Effect of Triple Fillers in Thermoelectric Performance of *p*- type Skutterudites

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Abstract

Up-to-date, the thermoelectric performance of *p*-type skutterudites lags that of the corresponding *n*-type materials. In this work, we report improved thermoelectric performance of *p*-type skutterudites by triple filling the voids. The samples were synthesized by hot pressing nano-powder made by ball milling the annealed ingots of $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ with varying concentration of x and y . By tuning the filler concentration and Fe/Co ratio, we achieved a lower thermal conductivity ($\sim 2.0 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature and $\sim 2.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 535 °C) and a higher power factor ($\sim 35 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 475 °C), leading to a peak ZT of about 1.1 at 475 °C. The observed lower thermal conductivity can be attributed to a broad range of phonon scattering due to multiple fillers and the enhanced mobility due to the light element Ca leading to a high power factor.

Introduction

A focused attention to develop the technologies that can reduce ozone layer depletion, greenhouse gas emissions, and fossil fuel usage has drawn a great attention of the scientific community [1]. Thermoelectric (TE) materials which can directly convert heat into electricity based on thermoelectric effects without moving parts is attractive for many applications in power generation using waste heat and active cooling. The ability of TE device to convert heat into electricity is determined by a dimensionless figure-of-merit, ZT , defined as,

$$ZT = \frac{S^2 \sigma}{\kappa_e + \kappa_l} T \quad [1]$$

where σ is the electrical conductivity and S is the Seebeck coefficient, κ_e and the lattice κ_l are the electronic and lattice thermal conductivity, respectively. The quantity $S^2 \sigma$ in the numerator is called power factor (PF). The efficiency of TE devices increases with ZT , where T is the mean operating temperature. From the definition of ZT , it is clear that to increase ZT , we have to increase the power factor ($S^2 \sigma$) and decrease the thermal conductivity of the material. The quantities S , σ , and κ_e mainly depend on electronic structure of the material and are inter-related to each other. However, the quantity κ_l is mainly related to lattice. One way to improve ZT is to reduce the lattice thermal conductivity without significantly affecting the electronic properties of the materials. This idea has been explored extensively in the past through phonon scattering mechanism [2, 3].

Recently, skutterudite compounds have attracted a great deal of attention as promising candidates for intermediate temperature applications [4, 5]. Skutterudite compounds have a general formula RM_4X_{12} , where R , called filler, may be alkali metal [6, 7], alkaline-earth metal [8, 9], rare earth or actinide [10, 11], M is transition metal (Co, Rh, or Ir), and X is the pnictogen atom (P, As, or Sb) [12]. By filling the voids in skutterudite, lattice thermal conductivity can be effectively reduced [12, 13, 14, 15]. The Einstein-like vibrations of weakly bound filler ions interact with normal modes of the structure and dramatically suppresses κ_l . Generally, the fillers atom with smaller ionic radii enhance the phonon scattering due to the increased amplitude of vibration and vibrating frequency of filling atom in the voids and reduce the lattice thermal conductivity significantly [16]. The vibrational frequencies of heavier fillers are significantly

different than that of lighter fillers [17]. Therefore, filling the voids with the elements having different atomic masses and smaller radii has been proven to be an effective way to reduce lattice thermal conductivity, leading to improved ZT values [18, 19, 20].

Recently, a significant improvement in ZT of n -type skutterudites is reported [18, 19, 20]. However, the peak ZT of p -type skutterudites [21, 22, 23] is lower compared to n -type skutterudites [18, 19, 20]. The lag in thermoelectric performance of p -type skutterudites is due to the unfavorable nature of the single, light (low effective mass, m^*), and nearly dispersed nature of valance band [24, 25]. The higher hole concentration in p -type skutterudite suggests that the Fermi level is deep inside the valance band, implying that the number of available energy state per unit energy range near Fermi level is small, leading to lower Seebeck coefficient. Nevertheless, when suitably modified by Fe/Co alloying on the transition metal site together with void filling, decent Seebeck coefficient can be achieved by pushing the Fermi level into heavier transition metal d-bands. But, the large effective mass (m^*) of the carriers coupled with alloy scattering result in poor mobility (μ) and a lower power factor ($S^2\sigma$), which is about half the magnitude of the corresponding n -type skutterudites. On top of that, at high temperatures both electrons and holes move across the band gap and transport heat, giving a bipolar conduction leading to a higher thermal conductivity. This combination of properties leads to the best p -type material with a peak ZT in the range of about 1.0 to 1.2 [22, 26]. In this paper, we report a systematic study in thermoelectric performance of triple filled p -type skutterudites $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ ($x = 0.25, 0.35$, and 0.40 ; and $y = 0.35, 0.5, 0.8$, and 1.0). Keeping all other elements fixed, we first tuned Ca concentration (x) and their studied thermoelectric properties. Based on the best calcium concentration giving the highest ZT , we tuned the cobalt concentration y for both higher power factor and lower thermal conductivity to achieve a peak ZT of 1.1 at 475 °C.

Experiment

Stoichiometric amount of elements Ca (99.98%, Alfa Aesar), Ce ingot (99.8%, Alfa Aesar), Nd ingot (99.6%, Alfa Aesar), Fe pieces (99.999%, Alfa Aesar), Co slugs (99.95% Alfa Aesar), and Sb chunk (99.999%, Chengdu Chemphys Chemical Industry, China) were weighed and kept in

carbon coated quartz tubes inside a glove box. The tubes were sealed at a low pressure of the order of 2×10^{-6} mbar, kept in a furnace, melted at 1080 °C for 24 hours, and quenched in water. The produced ingots were then annealed in the sealed quartz tubes at 650 °C for 5 days to ensure the transformation into pure skutterudites phase. The ingots were then taken out of the quartz tubes, cleaned using a steel brush and ultra-sonication in ethanol. The dried ingots were then transferred into a steel jar under argon environment and ball-milled for 2 hours to get the needed nano-powder. The nano-powder was then loaded into graphite dies and hot pressed at 650 °C at a pressure of about 80 MPa for 5 minutes to get sample disks of about 4 mm thickness. The disks were cut into two half-disks of about 2 mm thick each. One of them was polished to get a uniform thickness for thermal diffusivity measurement (LFA 454, Netzsch) while the other disk was used to make a $2 \times 2 \times 12 \text{ mm}^3$ bar for electrical conductivity and Seebeck coefficient (ZEM-3, Ulvac) measurements. It is worth pointing out that the samples were tested along both directions and found isotropic due to the cubic structure and randomness of the small grains. We also made thin samples of about $4 \times 4 \times 0.5 \text{ mm}^3$ for carrier concentration measurement. The room temperature carrier concentration is measured using Physical Properties Measurement System (PPMS). A sample disk of about 6 mm in diameter and 0.7 mm in thickness was made for specific heat capacity measurement. The specific heat capacity was measured by differential scanning calorimetry (DSC 200F, Netzsch) and the mass density of all samples was measured using an Archimedes' kit. The total thermal conductivity was then calculated as $\kappa = \alpha C_p \rho$, where α is the thermal diffusivity, C_p is the heat capacity at constant pressure, and ρ is the mass density of the sample. The error in the measurement of electrical conductivity, Seebeck coefficient, and thermal conductivity is ~5% each. Based on the individual errors, the error in ZT is ~ 10-15%.

The phase formation of the samples was characterized by X-ray diffraction (XRD) on an X'pert PRO PANalytical diffractometer with Cu K α radiation source. The microstructure of the samples was studied by scanning electron microscopy (SEM, LEO 1500, JEOL) and transmission electron microscopy (TEM, JEM-2100F, JEOL). The hot-pressed samples were cut into blocks (2 mm by 3 mm by 1 mm) and mechanically polished. Then the polished specimen was glued to copper grids and ion-milled on a Precision Ion Polishing System (Gatan, Inc.) with an incident energy of 3.5 kV and an incident angle of 3.5° to electron transparent as the TEM

specimen. The chemical composition of the hot pressed samples was analyzed by energy dispersive X-ray spectrometer (JSM 6330F, EDAX). The error in the measurement of Fe, Co, and Sb is less than 5%, while the measurement error is about 10% for Ca, Ce, and Nd.

Results and Discussion

Fig. 1 shows the XRD patterns of six samples ($\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ with $x = 0.25, 0.35$, and 0.40 ; and $y = 0.35, 0.5, 0.8$, and 1.0) studied. All of the samples show pure skutterudites phase except with $x = 0.40$ and $y = 0.5$. The impurity observed in the sample with $x = 0.40$ and $y = 0.5$ may be Fe/FeSb_2 secondary phase(s). The sample with higher y shows the peak shift toward right, showing the change in lattice parameter with different Co concentration.

Fig. 2 shows SEM images at low (Fig. 2a) and higher (Fig. 2b) magnification of the freshly broken surface of the hot pressed samples. From the SEM images, we have observed that the grain size is ranged from 200 nm to 1000 nm and they are closely packed. The grain size is further confirmed by low magnification TEM image (Fig. 2c). With bigger grains, we have fewer interfaces for phonon scattering. But, the non-uniform distribution of grain size can help scatter phonons with different mean free paths [27], although the grain size distribution is not in a multiple scale range as reported in Ref. [27]. The SEM image shows that the crystallized grains are closely packed, an indication of high volume mass density. The measured densities of all samples (listed in Table 1) are more than 97% of the theoretical density, which is consistent with the close packing shown in the SEM images. The high resolution TEM image in Fig. 2d shows that the grain boundaries are clean, which facilitate the charge transport.

Table 1 shows the composition studied with their actual composition and various physical parameters measured at room temperature.

Fig. 3a shows the temperature dependent electrical conductivity of the samples. The electrical conductivity of all samples decreases with temperature, showing that all samples are heavily doped with metal-like behavior. For fixed y concentration, we observed decreased electrical conductivity for the sample with higher calcium concentration (x). Since Ca is in +2 state, increasing calcium gives more electrons to the host and effectively lowers the hole concentration, consistent with carrier concentration measurement shown in Table 1, leading to

reduced electrical conductivity. However, for fixed filler concentration, the electrical conductivity is determined by cobalt concentration y . Since Co has one more electron compared to Fe, increasing Co concentration gives more electrons to the host and effectively lowers the carrier density, in an agreement with the experimental observation (Table 1), which lowers the electrical conductivity, consistent with measurement.

Fig. 3b shows the temperature dependent Seebeck coefficient of the samples. The Seebeck coefficients of all samples are positive, implying that holes are the majority charge carrier. Since the Seebeck coefficient of degenerate semiconductor or metal depends on carrier concentration (n) as $n^{-2/3}$, sample with higher carrier density gives lower Seebeck coefficient, consistent with electrical conductivity measurement. The Seebeck coefficients of most of the samples increase with temperature in the entire temperature range. The Seebeck coefficients of the samples with higher cobalt concentration y decrease after about 425 °C. Above this temperature both electrons and holes move across the band-gap and contribute to the Seebeck voltage, an intrinsic bipolar behavior of p -type skutterudites. A high Seebeck voltage of $\sim 170 \mu\text{V K}^{-1}$ at 525 °C is achieved for the sample composition $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$, the composition that yielded the best ZT value.

Fig. 3c shows the temperature dependent power factor. The power factor, PF , of all samples increases with temperature. For fixed filler concentration ($x = 0.35$), the PF of the sample with higher cobalt concentration ($y = 0.8$ and 1) is lower and decreases after 425 °C. The lower power factor of these samples is due to their lower electrical conductivity compared to other samples. A maximum power factor of $\sim 35 \mu\text{W cm}^{-1} \text{K}^{-2}$ at around 475 °C is achieved in $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$, and is comparable to the PF of the best p -type results reported previously [22, 26].

Fig. 3d shows the temperature dependent thermal diffusivity. For fixed concentration of y , the thermal diffusivity of sample first decreases with increasing Ca concentration x from 0.25 to 0.35 and then increases for $x = 0.40$. However, for fixed x concentration, the thermal diffusivity of the samples decreases with increasing cobalt concentration y . Fig. 3e shows the temperature dependent specific heat capacity. The specific heat capacity of all samples increases with temperature. The specific heat capacity of sample at room temperature is in the range of

$\sim 0.215\text{-}0.225 \text{ J g}^{-1} \text{ K}^{-1}$ and attains a maximum value of $\sim 0.245\text{-}0.251 \text{ J g}^{-1} \text{ K}^{-1}$ at 525°C , consistent with the theoretical values.

Fig. 3f shows the temperature dependent thermal conductivity. The thermal conductivity of all samples increases with temperature. The increment in thermal conductivity up to about 425°C is small. Above this temperature, an upturn in thermal conductivity is observed for all samples. Such an upturn in thermal conductivity at higher temperature can be attributed to the bipolar contribution, an inherent phenomenon in *p*-type skutterudites due to the small band gap. In this experiment, we observe a significant bipolar contribution for the samples with $x = 0.35$ and $y = 0.8$ and $x = 0.35$ and $y = 1.0$, which is due to the increased contribution of electrons in thermal transport at elevated temperatures. Assuming that the contribution of minority charge carriers at high temperature is small, the total thermal conductivity can be written as the sum of the thermal contribution from the carriers and from the lattice vibration. The carrier contribution to the total thermal conductivity can be calculated using Wiedemann-Franz relation given by $\kappa_e = \sigma LT$, where σ is the electrical conductivity, L is the Lorenz number, and T is the absolute temperature. The Lorenz number can be calculated as [28]

$$L = \left(\frac{\kappa_B}{e}\right)^2 \left[\frac{\left(r + \frac{7}{2}\right) F_{r+\frac{5}{2}}(\xi)}{\left(r + \frac{3}{2}\right) F_{r+\frac{1}{2}}(\xi)} - \left(\frac{\left(r + \frac{5}{2}\right) F_{r+\frac{3}{2}}(\xi)}{\left(r + \frac{3}{2}\right) F_{r+\frac{1}{2}}(\xi)} \right)^2 \right] \quad [2]$$

where r is the scattering parameter, and $F_n(\xi)$ is the Fermi integral given by,

$$F_n(\xi) = \int_0^\infty \frac{x^n}{1 + x^{y-\xi}} dx \quad [3]$$

where ξ is the reduced Fermi energy that can be deduced from the Seebeck coefficient S as well as the scattering parameter r , given as

$$S = \pm \frac{\kappa_B}{e} \frac{\left(r + \frac{5}{2}\right) F_{r+\frac{3}{2}}(\xi)}{\left(r + \frac{3}{2}\right) F_{r+\frac{1}{2}}(\xi)} - \xi \quad [4]$$

In this calculation, we assumed that the acoustic phonon scattering is the dominant mechanism for carrier scattering and evaluated the temperature dependent Lorenz number from the reduced Fermi energy deduced from the Seebeck coefficient at room temperature based on two band model with a temperature dependent band gap $E_g = 0.55-3 \times 10^{-4}T$ (eV) [29]. Since we do not exactly know the effective mass of carriers in conduction band and valance band, the bipolar thermal conductivity is overestimated by a small amount. The lattice part of thermal conductivity is then enumerated by subtracting both the carrier contribution and bipolar contribution from total thermal conductivity. The temperature dependent lattice thermal conductivity is plotted in Fig. 3g. The lattice thermal conductivity of the samples with fixed y first decreases with increasing Ca concentration (x) from $x = 0.25$ to $x = 0.35$, an indication of maximum rattling effect scattering a broad range of phonons. Further increasing Ca concentration increases the lattice part of thermal conductivity, possibly because of the reduced rattling effect due to higher rattler concentration above the solubility limit. The lowest lattice thermal conductivity is achieved in $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ and varies from $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature to $\sim 0.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 525°C .

The temperature dependent ZT is calculated from the measured values of temperature dependent electrical conductivity (σ), the Seebeck coefficient (S), and the thermal conductivity (κ) and is plotted in Fig. 3h. The ZT value of all samples increases with temperature, attain a maximum value at around $425\text{-}475^\circ\text{C}$, and then decreases. We have achieved a peak ZT of 1.1 at 475°C in $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$. This ZT value is fairly comparable to the highest reported ZT of p -type skutterudites [22, 26].

Conclusion

Triple filled (Ca, Ce, and Nd) p -type skutterudites $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ ($x = 0.25, 0.35$, and 0.40 ; $y = 0.35, 0.5, 0.8$, and 1.0) were synthesized by melting-quenching-annealing method followed by hot pressing the ball milled nano-powder. For fixed y concentration, the electrical conductivity of the sample decreased with increasing calcium concentration (x), which is due to lower carrier concentration. However, for fixed concentration of x , the electrical conductivity of sample depends on cobalt concentration y . The Seebeck coefficient of all samples is consistent

with electrical conductivity measurement. By tuning the filler concentration and Fe/Co ratio, we achieved a low thermal conductivity ($\sim 2.0 \text{ W m}^{-1} \text{ K}^{-1}$ at room temperature and $\sim 2.6 \text{ W m}^{-1} \text{ K}^{-1}$ at 525°C) and a high power factor ($\sim 35 \mu\text{W cm}^{-1} \text{ K}^{-2}$ at 475°C) in $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$. Such a low thermal conductivity may be due to the broad range of phonon scattering due to the vibration of multiple fillers with different ionic radii and atomic masses while the high power factor may be due to the enhanced mobility coming from lighter element Ca. Due to high power factor and low thermal conductivity, we achieved a peak ZT of 1.1 at 475°C in $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$.

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Figure Captions

- Fig. 1** XRD patterns of the dc hot pressed skutterudites $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ samples with $x = 0.25, 0.35$, and 0.40 ; $y = 0.35, 0.5, 0.8$, and 1.0 . All samples except for $x = 0.40$ & $y = 0.50$ show pure skutterudite phase.
- Fig. 2** SEM images at (a) low and (b) high magnification and TEM images at (c) low and (d) high magnification of $\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$ sample showing the grain size, crystallinity, and clean grain boundary.
- Fig. 3** Temperature dependent thermoelectric properties of $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ samples with $x = 0.25, 0.35$, and 0.40 ; $y = 0.35, 0.5, 0.8$, and 1.0 : (a) electrical conductivity (σ), (b) Seebeck coefficient (S), (c) power factor (PF), (d) thermal diffusivity (α), (e) specific heat capacity (C_p), (f) thermal conductivity (κ), (g) lattice thermal conductivity (κ_l), and (h) figure of merit, ZT .

Table 1: Room temperature thermoelectric properties of $\text{Ca}_x\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{4-y}\text{Co}_y\text{Sb}_{12}$ with varying nominal concentration of x and y and their actual composition.

Nominal composition	Actual Composition	a (°Å)	n (10^{21} cm^{-3})	μ ($\text{cm}^2 \text{ V}^{-1} \text{ S}^{-1}$)	ρ (g cm^{-3})	σ (10^5 S m^{-1})	S ($\mu\text{V K}^{-1}$)	κ ($\text{W m}^{-1} \text{ K}^{-1}$)	ZT
$\text{Ca}_{0.25}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	$\text{Ca}_{0.21}\text{Ce}_{0.30}\text{Nd}_{0.33}\text{Fe}_{3.53}\text{Co}_{0.54}\text{Sb}_{11.48}$	9.1278	6.61	1.92	7.64	2.01	95	2.22	0.25
$\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	$\text{Ca}_{0.32}\text{Ce}_{0.29}\text{Nd}_{0.33}\text{Fe}_{3.56}\text{Co}_{0.55}\text{Sb}_{11.42}$	9.1254	5.80	1.95	7.67	1.82	102	2.07	0.28
$\text{Ca}_{0.40}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.5}\text{Co}_{0.5}\text{Sb}_{12}$	$\text{Ca}_{0.37}\text{Ce}_{0.32}\text{Nd}_{0.31}\text{Fe}_{3.53}\text{Co}_{0.52}\text{Sb}_{11.17}$	9.1225	3.98	2.47	7.73	1.58	101	2.16	0.23
$\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.65}\text{Co}_{0.35}\text{Sb}_{12}$	$\text{Ca}_{0.29}\text{Ce}_{0.31}\text{Nd}_{0.29}\text{Fe}_{3.60}\text{Co}_{0.37}\text{Sb}_{11.47}$	9.1293	4.94	2.63	7.73	2.10	95	2.30	0.21
$\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_{3.2}\text{Co}_{0.8}\text{Sb}_{12}$	$\text{Ca}_{0.27}\text{Ce}_{0.30}\text{Nd}_{0.31}\text{Fe}_{3.17}\text{Co}_{0.83}\text{Sb}_{11.53}$	9.1232	3.48	2.42	7.70	1.37	111	2.00	0.25
$\text{Ca}_{0.35}\text{Ce}_{0.35}\text{Nd}_{0.35}\text{Fe}_3\text{CoSb}_{12}$	$\text{Ca}_{0.28}\text{Ce}_{0.31}\text{Nd}_{0.30}\text{Fe}_{3.03}\text{Co}_{1.03}\text{Sb}_{11.58}$	9.1220	2.07	3.08	7.68	1.03	122	1.78	0.26

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Fig. 3, T. Dahal *et al.*