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Effect of partial void filling on the transport properties of $Nd_xCo_4Sb_{12}$ skutterudites

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Abstract

Polycrystalline samples of the partially filled skutterudites $Nd_xCo_4Sb_{12}$ have been prepared and characterized by x-ray powder diffraction and differential thermal analysis. The saturation limit of the Nd void filling in $CoSb_3$ was found to be around 13%. All samples decompose incongruently at a temperature of 1149 ± 6 K. Room temperature Hall measurements show that each Nd atom donates approximately 0.8 electrons, which is significantly less than the Nd oxidation state (3+). The temperature dependence of the electrical and thermal transport properties has been measured over the range of 11–700 K. The electrical resistivity and absolute value of the Seebeck coefficient decrease with increasing Nd content and for samples with $x > 0.02$ the temperature dependence is typical of heavily doped semiconductors. Filling $CoSb_3$ with Nd causes a rapid initial decrease in the lattice thermal conductivity with a minimum at the composition $Nd_{0.1}Co_4Sb_{12}$. Nd-filled skutterudites exhibit the lowest value of the lattice thermal conductivity in comparison with other partially filled skutterudites at $x < 0.1$, which could be attributed to a smaller radius of Nd than that of other filling elements. At high temperature the ZT value of the Nd-filled skutterudites is limited due to intrinsic conduction caused by the relatively low carrier concentration. The effect of the partial Nd filling on the transport properties of the filled skutterudite compounds is discussed in the context of potential thermoelectric materials.

1. Introduction

During the last decade there has been renewed effort in the search for novel improved thermoelectric materials for cooling and power generation applications. For a given temperature range of operation the thermoelectric efficiency of a material is determined by its dimensionless figure of merit $ZT = \alpha^2 T/\lambda\rho$, where α is the Seebeck coefficient, ρ is

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the electrical resistivity and λ is the thermal conductivity ($\lambda = \lambda_e + \lambda_L$, where λ_e and λ_L are the electronic and lattice contributions, respectively). One promising group of materials, which possess good thermoelectric properties at elevated temperatures, is the skutterudite compounds [1–3].

Partially filled $CoSb_3$-based skutterudites have recently attracted considerable attention since they possess a significantly higher ZT value compared to 'unfilled' $CoSb_3$ [3–6]. The skutterudite crystal structure is cubic (Pearson symbol $cI32$) with the unit cell containing 32 atoms. There are also two large voids in the unit cell, which can be filled with a rare earth or alkali earth element. The loose bonds of the filling atoms within the oversized voids cause anharmonic 'rattling' of the former, which greatly lowers the lattice thermal conductivity value. It has been found that even a relatively small concentration of filling atoms leads to a large decrease in the lattice thermal conductivity of $CoSb_3$ [4, 5]. This could be attributed to an additional mass fluctuation scattering in partially filled skutterudites occurring between randomly distributed filling atoms and empty voids of the skutterudite crystal structure [5, 7]. As a result, partially filled skutterudites possess substantially reduced lattice thermal conductivity compared to the 'unfilled' $CoSb_3$. On the other hand, the relatively small concentration of filling atoms does not cause significant degradation of the electrical transport properties and the power factor $\alpha^2\rho$ remains comparable to that of doped $CoSb_3$ [1, 3, 4, 8].

There are many possible 'guest' atoms that can be inserted into the voids of the skutterudite crystal structure and, consequently, alter the properties of the materials. This gives an opportunity to tune the transport properties of skutterudites by altering the size, oxidation state and occupancy parameter of the filling atoms. All partially filled $CoSb_3$-based skutterudites exhibit n-type conductivity since filling atoms introduce additional electrons to the unfilled semiconductor $CoSb_3$. Several elements (Yb, Ce, La, Tl, Ba, Sn and Eu) have been used for partial filling of $CoSb_3$ [3–6, 8–10]. Recently, a ZT value of around unity at 600 K was reported for partially filled skutterudites [3, 8].

It has been suggested [11] that the decrease in lattice thermal conductivity is proportional to the ratio between the void and filling atom radii as well as to the mass of the filling atom, i.e. the smaller and heavier the filling atom, the lower the lattice thermal conductivity. Using Nd instead of La, Ce or Yb could bring additional improvements to the thermoelectric properties of $CoSb_3$-based filled skutterudites. The Nd^{3+} ion is smaller than La^{3+}, Ce^{3+}, Yb^{2+} or Ba^{2+} ions and, therefore, is freer to 'rattle' inside the voids. These localized vibrations may provide more prominent phonon scattering than many other lanthanide ions. At present there is no information in the literature on the thermoelectric properties of the partially filled Nd-based skutterudites. The present work reports on the preparation and characterization of $Nd_xCo_4Sb_{12}$ skutterudites and measurement of their electrical and thermal transport properties over a wide temperature range.

2. Experiment

Polycrystalline samples of the partially filled skutterudites $Nd_xCo_4Sb_{12}$ have been prepared by melting and hot pressing. Details of the synthesis procedure were described previously [12]. The phase composition of the samples was analysed by x-ray powder diffraction using a Philips PW1710 diffractometer with Cu Kα radiation. Differential thermal analysis (DTA) was performed using standardized chromel–alumel thermocouples. Heating and cooling rates were in the range of 3–5 K min^{-1}.

Low temperature (11–300 K) measurements of the Seebeck coefficient and electrical resistivity were performed using a Leybold–Heraeus closed-cycle helium refrigerator cryostat

and an in house designed and constructed sample holder. Samples were placed between two copper blocks using a spring plunger. The Seebeck voltage was measured with reference to copper maintaining the temperature difference across the sample in the range of 3–4 K using an electrical heater. The absolute temperature of the copper plates was measured using calibrated copper–constantan thermocouples, the copper wires of the thermocouples were simultaneously used to measure the Seebeck voltage. The temperature of the copper blocks and the Seebeck voltage were recorded using an automated temperature/voltage data logger. The Seebeck coefficient of the samples was corrected for the small absolute Seebeck coefficient of copper. A standard four-probe method with a dc power supply of 40 mA was used for resistivity measurements; the current was reversed at each measurement to eliminate the effect of unwanted Seebeck voltage.

Low temperature (15–300 K) thermal conductivity was measured using a steady-state technique. The samples with typical dimensions of approximately $1.5 \times 1.5 \times 6.0$ mm^3 were cut from the hot-pressed samples previously used for electrical transport property measurements and mounted between two copper plates using a silver paste. Copper–constantan thermocouples 0.055 mm in diameter were soldered to each copper plate. A heater (1 kΩ resistor) was attached to one plate and the other plate soldered to a copper sink, which was thermally connected to the cryostat heat exchanger via a double-sided soldered alumina plate. All the thermocouple and heater wires were thermally connected to the copper sink. Thermal losses through the wires were calculated and taken into account. To minimize radiation losses the sample and heater were shielded by a copper cap attached to the cryostat heat exchanger. The copper cap was at approximately the same temperature as the cold end of the sample. Radiation losses as well as the thermal contact resistance between the sample and copper plates were determined in separate experiments using standard samples and employed to correct experimental data.

Over the temperature range 280–410 K the thermal conductivity was measured using a computerized comparative method with a calibrated heat flux sensor [13]. The temperature difference across the sample and heat flux sensor was measured under steady state conditions using calibrated copper–constantan thermocouples. During both low and mid-temperature thermal conductivity measurements the Seebeck coefficient was also measured using the copper wires of the thermocouples and was compared to the preliminary obtained temperature dependence of the Seebeck coefficient to verify the temperature drop across the sample.

High temperature (300–700 K) Seebeck coefficient and electrical resistivity were measured using techniques described previously [14]. The room temperature Hall coefficient was determined using a 29 Hz frequency ac power supply and magnetic induction of 0.9 T. The carrier concentration was calculated from the Hall coefficient, assuming a single-carrier model and a Hall scattering factor of unity [15].

The absolute error of thermal conductivity measurements below 300 K was estimated to be 5% and arises primarily from the error in measuring the sample dimensions. The errors of the Seebeck coefficient and resistivity measurements were estimated to be 3%. Since the density of the samples was more than 95% the porosity was not corrected for in either thermal conductivity or electrical resistivity data.

3. Results and discussion

Typical x-ray diffraction pattern of $CoSb_3$ and $Nd_{0.25}Co_4Sb_{12}$ samples are shown in figure 1. All peaks visible in the $CoSb_3$ diffractogram can be indexed to the skutterudite crystal structure. For the $Nd_{0.2}Co_4Sb_{12}$ and $Nd_{0.25}Co_4Sb_{12}$ samples several additional small peaks were observed, which are identified by filled arrows in figure 1. These peaks can be indexed to impurity

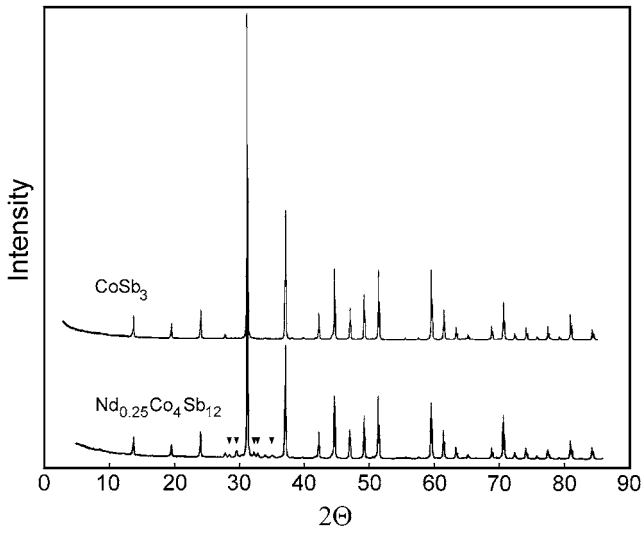

Figure 1. X-ray diffraction patterns of $CoSb_3$ and $Nd_{0.25}Co_4Sb_{12}$ skutterudites. The filled arrows indicate the peaks of impurity phase.

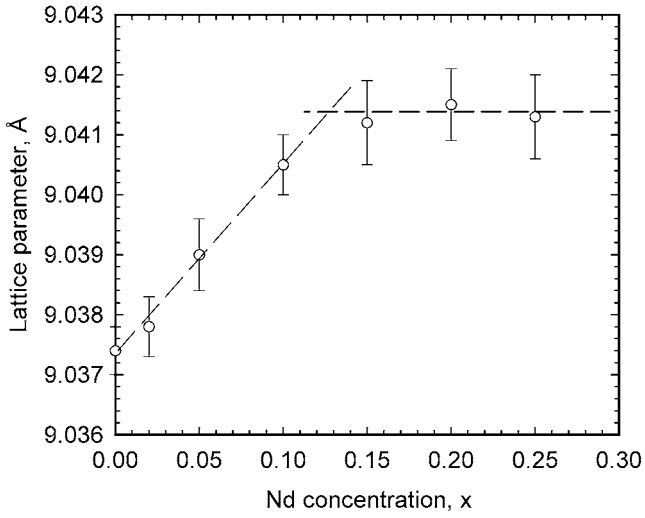

Figure 2. Lattice constant of $Nd_xCo_4Sb_{12}$ skutterudites as a function of Nd concentration.

phases such as NdSb and $CoSb_2$. The intensity of the highest peak of the second phase does not exceed 1.5% of the intensity of the strongest (130) peak of the skutterudite phase.

The room temperature lattice constant of the partially filled $Nd_xCo_4Sb_{12}$ skutterudites is presented in table 1 and figure 2. Incorporation of Nd into the voids of $CoSb_3$ crystal structure causes an expansion of the unit cell. Initially, the lattice constant increases in proportion to the amount of Nd in the samples and then remains practically unchanged. The linear increase of the lattice constant with x indicates the incorporation of the Nd filling atoms into the voids of the $CoSb_3$ crystal structure. Two straight lines on the concentrational dependence of lattice parameters (figure 2) intersect at the Nd concentration of around 13%, indicating a possible saturation limit of the void filling. Further addition of Nd above this limit could presumably

Table 1. Summary of room temperature crystallographic, thermodynamic and transport properties of the partially filled $Nd_xCo_4Sb_{12}$ skutterudites.

	$CoSb_3$	$Nd_{0.02}Co_4Sb_{12}$	$Nd_{0.05}Co_4Sb_{12}$	$Nd_{0.1}Co_4Sb_{12}$	$Nd_{0.15}Co_4Sb_{12}$	$Nd_{0.2}Co_4Sb_{12}$	$Nd_{0.25}Co_4Sb_{12}$
Lattice constant (Å)	9.0374 ± 0.0004	9.0378 ± 0.0005	9.0390 ± 0.0006	9.0406 ± 0.0005	9.0412 ± 0.0007	9.0415 ± 0.0006	9.0413 ± 0.0007
X-ray density (g cm^{-3})	7.637	7.649	7.665	7.694	7.725	7.756	7.789
Density (g cm^{-3})	7.534	7.576	7.368	7.330	7.568	7.439	7.548
Peritectic temperature (K)	1149 ± 4	1150 ± 3	1148 ± 4	1146 ± 4	1148 ± 6	1150 ± 5	1150 ± 3
Liquidus temperature (K)	1325 ± 6	1322 ± 5	1320 ± 5	1323 ± 4	1322 ± 5	1321 ± 6	1320 ± 5
Electrical resistivity (mΩ cm)	26	11	4.1	3.3	2.4	1.9	2.0
Seebeck coefficient (μV K^{-1})	-360	-278	-236	-210	-193	-170	-162
Lattice thermal conductivity (W cm^{-1} K^{-1})	0.087	0.055	0.034	0.030	0.036	0.037	—
Electron concentration (cm^{-3})	1.3×10^{18}	1.2×10^{19}	2.6×10^{19}	4.1×10^{19}	5.3×10^{19}	7.0×10^{19}	8.8×10^{19}
Electron mobility (cm^2 V^{-1} s^{-1})	185	47	59	46	49	47	35
Electron effective masses, m^*/m_0	0.59	1.35	1.60	1.74	1.79	1.75	1.89
Reduced Fermi energy, η	-2.122	-1.076	-0.488	-0.089	0.189	0.609	0.767

form an impurity phase, which was observed in x-ray diffraction patterns of $Nd_{0.2}Co_4Sb_{12}$ and $Nd_{0.25}Co_4Sb_{12}$ samples.

The results presented in figure 2 are qualitatively similar to previous studies of $CoSb_3$-based skutterudites partially filled with Ce, La, Tl, Yb or Ba [4–6, 8, 16]. The solubility limit of the filling atoms was reported to be around $x = 0.1$ in $Ce_xCo_4Sb_{12}$ [4], $x = 0.23$ in $La_xCo_4Sb_{12}$ [5], $x = 0.22 \pm 0.01$ in $Tl_xCo_4Sb_{12}$ [6], $x = 0.44$ in $Ba_xCo_4Sb_{12}$ [8] and around $x = 0.25$ in $Yb_xCo_4Sb_{12}$ [16]. The expansion of the crystal structure due to incorporation of Nd into the voids is significantly smaller than that observed in other $CoSb_3$-based partially filled skutterudites. This is consistent with the fact that the metallic radius of the Nd^{3+} ion for the ligancy 12 is smaller than the radii of other filling ions of the same crystallographic co-ordination [17].

DTA indicates that the addition of Nd does not affect the temperature and nature of phase transitions in partially filled skutterudites in comparison with those observed in $CoSb_3$ (table 1). All samples decompose incongruently at a temperature of around 1149 K and then exhibit a second incongruent transformation at 1205 ± 5 K (not shown in table 1). The incongruent nature of thermal effects is evident from the appearance of additional invariant thermal effects during the repeated cooling and heating of the samples. The liquidus temperature of $CoSb_3$ and all Nd-filled samples is also the same within experimental error. No additional thermal effects, which could be associated with a possible presence of the second phase in the samples, were observed.

The room temperature electrical transport properties of the $Nd_xCo_4Sb_{12}$ skutterudites are summarized in table 1. Prepared pure $CoSb_3$ exhibits n-type conductivity. $CoSb_3$ is a compound known to exhibit both n- and p-type conductivity depending on a small deviation from stoichiometry in the Sb sublattice [18]. It was reported in the literature [1] that single-crystalline $CoSb_3$ samples prepared from an Sb-rich melt possess p-type conductivity. N-type conductivity was previously observed in hot-pressed $CoSb_3$ samples [4, 16] and was attributed to a small change from stoichiometry into an Sb-deficient condition presumably due to the evaporation of a small amount of Sb during the synthesis procedure.

Relative to $CoSb_3$, the filling of the voids with Nd implies an increase in the number of electrons per unit cell, causing an increase in electron concentration and, consequently, a decrease in electrical resistivity and absolute value of the Seebeck coefficient. The mobility of electrons in $Nd_xCo_4Sb_{12}$ with $x \leqslant 0.2$ is around 50 $cm^2\ V^{-1}\ s^{-1}$ and does not depend on the Nd content. $Nd_{0.25}Co_4Sb_{12}$ samples exhibit slightly higher electrical resistivity and lower mobility of electrons in comparison to those of $Nd_{0.2}Co_4Sb_{12}$, which could be due to the presence of the second phase. A second phase could also cause the change in carrier concentration observed in the $Nd_xCo_4Sb_{12}$ samples with the Nd concentration exceeding the solubility limit.

A comparison of the concentration of the filling atoms with the experimentally measured carrier concentration enables an assessment to be made of the degree of ionization of filling atoms. In figure 3 are displayed the results of the present work together with literature data for Ce-, La- and Tl-filled skutterudites [4–6]. The concentration of the filling atoms in figure 3 was recalculated to the number of atoms per cubic centimetre. The experimental data for $Nd_xCo_4Sb_{12}$ fall on a straight line, indicating a doping effect of Nd atoms. The slope of the dependence represents the average number of electrons contributing to the conduction band by each filling atom. The slope of a solid line in figure 3 corresponds to the case when each filling atom donates one electron. As seen, different filling atoms give rise to a different slope of the dependence. Each Nd atom leads to the formation of around 0.8 electrons, whereas each Ce atom within the solubility range gives 2.2 electrons and La and Tl filling atoms produce around 1.6 and 1.3 electrons, respectively. By comparing the number of electrons donated by

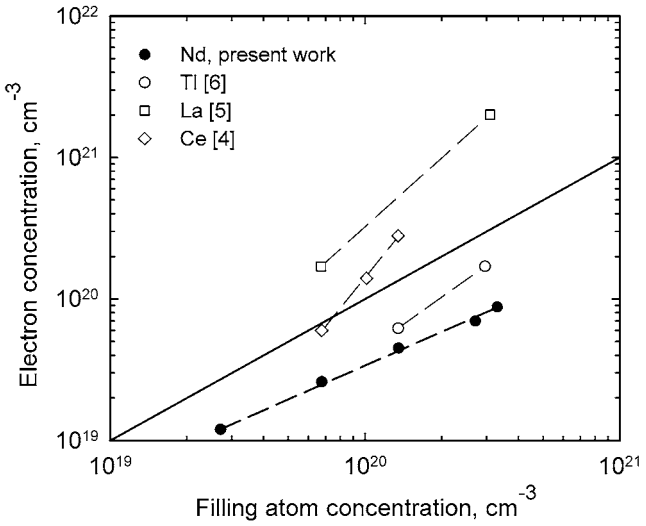

Figure 3. Room temperature carrier concentration as a function of concentration of filling atoms R in partially filled $R_xCo_4Sb_{12}$ skutterudites.

different filling atoms with their oxidation state (3+ for La and Nd, 3+ or 4+ for Ce and 1+ or 3+ for Tl), it can be seen that the filling atoms are not fully ionized. Partial ionization of the filling atoms was also suggested in $CeFe_4Sb_{12}$ skutterudites on the basis of density-functional calculations [19].

The largest difference between the oxidation state of the filling atoms and the number of donated electrons occurs in Nd-filled $CoSb_3$-based skutterudites. Nd atoms donate only around one-quarter of their available valence electrons. As a result, the carrier concentration in Nd-filled skutterudites is the lowest among other partially filled skutterudites at a given concentration of filling atoms (figure 3). It is suggested that due to their small metallic radius Nd ions tend to reside in an off-centre position rather than occupy the centre of the voids. The off-centre position could lead to the formation of partially covalent bonding with the nearest antimony atoms reducing the number of Nd electrons donating to the conduction band.

The variation of the electrical resistivity of the $Nd_xCo_4Sb_{12}$ skutterudites as a function of temperature is shown in figure 4 over the range of 11–750 K. $CoSb_3$ possesses the lowest electron concentration and its electrical resistivity decreases with increasing temperature over the whole temperature range of measurements. Although carrier concentration in $Nd_{0.02}Co_4Sb_{12}$ is relatively high, the sample also displays a negative temperature coefficient of electrical resistivity at $T < 50$ K. The dependence of electrical resistivity of $Nd_xCo_4Sb_{12}$ with $x > 0.02$ is typical of heavily doped semiconductors with the doping level dependent on the concentration of the filling atoms. Electrical resistivity increases with increasing temperature, exhibits a maximum at temperatures of around 600 K and then starts to decrease. The maximum and further decrease in electrical resistivity at a high temperature is caused presumably by intrinsic conduction. The onset of intrinsic conduction is shifted to a higher temperature with an increase in carrier concentration.

The temperature dependence of the electrical transport properties of $Nd_xCo_4Sb_{12}$ has been calculated assuming acoustic phonon scattering in a single-parabolic-band model. This model has been used previously to describe transport properties of skutterudites [1, 2]. The predominance of acoustic phonon scattering is evident from the temperature dependence of

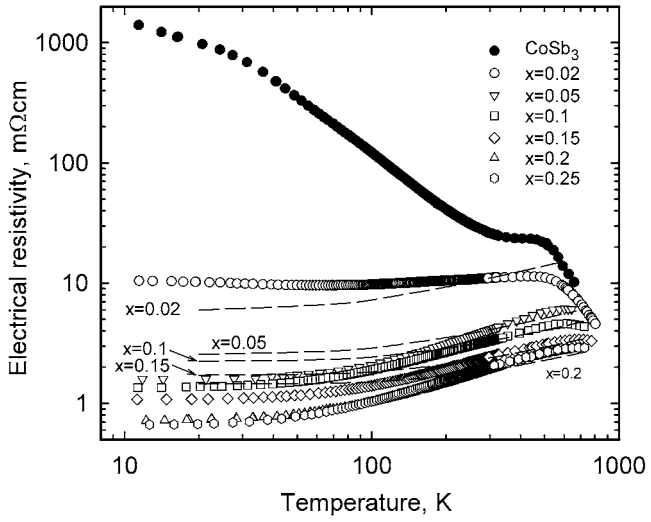

Figure 4. Temperature dependence of the electrical resistivity of $Nd_xCo_4Sb_{12}$ skutterudites. The dashed curves represent the model calculation using equation (3).

Hall mobility in partially filled $Ba_xCo_4Sb_{12}$ at $T > 50$ K [20] and in $CoSb_3$ at $T < 500$ K [1]. Using these assumptions, the Seebeck coefficient and carrier concentration can be expressed as

$$\alpha = \pm\frac{k_B}{e}\left(\frac{2F_1(\eta)}{F_0(\eta)} - \eta\right) \tag{1}$$

$$n = \frac{4\pi(2m^*k_BT)^{3/2}}{h^3}F_{1/2}(\eta), \tag{2}$$

where k_B is the Boltzmann constant, h is the Planck constant, $F_r(\eta)$ are the Fermi integrals of order r and $\eta = E_F/k_BT$, where E_F is the Fermi level. The Fermi levels were first calculated from the experimental Seebeck coefficient values using equation (1) and then these values together with measured carrier concentration were used to determine effective masses from equation (2). In the assumption that for scattering by acoustic phonons the relaxation time is given by $\tau = \tau_0 E^{-1/2}$ the temperature dependence of electrical conductivity can be expressed as

$$\sigma = \frac{1}{\rho} = \frac{16\pi e^2\tau_0 k_BT}{3h^3}\sqrt{2m^*}F_0(\eta). \tag{3}$$

The experimental room temperature values of electrical conductivity were used to fix the constant τ_0. The results of calculations are presented in figure 4 as dashed curves. The more significant increase in experimental electrical resistivity values with increasing temperature for samples with $x \geqslant 0.05$ can be associated with additional scattering processes, presumably with the Coulomb scattering on Nd filling ions.

The temperature dependence of the Seebeck coefficient of the $Nd_xCo_4Sb_{12}$ skutterudites is displayed in figure 5. The absolute value of the Seebeck coefficient rises with increasing temperature in the extrinsic region and then decreases due to the increasing number of minority carriers. This behaviour is consistent with the variations of the electrical resistivity over this temperature range. As with the temperature dependence of electrical resistivity, the maximum value of the absolute Seebeck coefficient is shifted to higher temperatures with the increase in the carrier concentration.

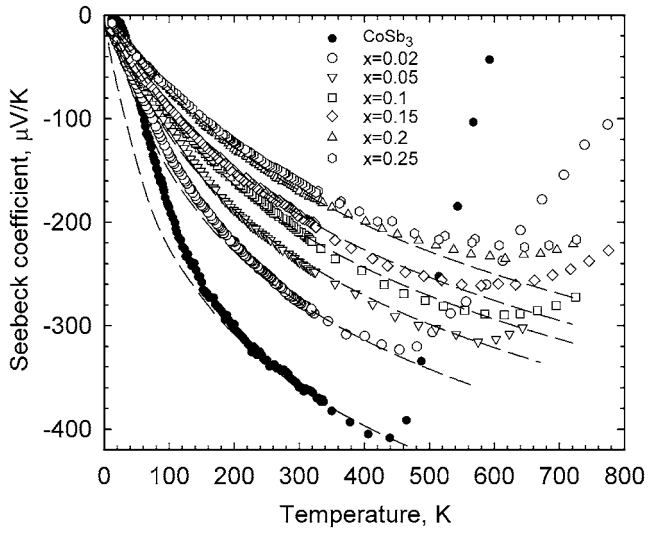

Figure 5. Temperature dependence of the Seebeck coefficient of $Nd_xCo_4Sb_{12}$ skutterudites. The dashed curves represent the model calculation using equation (1).

The temperature variation of the Seebeck coefficient of $Nd_xCo_4Sb_{12}$ skutterudites was evaluated using equation (1). The results are presented in figure 5 as dashed curves. The agreement between the measured and calculated data over the extrinsic region of $Nd_xCo_4Sb_{12}$ skutterudites is reasonably good.

Over the whole temperature range of measurements the values of the Seebeck coefficient and electrical resistivity of the $Nd_{0.2}Co_4Sb_{12}$ samples are very close to those of $Nd_{0.25}Co_4Sb_{12}$, confirming that in both samples the Nd concentration exceeds the solubility limit and the degree of void filling is similar.

An estimate of the density of state electron effective masses m^*/m_0 was obtained from equations (1) and (2). The resultant effective masses are shown in table 1 and range from 0.6 for $CoSb_3$ to 1.9 for $Nd_{0.25}Co_4Sb_{12}$. In figure 6 are displayed the room temperature effective masses as a function of electron concentration for $Nd_xCo_4Sb_{12}$ as well as literature data for Ce-, La-, Tl-, Ba- and Yb-filled $CoSb_3$ [4–6, 8, 20, 21]. As seen in figure 6, the effective masses in the $Nd_xCo_4Sb_{12}$ skutterudites are typical of those found in other n-type partially filled $CoSb_3$-based skutterudites. Relatively large m^* values are consistent with band structure calculations for La-filled skutterudites [22] and n-type skutterudites, for which a heavy conduction band mass is predicted [23].

The electron effective masses in all n-type $CoSb_3$-based partially filled skutterudites rise with an increase in carrier concentration value, which could result from some degree of nonparabolicity of the conduction band or from changes in the band structure with increasing concentration of filling atoms. The influence of nonparabolicity on the effective masses can be described by a two-band Kane model, which was previously used to analyse the effective masses of skutterudites [1, 20]:

$$m^* = m_e\left(1 + \frac{2\eta}{\Delta E}\right), \tag{4}$$

where m_e is the effective mass at the bottom of the band and $\Delta E = E_g/k_BT$ is the reduced energy gap. The results of calculation using equation (4) with $\Delta E = 0.15$ eV and $m_e = 1.9\,m_0$ are shown in figure 6 by a solid curve. The dashed line in figure 6 represents the predicted

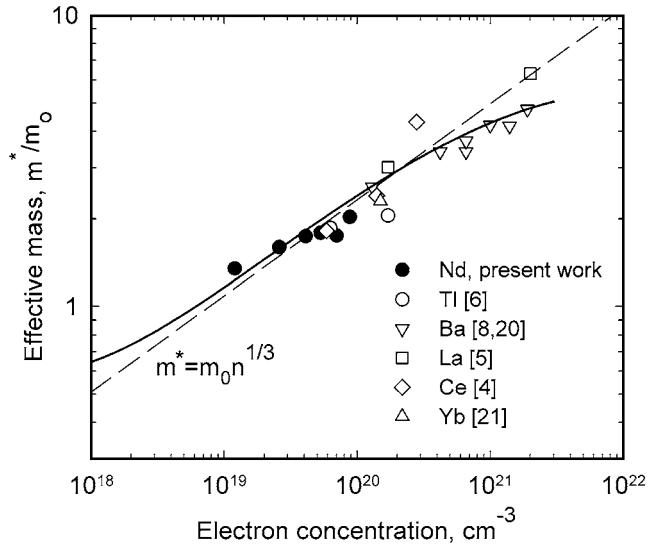

Figure 6. Room temperature effective masses as a function of electron concentration in partially filled $R_xCo_4Sb_{12}$ skutterudites. The dashed and solid lines are results of fits using the linear dispersion and Kane models, respectively (see the text for details).

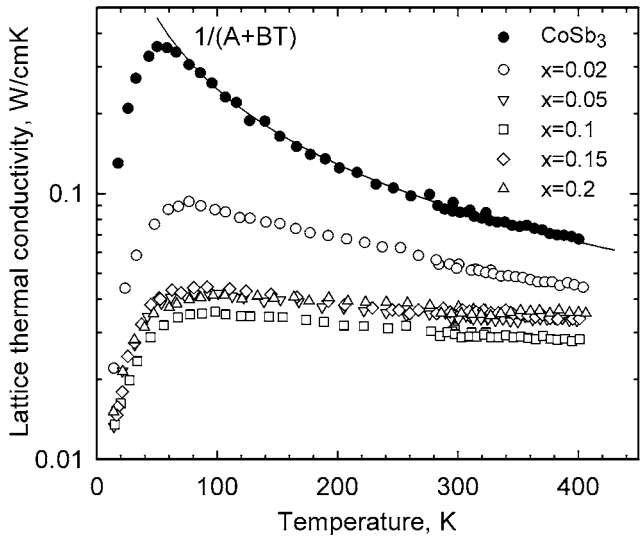

Figure 7. Temperature dependence of the lattice thermal conductivity of $Nd_xCo_4Sb_{12}$.

concentrational dependence of effective mass in the linear dispersion model [23] in which m^* varies as $n^{1/3}$. Both the Kane and linear dispersion models demonstrate good agreement with experimental data for all partially filled skutterudites. From figure 6 it can be suggested that electron effective mass in partially filled skutterudites depends mainly on carrier concentration and not on the type on filling atoms.

The lattice thermal conductivity λ_L of $Nd_xCo_4Sb_{12}$ skutterudites over the range of 15–410 K is shown in figure 7. λ_L values were obtained by subtracting the electronic component

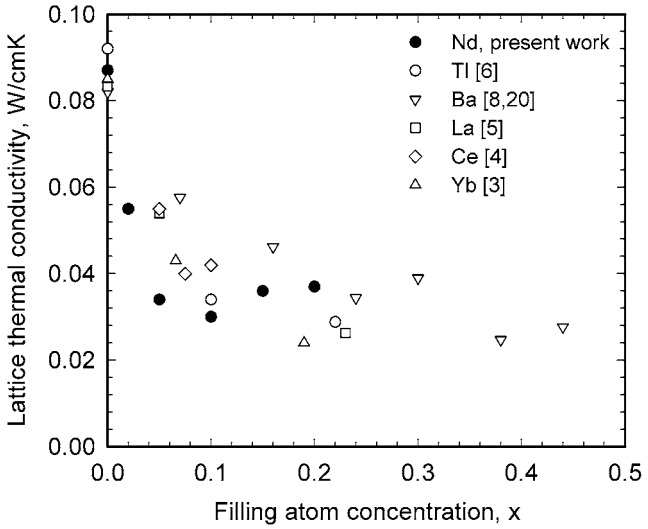

Figure 8. Room temperature lattice thermal conductivity of partially filled $R_x Co_4Sb_{12}$ skutterudites as a function of filling atom concentration.

of thermal conductivity from the experimentally measured total thermal conductivity. The electronic thermal conductivity λ_e was calculated using the experimental electrical resistivity values and the Wiedemann–Franz law $\lambda_e = LT/\rho$ with the Lorenz number

$$L = \frac{k^2}{e^2}\frac{3F_0(\eta)F_2(\eta) - 4F_1^2(\eta)}{F_0^2(\eta)}, \tag{5}$$

where the reduced Fermi energies were obtained from equation (1) and the measured Seebeck coefficient values.

For all the samples λ_e was less than 8% of the total thermal conductivity over the range of 15–410 K. $CoSb_3$ exhibits a temperature dependence of the lattice thermal conductivity typical of crystalline insulators. Above 80 K λ_L of $CoSb_3$ is adequately described by a $1/(A + BT)$ dependence with $A = 0.328$ cm K W^{-1} and $B = 0.0372$ cm W^{-1} and is shown by a solid curve in figure 7. The addition of Nd dramatically reduces the lattice thermal conductivity of $CoSb_3$ due to a combination of resonant scattering produced by 'rattling' of filling atoms in oversized voids and mass fluctuation scattering between filled and unfilled voids of the crystal structure. After a rapid initial decrease the lattice thermal conductivity exhibits a minimum for the $Nd_{0.1}Co_4Sb_{12}$ sample. The lattice thermal conductivity reduction is most noticeable at low temperatures, where the peak of λ_L of unfilled $CoSb_3$ is strongly suppressed by Nd filling. $Nd_xCo_4Sb_{12}$ samples with $x \geqslant 0.05$ demonstrate almost flat temperature dependence of λ_L between 50 and 400 K similar to that observed in charge compensated $R_xFe_{4-y}Co_ySb_{12}$ skutterudites [2, 4, 7].

In figure 8 the room temperature lattice thermal conductivity of $Nd_xCo_4Sb_{12}$ and other partially filled skutterudites is shown as a function of filling atom concentration [3–6, 8, 20]. Although the preparation techniques, grain size and density of the filled skutterudites presented in figure 8 are different, the calculated room temperature lattice thermal conductivity of pure $CoSb_3$ is very similar [3, 5, 6, 8, 20], that could justify the comparison of literature data. It is necessary to note that the additional charge compensation by substitution of Fe for Co or Sn for Sb was used to increase the solubility of filling atoms [4–6]. This substitution, however,

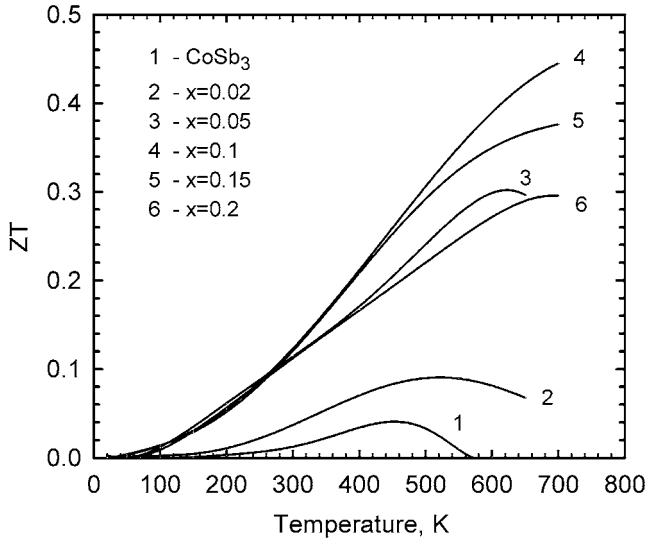

Figure 9. Temperature dependence of dimensionless figure of merit of $Nd_xCo_4Sb_{12}$.

could also decrease the lattice thermal conductivity due to the additional point-defect-type scattering [4], that is why these data are not shown in figure 8.

As seen in figure 8, for a small Nd concentration there is a rapid initial decrease in the lattice thermal conductivity with a minimum for $Nd_{0.1}Co_4Sb_{12}$ and a further small rise in λ_L for the $Nd_{0.15}Co_4Sb_{12}$ and $Nd_{0.2}Co_4Sb_{12}$ samples. A similar minimum in the lattice thermal conductivity was also observed for Ba-filled skutterudites at a filling fraction of 0.35–0.4 [8]. In both these cases the λ_L minimum occurs at a filling atom concentration approximately corresponding to a solubility limit of the filling elements in $CoSb_3$. It appears that the lattice thermal conductivity of partially filled skutterudites decreases as long as the $CoSb_3$ crystal structure can accommodate filling atoms and further increase in λ_L could be associated with the presence of the second phase with a high thermal conductivity.

The significant difference in λ_L between partially filled skutterudites having the same content of filling atoms indicates that the mass fluctuation scattering between filled and unfilled voids does not play a major role in the reduction of lattice thermal conductivity. If this were the case, λ_L values of all filled skutterudites in figure 8 would depend on the atomic mass of filling atoms. However, no such dependence could be observed in figure 8. It is also interesting to note that the minimum of the lattice thermal conductivity of partially filled skutterudites is similar in value, but it is achieved at a significantly different concentration of filling atoms.

At a given content of filling atoms the lattice thermal conductivity of $Nd_xCo_4Sb_{12}$ with $x \leqslant 0.1$ is lower than that of other filled skutterudites. This could be attributed to a smaller ionic radius of Nd than that of other filling elements resulting in the freer rattling of Nd atoms inside the voids and more efficient resonant scattering of the heat carrying phonons. Another factor which could further suppress the λ_L value of $Nd_xCo_4Sb_{12}$ is a possible additional static disorder in the lattice due to the off-centre position of small Nd ions [24] as opposed to the larger size ions, which occupy the centre of the voids.

In figure 9 is displayed the dimensionless figure of merit (ZT) of $Nd_xCo_4Sb_{12}$ as a function of temperature. To evaluate ZT values at $T > 410$ K an estimate of the total thermal conductivity has been obtained by extrapolation of the lattice thermal conductivity to higher

temperatures (figure 7). The electronic part of the thermal conductivity was calculated from the electrical resistivity using the Wiedemann–Franz law. Obtained ZT values rise with an increase in Nd content up to $x = 0.1$ and then diminish, mainly due to the rise of the total thermal conductivity (figure 9). A maximum ZT value of 0.45 is predicted at 700 K for $Nd_{0.1}Co_4Sb_{12}$. It is seen that at high temperature the ZT value of the Nd-filled skutterudites is limited due to intrinsic conduction caused by relatively low carrier concentration.

In comparison with other partially filled skutterudites [4–6, 8, 20, 21] the doping level in $Nd_xCo_4Sb_{12}$ is significantly lower due to a small number of electrons donated by each Nd atom. It is expected that further improvement to the thermoelectric properties of the $Nd_xCo_4Sb_{12}$ skutterudites might be achieved through additional n-type doping by substituting Pd, Pt or Ni for Co. These n-type dopants are reported to decrease markedly both the electrical resistivity and lattice thermal conductivity of $CoSb_3$ and partially filled skutterudites [20, 25]. Such a substitution could enable the carrier concentration in the material to be controlled independently as well as an accompanying further reduction in the lattice thermal conductivity due to an additional ionized impurity scattering. The lowest λ_L values might also be achieved in skutterudites partially filled with several different elements chosen to scatter a wider range of the heat-carrying phonons. The existence of a solid solution in some double-filled skutterudites has been reported [26, 27], which can facilitate further optimization of this class of materials for thermoelectric applications.

4. Conclusions

Partially filled skutterudites $Nd_xCo_4Sb_{12}$ have been synthesized. The saturation limit of the Nd void filling in $CoSb_3$ was found to be around 13%. Nd does not affect the temperature and nature of phase transitions in $Nd_xCo_4Sb_{12}$ in comparison with those observed in $CoSb_3$. The effect of the Nd filling on the electrical and thermal transport properties has been investigated. It was found that each Nd atom donates significantly fewer electrons than the Nd oxidation state, which could be a result of incomplete ionization of the filling atoms. The temperature dependence of the electrical resistivity and Seebeck coefficient of $Nd_xCo_4Sb_{12}$ with $x > 0.02$ is typical of heavily doped n-type semiconductors with a doping level dependent on the concentration of the filling atoms. A simple semiconductor transport model adequately describes the temperature variations of the Seebeck coefficient in the $Nd_xCo_4Sb_{12}$ skutterudites. The marked reduction in the lattice thermal conductivity of $Nd_xCo_4Sb_{12}$ upon filling with Nd can be attributed to the combination of a 'rattling' effect and a possible additional static disorder in the lattice due to the off-centre position of small Nd ions. The minimum of the lattice thermal conductivity is observed at the Nd concentration close to the solubility limit of Nd in $CoSb_3$. ZT value reaches 0.45 at 700 K for $Nd_{0.1}Co_4Sb_{12}$ and could be further enhanced by optimizing the doping level.

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