated to 1200 K and maintained at this temperature for 7 hours whilst being mechanically vibrated at 30–40 Hz to ensure homogenization of the melt. The ampoules were subsequently removed from the furnace, quenched in water followed by annealing at 900 K for 10 days and quenched again in water. There was no evidence of the material reacting with the quartz ampoule during synthesis and heat treatment. The material was ground into fine powder in an argon atmosphere and hot-pressed in vacuum into dense pellets at a pressure of 1.5–3 Mn m^{-2} and temperature 750 K. Several hot-pressed samples of each compound were prepared. Depending on hot-pressing conditions the measured densities of the samples were in the range 92–97% of the theoretical density as calculated from the lattice cell parameter.

Differential thermal analysis (DTA) was carried out in vacuum-sealed quartz ampoules using chromel–alumel thermocouples and Al_2O_3 powder as a standard. Heating and cooling rates were 3–5 K min^{-1}. The thermocouples were standardized at the melting points of pure Sn, Sb, Ge and Cu; the error of temperature measurements did not exceed 4 K.

The phase composition of samples was analysed by powder x-ray diffraction using a Guinier camera with Cu Kα radiation. Lattice parameters were obtained from x-ray spectra employing an inner standard of high purity KCl powder.

Room temperature Hall effect and electrical resistivity measurements were carried out using the van der Pauw method. The Hall coefficient was determined using an a.c. technique with a constant magnetic field of 0.9 T. The carrier density was calculated from the Hall coefficient assuming a single carrier model and a Hall scattering factor of unity. Electrical resistivity and Seebeck coefficient as a function of temperature were measured over the range 100–870 K using the method described in a previous paper [15].

3. Results and discussion

The x-ray analysis of as-cast quenched ingots revealed that the ingots consisted of skutterudite phase (not more than 30% of the total amount) and impurity phases $FeSb_2$, Sb and $EuSb_2$ or $YbSb_2$. After annealing at 900 K the same ingots contained predominantly the filled skutterudite phase. Very weak remaining impurity peaks observed in the x-ray powder diffraction patterns were attributed to a small amount (1–2 at.%) of impurity phases. The presence of impurity phases resulted from the peritectic reaction of the compound formation.

Table 1. Measured properties of filled skutterudite compounds $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$: lattice parameter (a), liquidus temperature ($T_{liq.}$), peritectic temperature ($T_{per.}$) and room temperature values of hole concentration (p), electrical resistivity (ρ), Seebeck coefficient (α) and Hall mobility (μ_H).

Property	$EuFe_4Sb_{12}$	$YbFe_4Sb_{12}$
a (nm)	0.9170 ± 0.0001	0.9156 ± 0.0002
$T_{liq.}$ (K)	1148 ± 15	1151 ± 15
$T_{per.}$ (K)	1023 ± 5	975 ± 5
p (cm^{-3})	5.6×10^{21}	3.6×10^{21}
ρ (mΩ cm)	0.43	0.62
α ($\mu V\ K^{-1}$)	65	67
μ_H ($cm^2\ V^{-1}\ s^{-1}$)	2.6	2.8

The results of differential thermal analysis of annealed samples of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are presented in table 1. Both compounds melt incongruently as is evident from the presence of several invariant thermal effects on DTA cooling curves and the appearance of additional invariant thermal effects during the repeated heating of the samples in comparison with the thermal effects observed during the first heating cycle.

Information on the melting and peritectic temperatures provides helpful guidelines for choosing the synthesis conditions for the preparation of filled skutterudites with a single-phase composition. Synthesis of a compound formed by peritectic reaction requires a fast quenching of the stoichiometric melt from temperature above the liquidus temperature and a prolonged annealing at a temperature below the peritectic temperature of the compound.

X-ray diffraction patterns of the hot-pressed samples were indexed to a cubic unit cell corresponding to the skutterudite structure. The lattice parameters obtained are presented in table 1 and agree well with those reported in the literature for $EuFe_4Sb_{12}$ [8] and $YbFe_4Sb_{12}$ [11, 12]. The lattice parameters of both $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are substantially larger than those of skutterudites filled with light lanthanides La and Ce [14] since the metallic radii of Eu and Yb ions for the ligancy 12 are bigger than corresponding radii of light lanthanide ions [16]. According to x-ray diffraction data [12], interatomic distances between the Yb ion and the nearest Sb atoms in the cage of the $YbFe_4Sb_{12}$ structure are 0.3409 nm, that is larger than the sum of the Sb metallic radius (0.1391 nm) and Yb metallic radius for the ligancy 12 (0.1933 nm) [16]. For all filled skutterudites rather large bonding distances in the $LnSb_{12}$ coordination are observed and they result in the 'rattling' of the filling atoms inside the cage. The 'rattling' of lanthanide atoms inside the cage was confirmed by the exceptionally large measured values of the thermal parameters for filling atoms obtained from the refinement of the x-ray and neutron diffraction data [6, 14]. This 'rattling' was predicted to lower significantly the lattice thermal conductivity of the filled skutterudites in comparison with their unfilled analogues [17].

Room temperature Hall concentration, electrical resistivity, Seebeck coefficient and carrier mobility of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are listed in table 1. It should be noted that both room temperature electrical resistivity and Seebeck coefficient of as-cast ingots, which contained more than 70% impurity phases, were around half of those of the annealed samples $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$. This indicates that impurity phases could affect transport properties of the filled skutterudites. However, the concentration of impurity phases in the annealed samples is small (1–2 at.%) and their effect on electrical resistivity and Seebeck coefficient is estimated to be within the experimental errors of measurements. The electrical transport properties of samples with different densities were readily reproducible. The room temperature properties

(table 1) and temperature dependence of electrical transport properties of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are presented for the samples with the highest density.

Both compounds possess p-type conductivity and a high carrier concentration. The p-type conductivity is observed in all ternary filled skutterudites and can be accounted for by a simple model taking into account the number of valence electrons per formula unit. The $[Fe_4Sb_{12}]$ group is electron deficient relative to the unfilled semiconductor skutterudite $CoSb_3$ since the Fe atom has one less electron than Co. The filling lanthanide atoms in $LnFe_4Sb_{12}$ compensate this deficiency by adding free electrons. However, the most stable oxidation state of lanthanide elements is 3+ (or 2+ for Eu) and the number of valence electrons donated by lanthanide atoms is insufficient to compensate this deficiency. This implies a high hole concentration in filled skutterudite compounds.

The low mobility value in filled skutterudites is thought to be due to the high carrier concentration and thermal vibrations of the lattice, which dominate the scattering of carriers [1].

Assuming a single-carrier model and a Hall factor of unity, the carrier concentration of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ corresponds to 2.1 and 1.4 holes per formula unit, respectively. These values indicate that each Eu atom donates 1.9 electrons, whereas Yb atoms donate 2.6 electrons. The latter value is in good agreement with the intermediate oxidation state of 2.68+ for Yb ions in $YbFe_4Sb_{12}$ obtained from the x-ray absorption spectroscopy data [12]. However, the effect of lanthanide filling on carrier concentration can be complicated by the fact that the occupancy parameter for filling atoms can be less than 100% and depends both on the type of filling atom and on the size of the cage which is determined by the type of the atoms comprising the A_4B_{12} frame [18]. For $YbFe_4Sb_{12}$ the occupancy parameter is known to be 99% [18] and it can be as low as 83% for $NdFe_4Sb_{12}$ [18]; however there are no comparable data for $EuFe_4Sb_{12}$.

Measured room temperature electrical resistivity of $YbFe_4Sb_{12}$ (table 1) is significantly lower than that reported in the literature [6] where the electrical resistivity reached 3 mΩ cm at room temperature. The reason for a high electrical resistivity of samples prepared in [6] could be the presence of the second phase of up to 5 vol.% and the low density of samples (80% of the theoretical one). The room temperature Seebeck coefficient values of both $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are almost identical (table 1) and close to the literature data for $CeFe_4Sb_{12}$ [2, 4, 10].

The temperature variations of the electrical resistivity of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ are shown in figure 1. This dependence is typical for heavily doped semiconductors. For $YbFe_4Sb_{12}$ the electrical resistivity gradually increases with increasing temperature, exhibits a broad maximum at 760–800 K and then tends to decrease due to intrinsic conductivity. For $EuFe_4Sb_{12}$ the electrical resistivity increases with temperature less steeply than that for $YbFe_4Sb_{12}$ and does not reach its maximum at temperatures up to 860 K, which can be attributed to the higher carrier concentration of the Eu-filled skutterudite compound. Although the room temperature value of electrical resistivity of $YbFe_4Sb_{12}$ samples is one-fifth of that reported in [6], the slope of the temperature dependence of resistivity over the range 100–300 K coincides well with the literature data [6, 11].

The temperature dependence of the Seebeck coefficient of filled skutterudites is presented in figure 2. As with the temperature dependence of electrical resistivity, the Seebeck coefficient of both compounds increases with increasing temperature and for $YbFe_4Sb_{12}$ exhibits a maximum at 760 K. The Seebeck coefficient of $EuFe_4Sb_{12}$ did not reach its maximum value in the temperature range of measurements.

An estimation of the total thermal conductivity of prepared $YbFe_4Sb_{12}$ samples can be obtained from the literature data on the lattice thermal conductivity of $YbFe_4Sb_{12}$ [6]. For fully

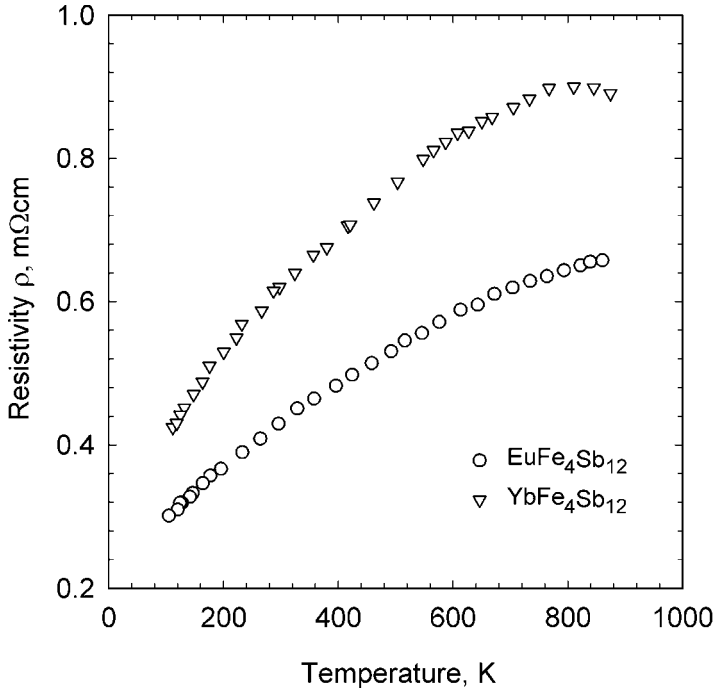

Figure 1. Temperature dependence of electrical resistivity of EuFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$.

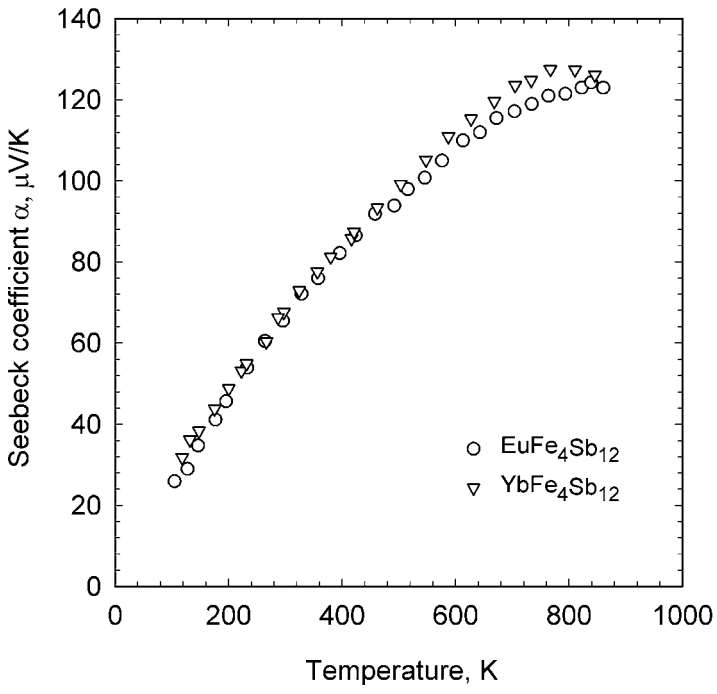

Figure 2. Temperature dependence of Seebeck coefficient of EuFe$_4$Sb$_{12}$ and YbFe$_4$Sb$_{12}$.

dense samples the room temperature value $\lambda_L = 22$ mW cm^{-1} K^{-1} was calculated from the total thermal conductivity λ_{total} of $YbFe_4Sb_{12}$ [6] by subtracting the electronic component of the thermal conductivity. The carrier contribution to the thermal conductivity was estimated from the electrical resistivity using the Wiedemann–Franz relationship $\lambda_e = LT/\rho$, where λ_e is the electronic part of the thermal conductivity, L is the Lorenz number and ρ is the electrical resistivity. Using the electrical resistivity from table 1 and calculated lattice thermal conductivity, the estimated value of 33.7 mW cm^{-1} K^{-1} was obtained for the room temperature total thermal conductivity of our $YbFe_4Sb_{12}$ samples.

The room temperature lattice thermal conductivity of $YbFe_4Sb_{12}$ (22 mW cm^{-1} K^{-1} [6]) is higher than that of other ternary filled skutterudites $CeFe_4Sb_{12}$ (17 mW cm^{-1} K^{-1} [19]) and $NdFe_4Sb_{12}$ (around 11 mW cm^{-1} K^{-1} [2]). This can be attributed to the smaller ion radii of Ce and Nd for the ligancy 12 than that of Yb. The Ce and Nd ions are more loosely bound inside the cages of the skutterudite structure and therefore more efficient in scattering the lower frequency phonons than in the case of the Yb ions. The Eu metallic radius is the largest among all other rare-earth elements and $EuFe_4Sb_{12}$ is expected to possess higher lattice thermal conductivity than $YbFe_4Sb_{12}$.

Analysis of the literature data for $CeFe_4Sb_{12}$ and $CeFe_{4-x}Co_xSb_{12}$ [2] indicates that the lattice thermal conductivity of these filled skutterudites decreases with increasing temperature up to 670 K following reasonably well a $1/T$ dependence, as expected for acoustic phonon scattering. Assuming the same scattering mechanism for $YbFe_4Sb_{12}$, a realistic value of the lattice thermal conductivity of $YbFe_4Sb_{12}$ at $T > 300$ K can be obtained from room temperature lattice thermal conductivity using a $1/T$ extrapolation of the temperature dependence of λ_L. The electronic part of the high temperature thermal conductivity was calculated from the measured temperature dependence of the electrical resistivity of $YbFe_4Sb_{12}$. The estimated total thermal conductivity of $YbFe_4Sb_{12}$ ranges from 33.6 mW cm^{-1} K^{-1} at room temperature to 28.7 mW cm^{-1} K^{-1} at 670 K with the electronic component being around 35% of the total thermal conductivity at room temperature, increasing to 65% at 670 K. To assess the figure of merit of $EuFe_4Sb_{12}$, information on the high temperature thermal conductivity is required.

The high temperature figure-of-merit value of $YbFe_4Sb_{12}$ was assessed based on experimental Seebeck coefficient and electrical resistivity data and taking into account the calculated thermal conductivity. The estimated ZT value of $YbFe_4Sb_{12}$ increases from 0.065 at room temperature to 0.4 at 670 K. The room temperature ZT value is more than three times higher than that reported in the literature [6] and close to that for $CeFe_4Sb_{12}$ [2]. However, the high temperature ZT value of $YbFe_4Sb_{12}$ is lower than that for $CeFe_4Sb_{12}$ mainly due to the steeper rise in electrical resistivity with temperature and the higher value of thermal conductivity.

The ZT value of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ might be enhanced by optimization of doping level and by further reduction in lattice thermal conductivity. Several approaches can be employed for this purpose including partial substitution of Fe with Co or Ni, which have more valence electrons than Fe and could reduce the high hole concentration in the material and increase the Seebeck coefficient. Partial filling of the lanthanide sites is also reported to be an efficient way to manipulate the transport properties of filled skutterudites [20].

4. Conclusion

The results of the measurements of electrical transport properties of $EuFe_4Sb_{12}$ and $YbFe_4Sb_{12}$ over the temperature range 100–860 K indicate that the materials are heavily doped p-type semiconductors. The ZT value of 0.4 was estimated for $YbFe_4Sb_{12}$ at 670 K. The high

temperature figure-of-merit value of $YbFe_4Sb_{12}$ is limited by the relatively high lattice thermal conductivity and steep rise in electrical resistivity. Further work is needed to optimize the electrical and thermal transport properties of these filled skutterudites to enhance the figure-of-merit value.

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