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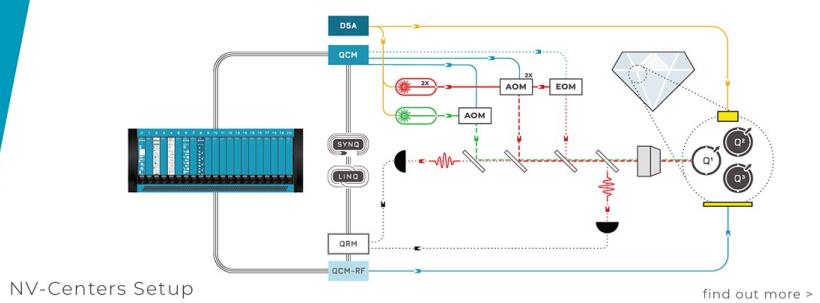
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# Influence of Ni impurities on the thermoelectric properties of Ca-partially filled skutterudites $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$

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Polycrystalline samples of the skutterudite compounds  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  were synthesized and investigated by means of electrical resistivity, thermal conductivity, and thermopower in the 300–800 K temperature range. Additional Hall effect measurements were performed between 2 and 300 K. Both Ni-free and Ni-containing Co powders were used as starting materials to elucidate the impact of Ni impurities at the ppm level on the thermoelectric properties. The presence of minute amounts of Ni atoms in the crystal structure leads to enhanced thermopower values with respect to the Ni-free samples, likely associated with the development of additional electron pockets near the Fermi level. Ni impurities, thus, play a significant role on the transport properties and lead to a spectacular increase in the dimensionless thermoelectric figure of merit  $ZT$  of up to 150% at 800 K. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4768439]

Chemical substitution and doping in the binary skutterudite  $\text{CoSb}_3$  compound, which crystallizes in the cubic  $\text{CoAs}_3$  structure-type, have unveiled a large class of thermoelectric materials.<sup>1,2</sup> The thermoelectric efficiency in these materials has attracted an ever-growing attention due to the good semiconducting properties of the binary compound and the large number of elements able to modulate its transport properties.<sup>1</sup> This enables a fine-tuning of both the electrical resistivity and thermopower, which represents a first essential requirement to optimize the thermoelectric efficiency typified by the so-called dimensionless thermoelectric figure of merit  $ZT$ . This parameter is defined at a temperature  $T$  as  $ZT = \alpha^2 T / \rho \kappa$ , where  $\alpha$  is the thermopower,  $\rho$  the electrical resistivity, and  $\kappa$  the total thermal conductivity.<sup>3</sup> The second qualification to fulfill is to achieve low thermal conductivity values. The  $\text{CoSb}_3$  skutterudite does not meet this requirement and several strategies were used to decrease its ability to transport heat. One of them benefits from the crystal structure of this compound that includes two voids per  $\text{Co}_4\text{Sb}_{12}$  formula.<sup>1</sup> Numerous studies have shown that a plethora of elements can partially fill these two voids resulting in a drastic decrease in the thermal conductivity.<sup>4–12</sup> These elements can as well effectively electron dope the parent compound yielding  $ZT$  values exceeding unity at high temperatures. This fruitful strategy was recently extended by designing novel compositions with double- or even multiple-filled compounds.<sup>13–18</sup> The basic idea of this approach is to influence different regions of the phonon spectrum using elements exhibiting distinct vibrational frequencies. This enables to scatter more efficiently the heat-carrying phonons thereby further reducing the lattice thermal conductivity. The maximum  $ZT$  achieved so far was obtained in the

multiple-filled skutterudite  $\text{Ba}_x\text{La}_y\text{Yb}_z\text{Co}_4\text{Sb}_{12}$  reaching 1.7 at 850 K.<sup>19</sup>

Filling the voids of the crystal structure is, however, not the only way to tune the electrical properties of skutterudites. Electron doping can be achieved via substituting Ni, Pd, or Pt for Co or Te for Sb.<sup>1</sup> Among these different possibilities, Ni proved to be a judicious choice. Replacing a minute fraction of Co by Ni effectively results in lower electrical resistivity values due to an increased electron concentration but, more surprisingly, does not lead to a concomitant decrease of the thermopower as usually observed. As a result, the power factor is markedly increased and hence the  $ZT$  values. The positive influence of Ni was noticed in both the  $\text{Ca}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  and  $\text{Ba}_{0.3}\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  systems for which, substituting only 0.75% and 1.25% Ni for Co was sufficient to push the  $ZT$  by 100% and 35% at 800 K, respectively.<sup>20,21</sup> This trend rapidly reverses when the Ni concentration is further increased. Yet, whether a lower limit of the Ni fraction exists below which, no enhancement of the power factor could be observed, remains an open question.

To address this issue, we report a transport property study on partially filled skutterudites  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  synthesized from both Ni-free and Ni-containing cobalt. Our results show a spectacular enhancement of the thermoelectric properties when Ni impurities are present. A minute amount of Ni indeed appears able to increase the  $ZT$  values by up to 150% at 800 K. Our results further confirm the beneficial effect of Ni in  $\text{CoSb}_3$ -based skutterudites, but also suggest that using Ni-containing Co as a starting material may obscure the intrinsic influence of the filler element on the transport properties of partially filled  $\text{CoSb}_3$  compounds.

Two series of  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  polycrystalline samples with nominal compositions  $x = 0.0, 0.05, 0.10$ , and  $0.20$  were prepared using Ca pellets (99.5%), Sb shots (99.999%) together with either Ni-free Co powders (99.998%) or Ni-containing

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Co powders (99.95% containing  $\approx$ 400 ppm of Ni as the main effective impurity) following a metallurgical route described in detail elsewhere.<sup>20</sup> Though difficult to reproduce exactly, we tried to keep constant the Ca content to allow for a direct comparison between the two series of samples. Hereafter, we shall use the labels Co\* and Co to refer to the Ni-containing and Ni-free samples, respectively.

The temperature dependence of the electrical resistivity, thermal conductivity, and thermopower was measured between 300 and 800 K as described in a previous paper.<sup>20</sup> The Hall effect measurements were performed by a five-probe method with an ac transport option of a physical property measurement system (PPMS, Quantum Design) in the 2–300 K temperature range by sweeping the magnetic field from −7 to +7 T. The Hall resistivity  $\rho_H$  was derived from the antisymmetric part of the transverse electrical resistivity  $\rho_{xy}$  under magnetic field reversal following the formula  $\rho_H = [\rho_{xy}(+\mu_0 H) - \rho_{xy}(-\mu_0 H)]/2$ .

The trends in the crystal structures of both series of compounds were determined by x-ray powder diffraction (XRPD) and the chemical homogeneity was checked by electron microprobe analyses (EPMA). The actual compositions measured by EPMA are summarized in Table I. As found for various filler elements,<sup>1</sup> the lattice parameter  $a$  of the cubic lattice, extracted from refinements against XRPD data, increases linearly with  $x$  following a Vegard's law (Figure 1). Though this behaviour remains unchanged upon introducing Ni impurities, the values of  $a$  are significantly higher. This clear change in the dimensions of the unit cell is in agreement with previous investigations on  $\text{Co}_{1-x}\text{Ni}_x\text{Sb}_3$  samples and indicate that a small fraction of Ni atoms substitute for Co.<sup>22,23</sup>

The comparison between the temperature dependences of the thermopower for both series is shown in Figure 2. The drastic influence of Ni impurities is clearly observed in  $\text{CoSb}_3$  where the electrical conduction switches from *p*-type to *n*-type. The maximum observed in both cases near 300 K reflects the activation of minority carriers resulting in a change of majority carriers above 550 K. A clear trend towards enhanced  $\alpha$  values in the Co\* series can be observed regardless of the Ca concentration. Previous detailed study of the electronic band structure of the  $\text{Ca}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  compounds has shown that an additional electron pocket near the Fermi level tends to open.<sup>20</sup> The main key features of the electronic band structure are preserved upon Ni doping thereby explaining the high thermopower values despite higher carrier concentrations. Liu *et al.*<sup>24</sup> further confirmed the beneficial influence of an additional electron pocket on

TABLE I. Nominal and measured compositions (EPMA) of the two series  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  and  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$ .

| Nominal composition                           | EPMA   |
|---|--|
| $\text{Co}_4\text{Sb}_{12}$                   | $\text{Co}_4\text{Sb}_{12.24}$                 |
| $\text{Ca}_{0.10}\text{Co}_4\text{Sb}_{12}$   | $\text{Ca}_{0.05}\text{Co}_4\text{Sb}_{12.43}$ |
| $\text{Ca}_{0.20}\text{Co}_4\text{Sb}_{12}$   | $\text{Ca}_{0.08}\text{Co}_4\text{Sb}_{12.45}$ |
| $\text{Co}_4^*\text{Sb}_{12}$                 | ...  |
| $\text{Ca}_{0.05}\text{Co}_4^*\text{Sb}_{12}$ | $\text{Ca}_{0.015}\text{Co}_4^*\text{Sb}_{12}$ |
| $\text{Ca}_{0.10}\text{Co}_4^*\text{Sb}_{12}$ | $\text{Ca}_{0.05}\text{Co}_4^*\text{Sb}_{12}$  |
| $\text{Ca}_{0.20}\text{Co}_4^*\text{Sb}_{12}$ | $\text{Ca}_{0.10}\text{Co}_4^*\text{Sb}_{12}$  |

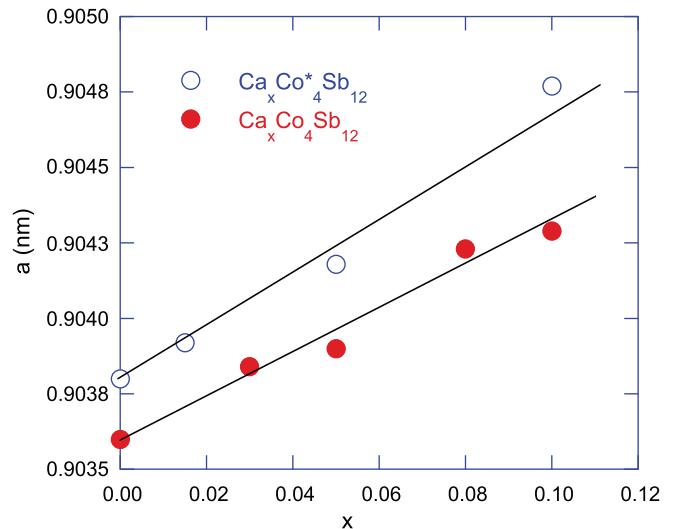


FIG. 1. Variation of the lattice parameter  $a$  as a function of the Ca content  $x$  in the  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  and  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  series. The solid lines are guides for the eyes.

the thermoelectric properties based on a multiband model. Their model raised two important key parameters to observe an enhancement of the power factor: the difference between the edge energy of the major electron pocket and the additional one should be less than  $5k_B T$  (where  $k_B$  is the Boltzmann constant) and acoustic phonon scattering should be the dominant source of diffusion of the charge carriers. The former condition may explain why the thermoelectric properties are only optimized at low Ni levels (typically  $\leq 2\%$ ), the positive impact of Ni being reversed at higher doping concentrations. Our data further corroborate this conclusion and suggest that the positive impact of Ni is retained down to the impurity-dilute limit.

The main effect of the electron-like pocket is to open another channel of electrical conduction giving rise to lower electrical resistivity values.<sup>20</sup> This picture is indeed confirmed by the temperature dependence of the electrical resistivity shown in Figure 3. Prior investigations have shown

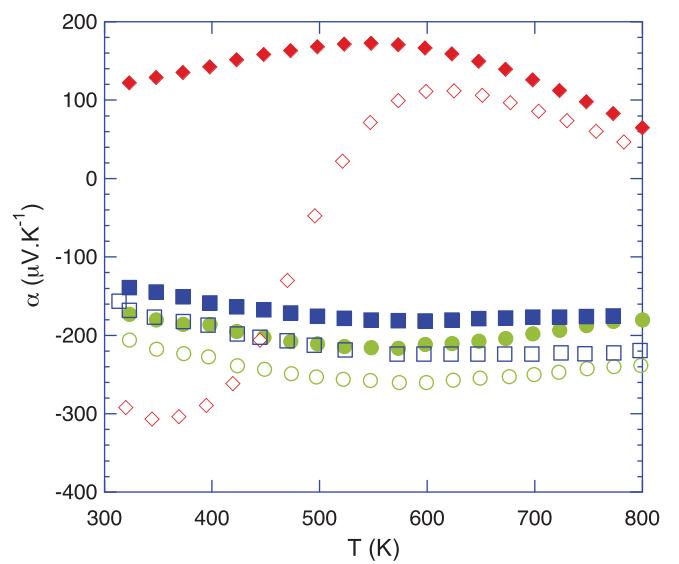


FIG. 2. Temperature dependence of the thermopower  $\alpha$  in  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  for  $x = 0$  ( $\blacklozenge$ );  $x = 0.05$  ( $\bullet$ ); and  $x = 0.10$  ( $\blacksquare$ ), and in  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  for  $x = 0$  ( $\diamond$ );  $x = 0.05$  ( $\circ$ ); and  $x = 0.10$  ( $\square$ ).

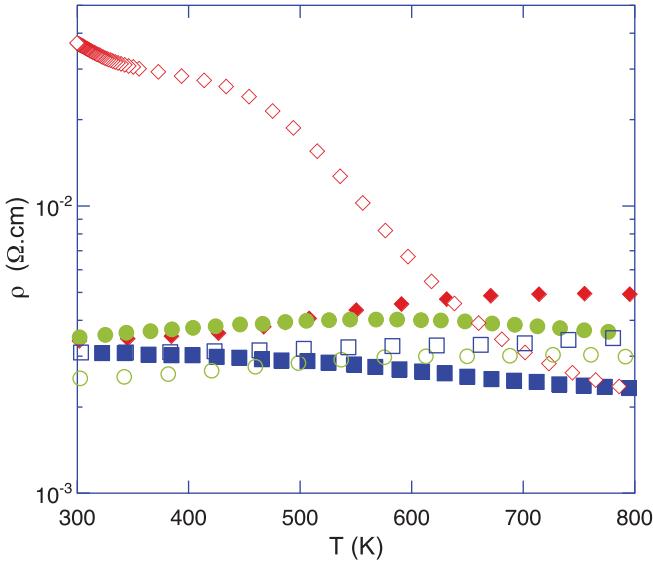


FIG. 3. Temperature dependence of the electrical resistivity  $\rho$  in  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  for  $x=0$  ( $\blacklozenge$ );  $x=0.05$  ( $\bullet$ ); and  $x=0.08$  ( $\blacksquare$ ), and in  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  for  $x=0$  ( $\diamond$ );  $x=0.05$  ( $\circ$ ); and  $x=0.10$  ( $\square$ ).

that Ca acts as an electron donor resulting in an increase in the electron concentrations. Here, the  $\rho$  values are decreased by two orders of magnitude below 475 K on going from  $x=0$  to 0.015. Ni has a similar influence on the carrier concentrations leading to lower  $\rho$  values in the  $\text{Co}^*$  series.

To determine whether the second requirement unveiled by the model of Liu *et al.*,<sup>24</sup> i.e., acoustic phonon scattering, is fulfilled in the present case, we performed Hall effect measurements (Figures 4(a) and 4(b)). The Hall coefficient  $R_H$  defined as the slope of the Hall resistivity  $\rho_H$  versus magnetic field  $\mu_0 H$  was found to be negative regardless of the Ca content in both series of samples (Figure 4(a)). The main difference is observed in the binary  $\text{CoSb}_3$  and  $\text{Co}^*\text{Sb}_3$  samples, which show positive (not shown) and negative  $R_H$  values, respectively, as a result of the presence of Ni in the latter. As presented in Figure 4(b), the Hall mobility  $\mu_H = R_H/\rho$  of the charge carriers drastically changed when Ca and/or Ni are present. The typical ionized-impurity-scattering mechanism responsible for the increase in  $\mu_H$  as a function of  $T$  in  $\text{CoSb}_3$  turns into two distinct mechanisms prevailing in different temperature ranges. Below 50 K,  $\mu_H$  remains practically temperature-independent indicating that neutral impurities dominate the diffusion of the electrons. Above this temperature,  $\mu_H$  starts to decrease following a  $T^{-3/2}$  law revealing that acoustic phonon scattering is at play at higher temperatures. The fact that these mechanisms are observed in both series of samples suggests that very small fractions of Ni have a minimal influence on the mobility. This conclusion is, however, no longer valid when the Ni content is substantially increased as demonstrated in the  $\text{Ca}_x\text{Co}_{4-y}\text{Ni}_y\text{Sb}_{12}$  compounds. For  $y \geq 0.02$ , the  $\mu_H(T)$  data show a significant departure from a  $T^{-3/2}$  law, likely related to light electrons originating from the additional electron pocket.<sup>20</sup>

Because of the very low concentration of Ni in the  $\text{Co}^*$  samples, the thermal transport is very similar in both series as shown in Figure 5. The decrease seen in the  $\kappa(T)$  data is mainly due to the presence of Ca in the voids of the crystal structure as widely demonstrated with other filling elements.<sup>1,2</sup>

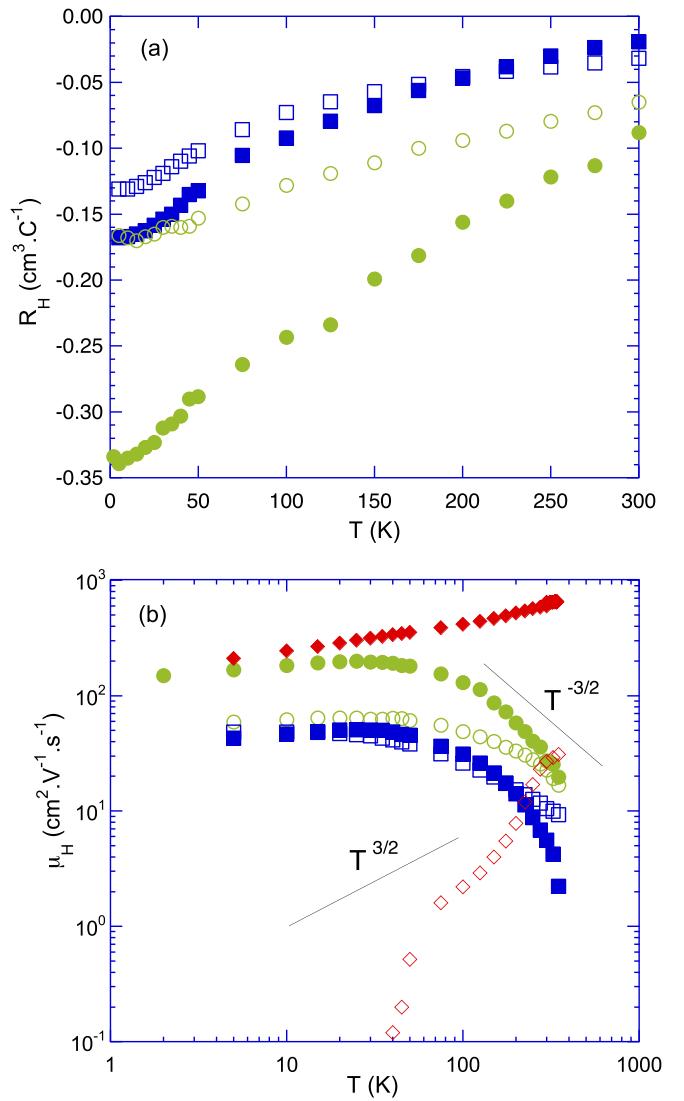


FIG. 4. Temperature dependence of the Hall coefficient  $R_H$  (a) and Hall mobility  $\mu_H$  on a log-log scale (b) in  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  for  $x=0.05$  ( $\bullet$ );  $x=0.08$  ( $\blacksquare$ ), and  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  for  $x=0.05$  ( $\circ$ );  $x=0.10$  ( $\square$ ). The theoretical dependences expected from scattering due to ionized impurities ( $T^{3/2}$ ) and acoustic phonons ( $T^{-3/2}$ ) are represented by solid lines.

Figure 6 presents the temperature dependence of  $ZT$  for the two series of samples. The presence of such a small amount of Ni results in a spectacular enhancement in the  $ZT$  values with respect to the Ni-free compounds. In the  $x=0.05$  and 0.10 samples, the maximum  $ZT$  value shows a remarkable rise of 150% and 70% at 800 K, respectively, to reach 0.5 in both samples. Noteworthy, this  $ZT$  is higher than the best value achieved in the Ni-free  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  compounds at the highest Ca content experimentally accessible, i.e.,  $x=0.20$ .

These results demonstrate that very small concentrations of Ni may have a sizeable impact on the transport properties. On one hand, if this effect can be extended to other filler elements, Ni-free Co could be replaced by lower-cost Co without being at the expense of the thermoelectric efficiency. On the other hand, such a pronounced influence shows that care should be taken regarding more fundamental studies aiming at determining the intrinsic influence of a given and/or a collection of filler elements on the transport properties of  $\text{CoSb}_3$ .

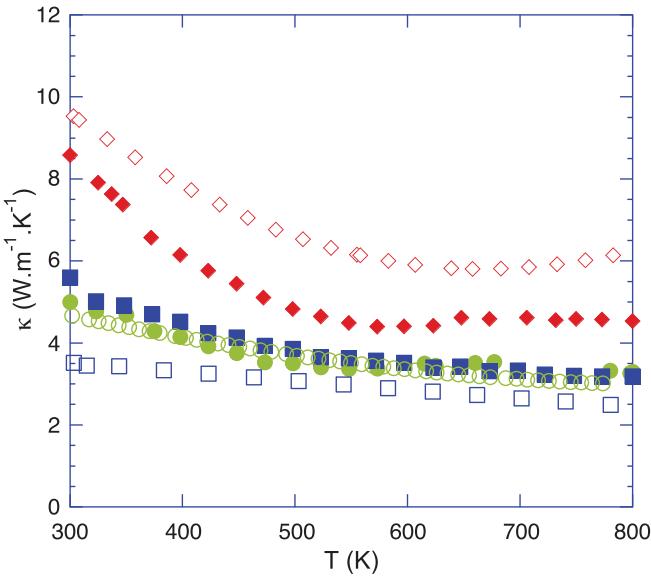


FIG. 5. Temperature dependence of the thermal conductivity  $\kappa$  in  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$ ;  $x=0$  ( $\blacklozenge$ );  $x=0.05$  ( $\bullet$ ); and  $x=0.08$  ( $\blacksquare$ ), and in  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  for  $x=0$  ( $\lozenge$ );  $x=0.05$  ( $\circ$ ); and  $x=0.10$  ( $\square$ ).

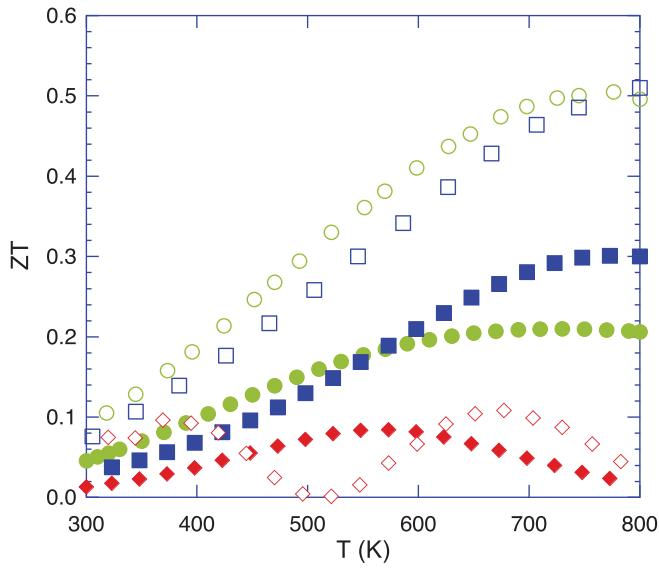


FIG. 6. Temperature dependence of the dimensionless figure of merit ZT in  $\text{Ca}_x\text{Co}_4\text{Sb}_{12}$  for  $x=0$  ( $\blacklozenge$ );  $x=0.05$  ( $\bullet$ ); and  $x=0.08$  ( $\blacksquare$ ), and in  $\text{Ca}_x\text{Co}_4^*\text{Sb}_{12}$  for  $x=0$  ( $\lozenge$ );  $x=0.05$  ( $\circ$ ); and  $x=0.10$  ( $\square$ ).

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