



Improvement on the High temperature Thermoelectric Performance of Ga-doped Misfit-layered $\text{Ca}_3\text{Co}_4\text{-xGa}_x\text{O}_9$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$)

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Improvement on the high temperature thermoelectric performance of Ga-doped misfit-layered $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ ($x = 0, 0.05, 0.1, \text{ and } 0.2$)

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ABSTRACT

Highly densified $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ ($0 \leq x \leq 0.2$) misfit-layered thermoelectric oxides are prepared by solid state reaction methods followed by hot-pressing. Thermoelectric properties of the samples are measured from room temperature to 1200 K. The results show that partial Ga substitution leads to a simultaneous increase of the electrical conductivity and thermopower. The Ga-doped samples have lower thermal conductivity than that of the non-doped sample in the high temperature region (>600 K). The $x = 0.05$ sample shows a higher figure of merit ($Z = 3.37 \times 10^{-4} \text{ K}^{-1}$) than that of the non-doped sample ($Z = 1.98 \times 10^{-4} \text{ K}^{-1}$) at 1073 K, indicating significant improvement of the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ by partial Ga substitution for Co.

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1. Introduction

Thermoelectric materials can be used to generate electricity via Seebeck effect and thus can be considered as one of the energy materials. Good thermoelectric materials require a large thermopower (S) for generating a large thermal voltage, a low electrical resistivity (ρ) for minimizing the Joule heating, and a low thermal conductivity (κ) for retaining the heat at the junctions in order to obtain a high figure of merit $Z = S^2/\rho\kappa$. Misfit-layered $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxide has recently attracted considerable attention since its single crystal shows a large figure of merit (ZT reaches ~ 0.87 at 973 K) and it has high thermal stability and lacks of toxicity [1]. Therefore, it can be considered as a potential candidate for power generation at high temperatures. However, single crystal is too small to be used in fabrication of the TE devices. More feasible method is to use the polycrystalline materials and enhance their TE properties by optimizing their compositions and preparing process.

Many studies have been carried out to improve the TE properties of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ [2–14]. Some of these studies adopt the spark plasma sintering (SPS) and hot-pressing (HP) methods to improve the microstructure [6–8]. Chemical substitution is also found to be an effective way to enhance the ZT value. Previous studies showed that the substitutions of Na, Bi, Ag, and Eu for the Ca site and Fe for the Co site are effective in improving the thermoelectric properties [9–14]. Besides the improvement on the microstructure and

preparation using spark plasma sintering (SPS) and hot-pressing (HP) methods, chemical substitution is also an effective method to enhance the ZT value. Previous researches showed that the substitutions of Na, Bi, Ag, and Eu for the Ca site and Fe for the Co site are effective in improving thermoelectric properties [9–14]. The X-ray absorption spectroscopy shows that there is a mixed valence of $\text{Co}^{3+}/\text{Co}^{4+}$ in $\text{Ca}_3\text{Co}_{4-x}\text{Fe}_x\text{O}_{9+\delta}$ [15]. Moreover, partial substitution of heavier ions with trivalence or tetravalence in the Co site might reduce the thermal conductivity since a heavier mass of the material is expected to reduce the lattice thermal conductivity. Therefore, the Ga ion with trivalence seems to be one of the candidates for serving the purpose of enhancing the figure of merit. In this paper, hot-pressed Ga-substituted $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ oxides were prepared to investigate their TE properties from room temperature to 1200 K. We find that the $x = 0.05$ sample has a higher figure of merit value ($Z = 3.37 \times 10^{-4} \text{ K}^{-1}$) than that of non-doped sample ($Z = 1.98 \times 10^{-4} \text{ K}^{-1}$) at 1073 K, which shows a significant improvement of the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ by the partial Ga substitution for Co.

2. Experimental

Polycrystalline samples of $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x = 0, 0.05, 0.1, \text{ and } 0.2$ were synthesized by the solid state reaction from CaCO_3 , Co_3O_4 and Ga_2O_3 powders. They were thoroughly mixed first by rocking mill for 2 h and then by ball milling with ethanol for 24 h. The mixtures were dried and calcined in air at 1173 K for 24 h. The calcined samples were ground into powders, pressed into pellets and sintered at 1223 K in the flow of O_2 gas for 24 h. The pellets of the samples were re-ground then hot-pressed at 1123 K in air for 2 h under a pressure of 60 MPa. The hot-pressed samples were then annealed at 1223 K in O_2 gas for 12 h. X-ray powder diffraction (XRD) analysis was carried out on a diffractometer equipped with $\text{Cu K}\alpha$ radiation.

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The relative densities of all the samples were measured using Archimedes' method. The microstructure of the hot-pressed samples was observed by scanning electron microscopy (SEM). Thermogravimetric and differential thermal analyses (TGA and DTA) were carried out from room temperature to 1300 K for the powder samples. The electrical resistivity and thermoelectric power were measured simultaneously from room temperature to 1200 K in air on an Ozawa RZ2001i thermoelectric property measurement system. The standard four-probe and steady techniques were adopted for the resistivity and thermoelectric power measurements, respectively. The thermal conductivity was determined from the thermal diffusivity and the specific heat capacity measured from room temperature to 1073 K on a LFA-502 laser flash measurement system.

3. Results and discussion

The XRD patterns for the first sintered powders of $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples are shown in Fig. 1. It can be seen from Fig. 1 that all the XRD peaks of each sample can be indexed as $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ phase. As shown in Fig. 2, the TGA and DTA data measured in air from room temperature to 1300 K reveal that there is no significant change up to 1200 K. This result indicates that $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ is thermally stable in air, which is an important property when used for thermoelectric applications within this temperature range. The samples are found to decompose at around 1230 K, which corresponds to a sharp endothermic peak. All the hot-pressed samples have a high bulk density with a relative value larger than 95% of the theoretical

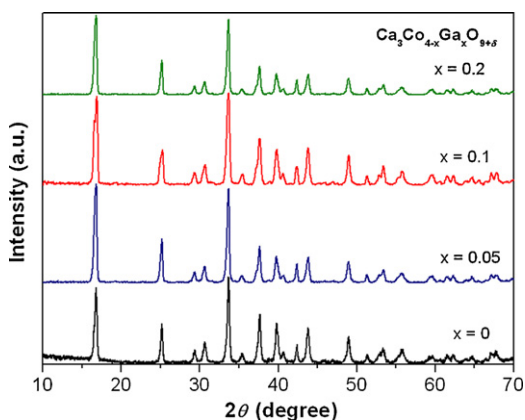


Fig. 1. The X-ray diffraction patterns of $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples.

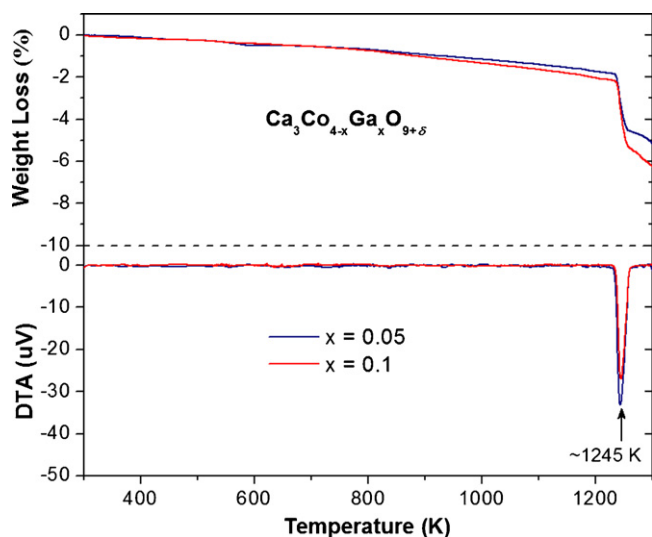


Fig. 2. The thermogravimetric and differential thermal analysis data for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0.05$ and 0.1 samples.



Fig. 3. SEM photograph of the fractured surfaces of the $x=0.05$ sample.

X-ray density [2]. Because the difference of the bulk density between each sample is less than 1%, the observed difference in the thermoelectric properties for all the samples in this study would not be associated with the bulk density.

Fig. 3 illustrates the SEM images of fractured surfaces for a typical $x=0.05$ sample. The plate-like grains can be clearly observed due to the layered crystal structure of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$. The SEM photograph also shows the local textured microstructure of the samples.

Fig. 4 shows the electrical resistivity (ρ) as a function of temperature for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples. For all the samples, the ρ - T curve shows a metal-like behavior below 450 K ($d\rho/dT < 0$) while nonmetallic behavior above 450 K ($d\rho/dT > 0$). The metal–nonmetal transition observed in the high temperature regime in the in-plane resistivity of a single crystal of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ has been ascribed to a pseudogap caused by the disappearance of quasiparticle resonance suggested by Limelette et al. [16].

The Ga substitution for Co results in a decrease of electrical resistivity over the measured temperature range. Among the Ga-doped samples, the resistivity tends to increase with increasing Ga concentration for $x > 0.05$. Hall measurements reveal that with partial substitution of Ga for Co, the hole carrier concentration (n) increases from $1.907 \times 10^{20} \text{ cm}^{-3}$ ($x=0$) to $2.339 \times 10^{20} \text{ cm}^{-3}$ ($x=0.05$). However, n slightly decreases with increasing Ga doping level for $x > 0.05$.

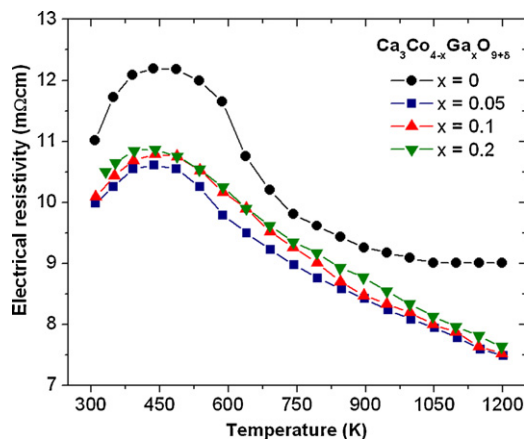


Fig. 4. Temperature dependence of the electrical resistivity for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples.

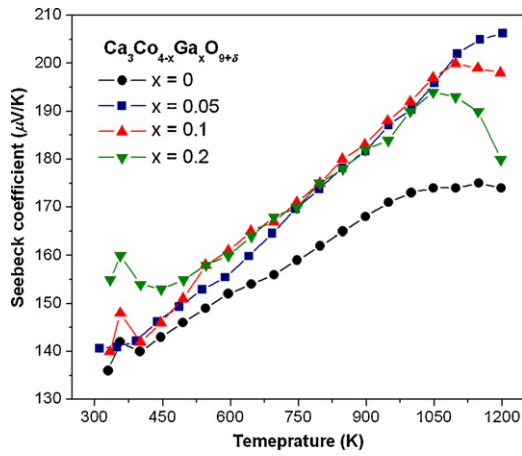


Fig. 5. Temperature dependence of the thermoelectric power for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{Co}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples.

The temperature dependence of the Seebeck coefficient (S) of the samples is shown in Fig. 5. The thermopower of all the samples shows a positive value over the measured temperature range, indicating the p -type conduction; the magnitude of thermopower increases with increasing temperature. It can be clearly seen from Fig. 5 that partial substitution of Ga results in an increase in the magnitude of the thermopower and the effect is more significant in the high temperature region (>600 K). However, the magnitude of thermopower tends to decrease with increasing Ga concentration at high temperatures (>800 K).

For a single and non-degenerate band, the diffusion thermopower can be expressed as [17]

$$S = \frac{k_B}{e\sigma} \int \sigma(E) \frac{(E - E_F)}{k_B T} \frac{\partial f}{\partial E} dE, \quad (1)$$

where f , σ , E_F and k_B are the Fermi distribution function, electrical conductivity, Fermi energy, and Boltzmann constant, respectively. For a system with one type of carrier, the electrical conductivity σ in Eq. (1) is proportional to the product of carrier concentration and mobility and can be expressed as

$$\sigma = ne\mu \quad (2)$$

where n and μ are the carrier concentration and mobility, respectively. In general, increasing the carrier concentration of materials would decrease the electrical resistivity and also decrease the thermopower for materials with one type of carrier. For example, the absolute magnitude of thermopower of many oxides decreases with increasing carrier concentration, which can be tuned by controlling the oxygen content, provided that mobility would not change significantly [18–20]; the magnitude of thermopower for p -type $(\text{Bi,Sb})_2\text{Te}_3$ thermoelectric materials in the extrinsic conduction region can be expressed as [21].

$$S = \frac{k_B}{e} (\delta + C - \ln n) \quad (3)$$

where n is the hole concentration; δ is associated with the scattering parameter; and C is a constant. The magnitude of thermopower apparently would decrease with increasing carrier concentration provided that the scattering parameter remains unchanged. In addition, the activated type conduction in resistivity is not reconciled with the metal-like temperature dependence of thermopower. Therefore, the facts of simultaneous decrease of the resistivity and increase of the thermopower suggest that the cobaltites $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ most likely have more than one type of independent carrier. A possible scenario is as follows. For materials

with more than one type of independent charge carriers, thermopower can be expressed by

$$S = \sum_i \frac{\sigma_i}{\sigma} S_i \quad (4)$$

where σ_i and S_i are the partial electrical conductivity and partial thermopower, respectively. Since $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ consists of CoO_2 and Ca_2CoO_3 sublattices, the first-principles calculation also suggest that both the CoO_2 and Ca_2CoO_3 sublattices contribute to the transport [22]. The former is of activated type, while the latter is of metal-like type. Provided that there are no interactions between the two sublattices, the thermopower for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ can be rewritten as

$$S = \frac{\sigma_{\text{Ca}_2\text{CoO}_3}}{\sigma_{\text{Ca}_2\text{CoO}_3} + \sigma_{\text{CoO}_2}} S_{\text{Ca}_2\text{CoO}_3} + \frac{\sigma_{\text{CoO}_2}}{\sigma_{\text{Ca}_2\text{CoO}_3} + \sigma_{\text{CoO}_2}} S_{\text{CoO}_2} \quad (5)$$

Suppose Ga substitutes for the Co site in the CoO_2 sublattice, the carrier concentration is expected to increase due to a decrease of the activation energy. It is evidenced by the Hall measurements that carrier concentration increases from $1.97 \times 10^{20} \text{ cm}^{-3}$ for the undoped sample to $2.34 \times 10^{20} \text{ cm}^{-3}$ for the $x=0.05$ sample. Since the increase of electrical conductivity, which is proportional to $e^{-E_a/k_B T}$ for the activated type conduction, is faster than the decrease of thermopower, which is proportional to $E_a/k_B T$, the situation of simultaneous increase of conductivity and thermopower could happen in this scenario.

Due to the simultaneous decrease of resistivity and increase of thermopower, the power factor is significantly improved for the Ga-doped samples, as shown in Fig. 6. The power factor is $5.7 \times 10^{-4} \text{ Wm}^{-1} \text{ K}^{-2}$ at ca. 1200 K for the $x=0.05$ sample, which is about 1.7 times larger than that of the non-doped sample.

The thermal conductivity (κ) and figure of merit (Z) as a function of temperature for the $x=0$ and 0.05 samples are shown in Fig. 7. For all the samples, κ decreases with increasing temperature and the value is lower for the Ga-doped sample than that for non-doped in high temperature region (>600 K). The κ values at 1078 K are 1.69 and $1.5 \text{ Wm}^{-1} \text{ K}^{-1}$ for the $x=0$ and 0.05 samples, respectively. The Z values at 1073 K are 1.98×10^{-4} and $3.37 \times 10^{-4} \text{ K}^{-1}$ for the $x=0$ and 0.05 samples, respectively. If the thermal conductivity of the $x=0.05$ sample still keeps the decreasing trend with increasing temperature, the thermal conductivity at 1200 K would not exceed $1.5 \text{ Wm}^{-1} \text{ K}^{-1}$. In that case, the figure of merit Z is $3.8 \times 10^{-4} \text{ K}^{-1}$ and the dimensionless figure of merit value, ZT should exceed 0.45 at 1200 K.

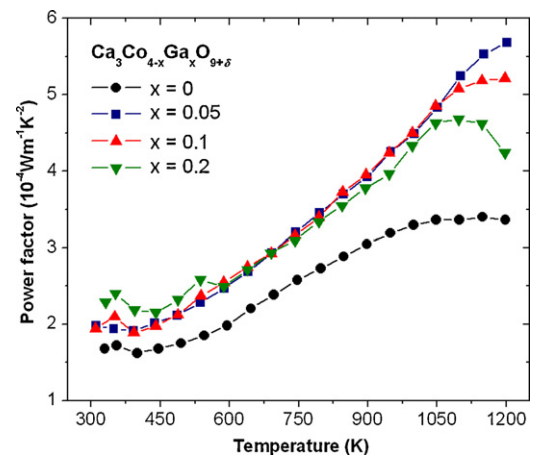


Fig. 6. The power factor versus temperature for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{Co}_{9+\delta}$ with $x=0, 0.05, 0.1,$ and 0.2 samples.

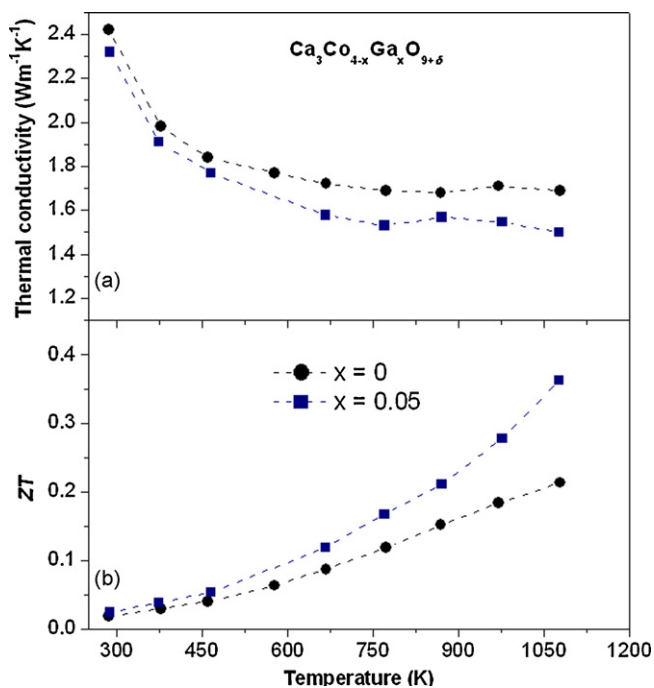


Fig. 7. Temperature dependence of the thermal conductivity and figure of merit for $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ with $x=0$, and 0.05 samples.

4. Conclusions

In summary, we have investigated high temperature thermoelectric properties of misfit-layered $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ ($0 \leq x \leq 0.2$) oxides prepared by conventional solid state reaction methods followed by hot-pressing. According to the TGA and DTA data, the $\text{Ca}_3\text{Co}_{4-x}\text{Ga}_x\text{O}_{9+\delta}$ is found to be thermally stable up to 1200 K in air, which is essential for high temperature applications of thermoelectric devices. Our results indicate that partial substitution of Ga for the Co site effectively improves the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ by simultaneously lowering the electrical conductivity, raising the thermopower, and reducing the thermal conductivity, which all favor enhancing the figure of merit. The $x=0.05$ sample exhibits a higher figure of merit of $Z=3.37 \times 10^{-4} \text{ K}^{-1}$ than that

of the non-doped sample with $Z=1.98 \times 10^{-4} \text{ K}^{-1}$ at 1073 K. Moreover, the ZT value of the $x=0.05$ sample could possibly reach 0.45 at 1200 K if the thermal conductivity keeps the decreasing trend with increasing temperature. This suggests that it is a promising oxide material for power generation at high temperatures.

Acknowledgments

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