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Electrical transport and thermoelectric properties of double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ at low temperatures

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The electrical transport and thermoelectric properties of CoSb_3 and double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$, and 0.15) were investigated in the temperature range from 5 to 300 K. The results indicated that double filling of Ca and Ce has a strong influence on the temperature dependence of the electrical resistivity. For samples CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, the relationship of $\ln \rho \propto 1/T$ existed only in the temperature regimes of 100–200 and 160–300 K, respectively, while Mott's law $\ln \rho \propto T^{-1/4}$ was obeyed at lower temperatures below 100 and 160 K for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, respectively. The results suggested a localization of charge carriers. Moreover, a transition from the semiconducting state (i.e., $d\rho/dT < 0$) ($x=0.05$) to the metallic state (i.e., $d\rho/dT > 0$) ($0.05 < x \leq 0.15$) took place owing to heavy filling. Due to the increase in carrier concentration, the electrical resistivity for $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x > 0.5$) was observed to be smaller than that of CoSb_3 . However, the increase in carrier concentration did not affect the absolute Seebeck coefficient values. In fact, a large absolute Seebeck coefficient was maintained, which was likely due to the large effective mass arising from the filler atoms. Moreover, the low-temperature lattice thermal conductivity of $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ was observed to decrease monotonously with increasing Ce content, which was attributed to the rattling motion of the Ca and Ce atoms in the Sb cages. As a result, the figure of merit, ZT , of heavily filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.1$ and 0.15) improved over the whole temperature range investigated. In particular, ZT of $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ was tenfold larger than that of CoSb_3 at 300 K. The current results showed that double filling Ca and Ce is an efficient way in improving the thermoelectric properties.

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I. INTRODUCTION

Extensive interest is currently focused on the search for efficient thermoelectric materials for solid-state cooling and power generation application based on thermoelectric effects. The efficiency of thermoelectric devices is determined by the materials' dimensionless figure of merit, defined as ZT ($=S^2T/\rho\kappa$, where S , ρ , κ , and T are the Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively¹). Therefore, a useful thermoelectric material should possess a large Seebeck coefficient, a low electrical resistivity, and a low thermal conductivity.

One family of compounds that has received much attention is the skutterudite CoSb_3 , which was reported to have a large Seebeck coefficient (220 $\mu\text{V/K}$) and a low electrical resistivity (1.89 $\text{m}\Omega\text{ cm}$) at room temperature.² However, due to its large lattice thermal conductivity (10 $\text{W K}^{-1}\text{ m}^{-1}$), its ZT value is too small for practical application. Therefore, reduction in its thermal conductivity is of great importance in improving its thermoelectric properties.

Filling the voids in the skutterudite structure of CoSb_3 with rare earth and alkaline earth atoms is an effective approach to lower the thermal conductivity of CoSb_3 . The rattling effect of the filler atoms in the voids generates low

frequency phonon that can interact strongly with the heat-carrying phonons of the pnictogen ring to reduce the thermal conductivity. So far, various kinds of rare earth atoms such as Ce, La, Nd, Sm, and Yb and alkaline earth atoms including Ca, Sr, and Ba have been used to fill the voids in the skutterudite structure.^{2–10} Since each type of filler ions has its own characteristic frequency that reflects its mass, size, and strength of coupling with atoms, filling with two or more different species of filler atoms into the voids of the skutterudite structure may give rise to different frequencies and hence introduce an extra phonon scattering mode. A combination of alkaline earth and rare earth atoms as different filler atoms to produce compounds such as $(\text{Ba,Ce})_y\text{Co}_4\text{Sb}_{12}$ and $(\text{Ba,La})_y\text{Co}_4\text{Sb}_{12}$ have been shown to exhibit a lower lattice thermal conductivity than that of Ba filled skutterudites.^{11,12} Similar results were also obtained for cases when two different rare earth filler atoms were introduced as in $\text{Ce}_m\text{La}_n\text{Co}_4\text{Sb}_{12}$.¹³

Atomic (or ionic) radius and atomic weight of the filler atoms play an important role in affecting the transport properties of double filled CoSb_3 compounds since these can affect their ability to scatter carriers and phonons. In the present work, Ca [ionic radius of Ca^{2+} is 0.99 Å with a light atomic weight (40.08)] and Ce (ionic radii of Ce^{3+} and Ce^{4+} are 0.92 and 1.03 Å, respectively, with a heavy atomic weight (140.12)) were chosen as filler atoms to synthesize

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Ca and Ce double filled $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ compounds. The low-temperature thermoelectric properties of double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ were investigated in an attempt to explore the mechanism of filler atoms on the transport and thermoelectric properties of CoSb_3 .

II. EXPERIMENTAL PROCEDURE

Polycrystalline samples of $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15) were prepared by melting method. High-purity Ca pellets (99.5%, Aldrich Chemical Co., Inc., USA), Co powders (99.9%, Aldrich Chemical Co., Inc., USA), Sb ingots (99%, International Laboratory, USA), and Ce shot (99.99%, Aldrich Chemical Co., Inc., USA) were used as the starting materials. The nominal Ca filling fraction of all the samples was fixed at 0.1 , and Ce filling fraction was varied from 0.05 to 0.15 . Excess 0.25 at. % Sb was added to compensate for the volatilization of Sb during the hot-pressing process. The starting metals were loaded into quartz tubes in an argon atmosphere glove box and sealed at a pressure of 6.5×10^{-5} Torr. They were heated slowly to 1000°C in a Nabertherm low-temperature box furnace (L5/11/S27) and isothermally held at this temperature for 48 h followed by quenching in water. The quartz tubes were then annealed at 620°C for 7 days. The solid obtained was then ground into fine powders using an agate mortar. The powders were compacted by hot pressing (Centorr series 60) under a pressure of 100 MPa in vacuum at 500°C for 2 h to form bulk samples of 13 mm in diameter and 2 – 3 mm in thickness.

X-ray diffraction (XRD) analysis to determine the phase structure of the hot-pressed samples was carried out using $\text{Cu } K\alpha$ radiation ($\lambda=1.5406$ Å) on a Shimadzu 6000 x-ray diffractometer over the 2θ range of 20° – 80° . Reitveld refinements were performed to determine the lattice parameters using the diffraction data over the 2θ range of 10° – 140° . Four probes (Cu straps) were electrically and thermally attached to the specimens by silver conductive adhesive paste (Phentex Corp., Ward Hill, MA) to measure their electrical resistance. When thermopower and thermal conductivity were to be measured, the middle two probes were used to explore the temperature gradient (difference) and potential difference. All the thermoelectric properties (electrical resistance, thermopower, and thermal conductivity) were measured simultaneously using a physical property measurement system (Quantum Design) in the temperature range from 5 to 300 K.

III. RESULTS AND DISCUSSION

The XRD patterns of CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15) are shown in Fig. 1. It can be seen from curve (a) of Fig. 1 that all the main diffraction peaks correspond to the CoSb_3 Phase¹⁴ with a body-centered cubic structure (space group $Im\bar{3}$). Trace amount of Sb was detected, which is due to the excess Sb used in the starting material. As compared with that of pristine CoSb_3 , no substantial changes were observed in the XRD patterns of the double filled samples. This suggests that all the double filled samples have the same crystallographic structure as that of CoSb_3 . The lattice constant a obtained from Rietveld analy-

FIG. 1. XRD patterns ($\text{Cu } K\alpha$ irradiation) for (a) CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$].

sis for all the samples is presented in Fig. 2. The lattice constant a of our synthesized CoSb_3 is ~ 9.036 Å, which is in good agreement with the value reported by Puyet *et al.*¹⁵ The lattice parameter a of the double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15) is observed to increase with increasing Ce content. Similar phenomenon, as pointed out elsewhere,¹⁶ indicates that the filler atoms have filled into voids of the skutterudite caged structure and give rise to lattice expansion.

The temperature dependence of electrical resistivity ρ for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ with different compositions x is shown in Fig. 3. The electrical resistivity of lightly double filled compound $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$ is obviously larger than that of CoSb_3 . In contrast, as compared to CoSb_3 , the electrical resistivity of the heavily filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.1$ and 0.15) decreased substantially with increasing Ce content for the temperature range investigated. Furthermore, the temperature behavior of the electrical resistivity for the double filled compound $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ is strongly affected by the filling content of Ce and Ca. For CoSb_3 , the ρ - T curve shows a metalliclike behavior (i.e., $d\rho/dT > 0$) as temperature decreases from 300

FIG. 2. Composition (x) dependence of lattice parameters a for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.10 , and 0.15) at room temperature.

FIG. 3. Temperature dependence of the electrical resistivity for (a) CoSb₃ and Ca_{0.1}Ce_xCo₄Sb₁₂ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$]. The inset shows the electrical resistivity as a function of temperature for CoSb₃.

to 220 K, which can be explained as Boltzmann-type electrical conduction.¹⁷ For temperatures below 220 K, the ρ - T curve of CoSb₃ exhibits semiconducting behavior (i.e., $d\rho/dT < 0$) instead. Semiconducting behavior was also observed when $x=0.05$ for sample Ca_{0.1}Ce_{0.05}Co₄Sb₁₂ [curve (b) in Fig. 3]. However, when x is increased to 0.1 [curve (c) in Fig. 3] and 0.15 [curve (d) in Fig. 3], metallic behavior was observed in these compounds.

In order to examine the temperature behavior of the resistivity for CoSb₃ and Ca_{0.1}Ce_{0.05}Co₄Sb₁₂, the logarithm of resistivity as a function of the reciprocal of temperature is plotted as shown in Fig. 4. A good linear relationship between $\ln \rho$ and $1/T$ existed from 100 to 200 K for CoSb₃ and

FIG. 4. Plot of $\ln \rho$ vs reciprocal of temperature for (a) CoSb₃ and (b) Ca_{0.1}Ce_{0.05}Co₄Sb₁₂. The solid lines are the best fit of Eq. (1) to the experimental data.

from 160 to 300 K for Ca_{0.1}Ce_{0.05}Co₄Sb₁₂. This linear behavior can be described by the simple band theory of semiconductor and can be expressed in terms of thermal activation:¹⁶

$$\rho = \rho_0 \exp(E_a/k_B T), \quad (1)$$

where ρ_0 is a constant, k_B is the Boltzmann constant, and E_a is the apparent activation energy for conduction. By fitting the experimental data to Eq. (1), the apparent activation energies E_a for CoSb₃ and Ca_{0.1}Ce_{0.05}Co₄Sb₁₂ were determined to be 1.8 and 29 meV, respectively. The activation energy reflects the magnitude of ionizing energy E_i , which is related to E_a by the relation $E_i = 2E_a$.¹⁸ Hence, E_i for CoSb₃ will be 3.6 meV, which suggests that the acceptor level is located very close to the edge of the valence band.

For the pure CoSb₃ prepared by Mandrus *et al.*,⁴ no excess Sb was used. A low-temperature semiconducting behavior was observed, and a room temperature electrical resistivity of $2.5 \times 10^{-4} \Omega \text{ m}$ and an energy gap of 50 meV were reported. As discussed above, our pure CoSb₃ sample showed a transition from semiconducting behavior to the metallic behavior, and a room temperature electrical resistivity of $2.0 \times 10^{-5} \Omega \text{ m}$ and an ionizing energy of 3.6 meV were obtained. Such a difference in behavior may arise due to the excess Sb in our sample. The excess Sb can produce acceptor levels in the CoSb₃ host, which leads to smaller ionizing energy at temperatures below 200 K and exhibiting metallic conduction behavior at temperatures above 200 K. The existence of Sb can also supply more carriers, and hence lowers the electrical resistivity. Metallic behavior at high temperature and low electrical resistivity were also observed by He *et al.*¹⁹ in their CoSb₃ samples due to the presence of excess Sb.

The filling of Ca and Ce into the voids of the skutterudite structure provides extra electrons. Such filling introduces donor level into the band gap of the host and gives rise to an increase in electron concentration. The increased electrons in the newly introduced donor levels will counteract holes in the original acceptor levels. As a result, the major carriers in the samples are electrons. This is supported by the Seebeck coefficient results, which will be discussed later. When the net number of electrons in the double filled compounds is less than the number of holes in CoSb₃, this will cause an increase in both resistivity and thermopower, as seen in CoSb₃ and Ca_{0.1}Ce_{0.05}Co₄Sb₁₂. However, with increasing Ce content, the donor levels broaden and shift toward the edge of the conduction band. Especially, in the case for the heavily double filled compounds, overlapping of the donor levels with the conduction band would occur, which could be responsible for the transition from semiconductor for Ca_{0.1}Ce_{0.05}Co₄Sb₁₂ to metallic state for Ca_{0.1}Ce_xCo₄Sb₁₂ ($x=0.1$ and 0.15).

At very low temperatures, however, the temperature dependences for CoSb₃ and Ca_{0.1}Ce_{0.05}Co₄Sb₁₂ were found to follow Mott's law $\ln \rho \propto T^{-1/4}$ at temperatures below 100 K for CoSb₃ and below 160 K for Ca_{0.1}Ce_{0.05}Co₄Sb₁₂, as shown in Fig. 4. This implies that variable-range hopping conduction occurs in these specimens. According to Mott's variable-range hopping conduction theory, the resistivity is expressed by¹⁵

FIG. 5. Plot of $\ln \rho$ vs $T^{-1/4}$ for (a) CoSb_3 and (b) $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$. The solid lines are the best fit of Eq. (2) to the experimental data.

$$\rho_{\text{hop}} = \rho_0 \exp(T_0/T)^{1/4}, \quad (2)$$

with

$$T_0 = 18.1\alpha^3/k_B N(E_F), \quad (3)$$

where ρ_0 is a constant, $N(E_F)$ is the density of localized states at Fermi energy, k_B is the Boltzmann constant, and α is the inverse decay length of the wave function for localized states near the Fermi level. By fitting the experimental data to Eq. (2), as shown in Fig. 5, T_0 were determined to be 20 and 151 K for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, respectively. T_0 increases with Ce filling, which may indicate that the density of the localized states, $N(E_F)$, decreases.

The temperature dependence of the Seebeck coefficient for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$ and 0.15) is shown in Fig. 6. The binary compound CoSb_3 obtained in this study is p type. The Seebeck coefficient values were negative for all the (Ca, Ce) double filled compounds in the temperature range investigated, indicating that they are n type. Filling the voids of the skutterudite with Ca and Ce atoms changes the sign of the Seebeck coefficient. The room temperature Seebeck coefficients for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$ and 0.15) are 90, -330 , -165 , and -165 $\mu\text{V/K}$, respectively. As presented in Fig. 6, except for $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$ whose absolute Seebeck coefficient $|S|$ decreased with increasing temperature above 290 K, the absolute Seebeck coefficient $|S|$ for the other samples decreased monotonically with decreasing temperature for the temperature range investigated. At temperatures above 150 K, the Seebeck coefficients for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$, and 0.15) showed approximately linear relationship with temperature. In particular, the slope for $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ decreased with increasing Ce content. The

FIG. 6. Variation in Seebeck coefficient S with temperature for (a) CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$]. The solid lines are the best fit of Eq. (3) to the experimental data.

diffusive part of the Seebeck coefficient (T -linear part) in the higher temperature range can be described by²⁰

$$S \propto \pi^2 k_B^2 T / e E_F, \quad (4)$$

where k_B , E_F , and e are the Boltzmann constant, Fermi level, and electron charge, respectively. This indicates that the slope of the plot of S versus T is inversely proportional to the Fermi level. Hence, the decrease in the slope of the plot of S versus T (Fig. 6) with increasing Ce content would reflect a rise in E_F , which is consistent with the increase in electron concentration originating from the charge transfer. It should be noted that the absolute values of the Seebeck coefficient for the double filled compounds at room temperature remained very large although the electrical resistivity decreased due to an increase in carrier concentration as compared to that of CoSb_3 . This may be caused by the large electron effective mass due to the introduction of Ca and Ce as filler atoms.

The temperature dependence of thermal conductivity for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05, 0.1$, and 0.15) is shown in Fig. 7. For the binary compound CoSb_3 , the thermal con-

FIG. 7. Variation in thermal conductivity κ with temperature for (a) CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$].

FIG. 8. Variation in lattice component of thermal conductivity κ_L with temperature for (a) CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$]. The solid lines are the best fit of Eq. (5) to the experimental data.

ductivity increased with increasing temperature and then decreased with further increase in temperature, leaving a peak located at 31 K. Such behavior is typical for crystalline materials. The thermal conductivity behavior of the $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ sample with $x=0.05$ is similar to that of CoSb_3 , but the thermal conductivity was already strongly suppressed. For higher Ce filling compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.1$ and 0.15), the thermal conductivity increased with increasing temperature. At temperatures above ~ 50 K, it exhibited weak temperature dependence. In general, it is observed that filling of Ca and Ce into the voids of CoSb_3 caused a decrease in thermal conductivity for the temperature range investigated. The values of the thermal conductivity at 300 K were $11.7 \text{ W m}^{-1} \text{ K}^{-1}$ for CoSb_3 , $9.9 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, $7.7 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Ca}_{0.1}\text{Ce}_{0.1}\text{Co}_4\text{Sb}_{12}$, and $6.5 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$.

Thermal conductivity can be expressed by the sum of lattice component (κ_L) and carrier component (κ_C) as $\kappa = \kappa_L + \kappa_C$. The κ_C values can be estimated from Wiedemann–Franz’s law as $\kappa_C = LT/\rho$, where L is the Lorentz number ($2.44 \times 10^{-8} \text{ V}^2 \text{ K}^{-2}$ for free electrons). Hence, κ_L can be obtained from κ and κ_C , and the results are presented in Fig. 8. By comparing Fig. 7 with Fig. 8, it can be determined that the total thermal conductivity of all the compounds arises mainly from the lattice thermal conductivity. According to the phononic heat transport theory,²¹ the relationship between lattice thermal conductivity and temperature above about 30 K can be written as

$$\kappa_L \propto T^n. \quad (5)$$

By fitting the experimental data (Fig. 8) to Eq. (5), $n = -0.9$, -0.7 , -0.2 , and -0.1 were obtained for CoSb_3 , $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, $\text{Ca}_{0.1}\text{Ce}_{0.1}\text{Co}_4\text{Sb}_{12}$, and $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$, respectively. The value of n for the binary CoSb_3 is fairly close to -1 . This suggests that phonon-phonon interactions are the primary source of thermal resistance. However, with double filling and increasing Ce content, the absolute value of n decreases. In particular, the

FIG. 9. Temperature dependence of ZT for (a) CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ [(b) $x=0.05$, (c) $x=0.1$, and (d) $x=0.15$].

weak temperature dependence for sample $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ indicates that it possesses the thermal transport characteristic of glass. It is worth noting that κ_L of all the double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15) were less than that of CoSb_3 . Higher Ce content lowered the lattice thermal conductivity. Such reduction in lattice thermal conductivity is attributed to the rattling motion of the Ca and Ce atoms in the Sb cages.

Figure 9 shows the temperature dependence of the figure of merit ZT for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15). The ZT values for all the samples were found to increase with increasing temperature. However, the ZT for the lightly Ce filled compound $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$ was smaller than that of CoSb_3 . This is mainly due to the large increase in its electrical resistivity, although its absolute Seebeck coefficient increased and its thermal conductivity decreased considerably. On the other hand, the ZT of the heavily filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.10$ and 0.15) improved substantially for the whole temperature range investigated. In particular, the ZT value of sample $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ is about one magnitude larger than that of CoSb_3 at 300 K. Evidently, this improvement in the thermoelectric properties of sample $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ is ascribed to the decreased resistivity, the increased absolute Seebeck coefficient, and the decreased lattice thermal conductivity.

IV. CONCLUSIONS

The temperature dependence of the electrical transport and thermoelectric properties of CoSb_3 and double filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.05$, 0.1 , and 0.15), prepared by melting method followed by hot pressing, were investigated in the temperature range from 5 to 300 K. The results showed that double filling of Ca and Ce into the voids of CoSb_3 has a strong influence on the temperature dependence of the electrical resistivity. For CoSb_3 and lightly filled compound $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, the relationship of $\ln \rho \propto 1/T$ existed only in the higher temperature regime (between 80 and 200 K and between 160 and 300 K for CoSb_3 and $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, respectively); however, at lower temperatures (below 80 and 160 K for CoSb_3 and

$\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$, respectively) Mott's law $\ln \rho \propto T^{-1/4}$ was obeyed, which suggested a localization of charge carriers. Double filling also led to a transition from the semiconducting state (i.e., $d\rho/dT < 0$) for sample $\text{Ca}_{0.1}\text{Ce}_{0.05}\text{Co}_4\text{Sb}_{12}$ to the metallic state (i.e., $d\rho/dT > 0$) for samples $\text{Ca}_{0.1}\text{Ce}_{0.1}\text{Co}_4\text{Sb}_{12}$ and $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$. In contrast, the large absolute Seebeck coefficient values were maintained although the electrical resistivity decreased as compared to that of CoSb_3 due to an increase in carrier concentration for $x > 0.05$, presumably resulting from the large effective mass arising from the Ca and Ce filler atoms. Moreover, the low-temperature lattice thermal conductivity of $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ was observed to decrease monotonously with increasing Ce content. This is attributed to the rattling motion of the Ca and Ce atoms in the Sb cages. As a result, the figure of merit ZT of heavily filled compounds $\text{Ca}_{0.1}\text{Ce}_x\text{Co}_4\text{Sb}_{12}$ ($x=0.1$ and 0.15) showed improvement over the whole temperature range investigated. In particular, the ZT of $\text{Ca}_{0.1}\text{Ce}_{0.15}\text{Co}_4\text{Sb}_{12}$ reached 0.11 at 300 K, which was tenfold larger than that of CoSb_3 . The present results showed that Ca and Ce double filling is an efficient way in improving the thermoelectric properties of CoSb_3 .

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- ¹M. Puyet, A. Dauscher, B. Lenoir, C. Bellouard, C. Stiewe, E. Muller, J. Hejtmánek, and J. Tobola, *Phys. Rev. B* **75**, 245110 (2007).
- ²T. Caillat, A. Borshchevsky, and J. P. Fleurial, *J. Appl. Phys.* **80**, 4442 (1996).
- ³L. D. Dudkin and N. Kh. Abrikosov, *Fiz. Tverd. Tela (Leningrad)* **1**, 142 (1999) [*Sov. Phys. Solid State* **1**, 126 (1959)].
- ⁴D. Mandrus, A. Migliori, T. W. Darling, M. F. Hundley, E. J. Peterson, and J. D. Thompson, *Phys. Rev. B* **52**, 4926 (1995).
- ⁵J. W. Sharp, E. C. Jones, R. K. Williams, P. M. Martin, and B. C. Sales, *J. Appl. Phys.* **78**, 1013 (1995).
- ⁶D. T. Morelli, T. Caillat, J.-P. Fleurial, A. Borshchevsky, J. Vandersande, B. Chen, and C. Uher, *Phys. Rev. B* **51**, 9622 (1995).
- ⁷D. J. Braun and W. Jeitschko, *J. Less-Common Met.* **72**, 147 (1980).
- ⁸N. T. Stetson, S. M. Kauzlarich, and H. Hope, *J. Solid State Chem.* **91**, 140 (1991).
- ⁹N. R. Dilley, E. J. Freeman, E. D. Bauer, and M. B. Maple, *Phys. Rev. B* **58**, 6287 (1998).
- ¹⁰M. E. Danebrock, C. B. H. Evers, and W. Jeitschko, *J. Phys. Chem. Solids* **57**, 381 (1996).
- ¹¹L. D. Chen, Proceedings of the 21st International Conference on Thermoelectrics, Long Beach, CA, 2002 (unpublished), p. 42.
- ¹²L. D. Chen, X. F. Tang, T. Kawahara, J. S. Dyck, and W. Chen, Proceedings of the 20th International Conference on Thermoelectrics, Beijing, China, 2001 (unpublished), p. 57.
- ¹³Q. M. Lu, J. X. Zhang, X. Zhang, Y. Q. Liu, and M. L. Zhou, *J. Appl. Phys.* **98**, 106107 (2005).
- ¹⁴JCPD Card No. 65-3144.
- ¹⁵M. Puyet, B. Lenoir, A. Dauscher, and P. Pécœur, *Phys. Rev. B* **73**, 035126 (2006).
- ¹⁶D. Berardan, C. Godart, E. Alleno, St. Berger, and E. Bauer, *J. Alloys Compd.* **351**, 18 (2003).
- ¹⁷D. Li, X. Y. Qin, Y. J. Gu, and J. Zhang, *J. Appl. Phys.* **99**, 053709 (2006).
- ¹⁸H. X. Xin and X. Y. Qin, *J. Phys. D: Appl. Phys.* **39**, 5331 (2006).
- ¹⁹Z. He, C. Stiewe, D. Platzek, G. Karpinski, and E. Müller, *J. Appl. Phys.* **101**, 053713 (2007).
- ²⁰D. Li, X. Y. Qin, J. Zhang, L. Wang, and H. J. Li, *Solid State Commun.* **135**, 237 (2005).
- ²¹D. Li, X. Y. Qin, Y. J. Gu, and J. Zhang, *J. Appl. Phys.* **99**, 053709 (2006).