Thermoelectric performance enhancement by manipulation of Sr/Ti doping in two sublayers of $\text{Ca}_3\text{Co}_4\text{O}_9$

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Abstract: Thermoelectric (TE) performance of $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO) has been investigated extensively via a doping strategy in the past decades. However, the doping sites of different sublayers in CCO and their contributions to the TE performance remain unrevealed because of its strong correlated electronic system. In this work, Sr and Ti are chosen to realize doping at the $[\text{Ca}_2\text{CoO}_3]$ and $[\text{CoO}_2]$ sublayers in CCO. It was found that figure of merit (ZT) at 957 K of Ti-doped CCO was improved 30% than that of undoped CCO whereas 1 at% Sr doping brought about a 150% increase in ZT as compared to undoped CCO. The significant increase in electronic conductivity and the Seebeck coefficient are attributed to the enhanced carrier concentration and spin-entropy of Co^{4+} originating from the Sr doping effects in $[\text{Ca}_2\text{CoO}_3]$ sublayer, which are evidenced by the scanning electron microscope (SEM), Raman, Hall, and X-ray photoelectron spectroscopy (XPS) analysis. Furthermore, the reduced thermal conductivity is attributed to the improved phonon scattering from heavier Sr doped Ca site in $[\text{Ca}_2\text{CoO}_3]$ sublayer. Our findings demonstrate that doping at Ca sites of $[\text{Ca}_2\text{CoO}_3]$ layer is a feasible pathway to boost TE performance of CCO material through promoting the electronic conductivity and the Seebeck coefficient, and reducing the thermal conductivity simultaneously. This work provides a deep understanding of the current limited ZT enhancement on CCO material and provides an approach to enhance the TE performance of other layered structure materials.

Keywords: layered structures; manipulation doping sites; $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO); spin-entropy; thermoelectric performance

1 Introduction

The need for sustainable and clean energy is more

urgent over the past decades. Thermoelectric (TE) materials are known to convert waste heat to electricity directly, driving extensive attention in the field of energy conversion and storage. The dimensionless figure of merit (ZT) is usually used to evaluate the TE performance of materials by $ZT = S^2\sigma T/\kappa$ [1], where S , σ , T , and κ are the Seebeck coefficient, electrical conductivity, temperature, and thermal conductivity,

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respectively. The most well-studied commercial TE materials with high ZT values, like Bi–Te [2], Pb–Te [3], and half-Heusler alloys [4], are unstable at higher temperatures due to their volatile/toxic elements and oxidation, resulting in the degradation of TE performance at high temperatures. Therefore, oxide TE materials attract great interests from researchers because of their chemical and thermal stability at high temperatures even in the oxidizing atmosphere along with non-toxic and low-cost elements [5].

Complex cobalt oxides, including Na_xCoO_2 and $\text{Ca}_3\text{Co}_4\text{O}_9$, possess similar crystal structural characteristic [6]: A hybrid lattice structure in commensurately stacked alternately by a CdI_2 -type $[\text{CoO}_2]$ layer and another layer along the c -axis, such as the $[\text{Na}]$ layer in Na_xCoO_2 and the $[\text{Ca}_2\text{CoO}_3]$ layer in $\text{Ca}_3\text{Co}_4\text{O}_9$, which have been widely studied due to their large power factor induced by the strong electronic correlations. The application of $\text{Na}_x\text{Co}_2\text{O}_4$ was limited because of the chemical instability nature of the Na element. Therefore, the $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO) was regarded as one of the most promising high-temperature TE materials. The $[\text{Ca}_2\text{CoO}_3]$ layer is commonly responsible for phonon transport and the $[\text{CoO}_2]$ layer provides carriers as the electronic transport pathway [7]. Although the high ZT of 0.87 at 973 K has been realized in single-crystal CCO [7], the complicated and expensive growth process of single-crystal limited its practical applications. Therefore, many efforts have been developed to improve the ZT values of polycrystalline CCO especially at higher temperatures over the past years.

Doping is one of the most effective strategies to enhance the TE performance by manipulation of carrier concentration. The carrier concentration could be optimized to 10^{19} – 10^{21} cm^{-3} to achieve a high ZT value through doping various elements [1,8]. Although Refs. [9–12] reported the remarkable enhancement of TE performance in CCO systems by manipulation of Sr doping, the mechanism of doping effect induced by different doping sites is still unclear because of the complexity of CCO sublayers offering several available doping sites. In addition, it is noted that three types of spin-state of Co ions exist in $[\text{CoO}_2]$ layer of CCO correlated system [13], low-spin, intermediate-spin, and high-spin, where contains both Co^{3+} and Co^{4+} ions. Klie *et al.* [13] demonstrated that the spin-entropy contribution plays an important role in achieving a large Seebeck coefficient of CCO materials, which was decided by the concentration of $\text{Co}^{3+}/\text{Co}^{4+}$

of the CCO system. Doping at $[\text{Ca}_2\text{CoO}_3]$ or $[\text{CoO}_2]$ layer will affect the concentration of $\text{Co}^{3+}/\text{Co}^{4+}$ to change the spin-entropy contribution. Furthermore, Refs. [14,15] suggested that doping at Ca site largely decreases the concentration of Co^{4+} and improves the spin-entropy enhancement, which further increases the Seebeck coefficient. However, the combined TE performance and spin-entropy contribution effects by doping at Co site in $[\text{CoO}_2]$ layer of CCO system have been rarely reported so far. Thus, it is essential to make clear the doping sites in different sublayers of CCO and their contributions to the TE performance.

In this work, we chose two typical elements Sr and Ti to realize the manipulation of doping at the desired site in $[\text{Ca}_2\text{CoO}_3]$ and $[\text{CoO}_2]$ sublayers and investigated the enhancement of TE performance through the induced Co spin-entropy via the doping effects of Sr and Ti within two sublayers. The Sr-doped CCO samples exhibit much higher ZT values than Ti-doped CCO samples. The highest ZT value of 0.38 at 957 K was obtained in a CCO sample with Sr doping level of 0.1, which increased ZT of ~150% than the pristine CCO sample with ZT of 0.15 at 957 K.

2 Experimental

In this experiment, the Ca/Co ratio of about 0.765 was used to reflect the stoichiometric ratio of $\text{Ca}_3\text{Co}_4\text{O}_9$ which is $(\text{Ca}_2\text{CoO}_3)_{0.62}(\text{CoO}_2)$. The dopant concentration range investigated is between 0% and 20%. Polycrystalline $\text{Ca}_{3-x}\text{Sr}_x\text{Co}_{3.92}\text{O}_9$ and $\text{Ca}_3\text{Co}_{3.92-x}\text{Ti}_x\text{O}_9$ ($x = 0, 0.05, 0.1, 0.2$) samples were synthesized by conventional solid-state method and sintered by spark plasma sintering (SPS, Syntex Inc., Japan). Commercially obtained CaCO_3 , Co_3O_4 , SrCO_3 , and TiO_2 were weighed and mixed as stoichiometric ratios, and then ground with ball milling in a zirconia jar with ethanol for 6 h. The obtained powders were calcined twice at 1173 K in the air for 20 h. The ball-milled samples were manually ground to fine powders and pre-pressed into pellets in a graphite die under 10 MPa before sintering by SPS technique. In SPS, the samples were heated at 80 K/min to 1073 K and dwelled for 5 min under 50 MPa uniaxial pressure. The SPS-sintered samples were polished to remove the graphite foil from the surfaces of pellets.

The phase identifications of all samples were carried out using Bruker D8 Cu $K\alpha$ X-ray diffraction (XRD). The crystal microstructures of SPS-sintered pellets

were investigated by field emission scanning electron microscopy (FE-SEM, FEI Verios 460, USA). The structural variations of samples induced by Sr and Ti doping effects were analyzed using the Raman spectra (LabRAM HR Evolution, HORIBA, France). The surface chemical state and oxidation were measured by the X-ray photoelectron spectrum (XPS, AXIS SUPRA, Kratos, UK). The obtained XPS spectra were fitted by XPSPEAK software. High-temperature resistivity and Seebeck coefficient of the samples were analyzed using the ULVAC-RIKO ZEM3 system between 360 and 960 K in a low-pressure helium atmosphere. Thermal conductivities (κ) were calculated from the equation $\kappa = \alpha \rho C_p$, where α , ρ , and C_p are thermal diffusivity, density, and specific heat, respectively. The thermal diffusivity and specific heat were carried out by a NETZSCH LFA-427 laser flash system and a NETZSCH STA (499F1 Jupiter) instrument, respectively. The densities of SPS-sintered pellets were obtained by a Micromeritics OccuPyc II 1340 Gas Pycnometer. The carrier concentration and mobility of samples were measured using the van der Pauw method by Hall effect measurement (Quantum Design PPMS-9). The error

bar of TE properties and Hall measurement is $\pm 5\%$.

3 Results and discussion

Figure 1(a) shows the calculated ZT values of Sr- and Ti-doped CCO SPS-sintered pellets as a function of temperature ranging from 360 to 960 K. Compared to the pure CCO, the ZT values are improved after Sr doping ($x \geq 0.05$) and Ti doping ($x > 0.05$). These results indicated that the TE performances of the CCO materials could be enhanced by modifying either the $[\text{Ca}_2\text{CoO}_3]$ sublayer or the $[\text{CoO}_2]$ sublayer, by incorporating the Sr or Ti donors. Moreover, the CCO samples doped by the Sr element had much higher ZT values than those doped by the Ti element in the investigated temperature range. The highest ZT value of 0.38 at 957 K measured in $\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Co}_{3.92}\text{O}_9$ sample with Sr doping level of 0.1, showing $\sim 150\%$ higher in ZT compared to undoped CCO ($ZT = 0.15$) at 957 K. However, ZT values of Ti-doped CCO samples ($x = 0.1, 0.2$) improved only $\sim 30\%$ compared to undoped CCO sample at 957 K. Figure 1(b) summarizes the reported

Fig. 1 (a) ZT values of Sr-doped CCO and Ti-doped CCO SPS-sintered pellets from 360 to 973 K. (b) ZT value comparison of various doped-CCO from Refs. [12, 14–17]. The XRD patterns of (c) $\text{Ca}_{3-x}\text{Sr}_x\text{Co}_{3.92}\text{O}_9$ and (d) $\text{Ca}_3\text{Co}_{3.92-x}\text{Ti}_x\text{O}_9$ samples with different x values ($x = 0, 0.05, 0.1, 0.2$).

ZT values of various doping CCO materials [12,14–17]. The ZT value of 0.38 at 957 K obtained in the $\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Co}_{3.92}\text{O}_9$ sample of this work is significantly higher than most of the reported doped CCO materials at the same temperature. By contrast, the Ti-doped CCO sample yields a limited ZT enhancement of ~ 0.2 . According to the literature in Fig. 1(b), the substitution elements of Bi, Cd, La, and Sr were reported to dope into Ca site of the rock-salt $[\text{Ca}_2\text{CoO}_3]$ layer in CCO crystal structure while the Ga element prefers to occupy the Co site of the rock-salt $[\text{Ca}_2\text{CoO}_3]$ layer [12,14–17]. The CCO system is known to consist of the rock-salt $[\text{Ca}_2\text{CoO}_3]$ sandwiched by two $[\text{CoO}_2]$ layers, potentially offering different pathways to dope at Ca or Co sites to tune the electronic and phononic properties. Therefore, the different Sr and Ti doping effects on the CCO system will be investigated.

To understand the remarkably TE performance improvement in Sr-doped CCO compared to Ti-doped CCO, as well as the different TE enhancement mechanism between Sr- and Ti-doped CCO TE materials, we first investigate the structure characteristic of both Sr- and Ti-doped CCO samples. Figures 1(c) and 1(d) show the XRD patterns of $\text{Ca}_{3-x}\text{Sr}_x\text{Co}_{3.92}\text{O}_9$ and $\text{Ca}_3\text{Co}_{3.92-x}\text{Ti}_x\text{O}_9$ samples with different x values ($x = 0, 0.05, 0.1, 0.2$). In Fig. 1(c), all diffraction peaks can be indexed to the CCO phase with the standard JCPD card (No. 00-058-0661). It appears to be no Sr- or Ca-related secondary phases (i.e., SrO, CaO) in the XRD patterns obtained, suggesting full substitution of Sr into CCO host lattice structure. Refs. [18–21] reported similar substitution effects of CCO crystal structure. When Ti added into CCO samples, the majority of the peaks are still associated with the CCO standard JCPD card (No. 00-058-0661) in Fig. 1(d). However, several minor peaks appeared, corresponding to the Co_3O_4 standard JCPD card (No. 97-006-3164). With increasing the Ti doping level from 0.05 to 0.2, the Co_3O_4 peak intensities increased sharply, indicating more Co atoms free from CCO host lattice. The appearance of Co_3O_4 impurity in Ti-doped CCO samples implies the Ti substitution of Co site of layered CCO crystal structure, either in rock-salt $[\text{Ca}_2\text{CoO}_3]$ or $[\text{CoO}_2]$ layer. All the relative densities of all Sr- or Ti-doped CCO samples are almost higher than $\sim 95\%$, confirming the very low porosity of the SPS-pressed samples in this study. The XRD patterns of all samples show strongly diffraction peaks along (0001) orientations, indicating the highly c -oriented grains in these samples. Therefore, the

samples for thermoelectric measurements were prepared by cutting along the perpendicular direction to the pressure axis and all thermoelectric measurements were performed along this direction. The orientation degrees of the samples can be determined from the Lotgering factor (f) [22], $f = (P - P_0)/(1 - P_0)$, where $P = \sum I(00l) / \sum I(hkl)$ for the grain-oriented samples, I is the intensity of the XRD diffraction peak, and P_0 could be calculated from the standard card. The Lotgering factors of the pure and Sr-/Ti-doped CCO samples are calculated and presented in Table 1, which demonstrates the doping does not change the orientation significantly [23–25].

To further investigate the substitution sites of Sr and Ti, Raman analysis in the range of 200–650 cm^{-1} was carried out to verify the different lattice vibrations of the CCO system induced by Sr and Ti doping effects. Figure 2(a) presents a series of Raman spectra for Sr doped CCO samples with different Sr doping levels ($x = 0, 0.05, 0.1, 0.2$). It is found that the broad peaks in the spectra of Sr-doped CCO samples are consistent with the single crystal CCO [26]. Each spectrum is dominated by four vibration modes at P1 ($\sim 275 \text{ cm}^{-1}$), P2 ($\sim 473 \text{ cm}^{-1}$), P3 ($\sim 600 \text{ cm}^{-1}$), and P4 ($\sim 662 \text{ cm}^{-1}$). Since the crystal structure of CCO is known to be complicated, the assignment of those vibration modes is challenging. By comparing our Raman spectra to other similar misfit layer structure systems Na_xCoO_2 [27,28] and (Bi, Pb)–Sr–Co–O [29], which possess the same $[\text{CoO}_2]$ layer connecting by edge-sharing CoO_6 octahedral, the Raman results show that the dominant peaks at 472 and 593 cm^{-1} in Na_xCoO_2 [28] and 452 and 615 cm^{-1} in $\text{Bi}_{2-x}\text{Pb}_x\text{Sr}_2\text{Co}_2\text{O}_y$ [29] system were assigned to the in-plane E_{1g} and out-of-plane A_{1g} vibration modes of $[\text{CoO}_2]$ layer. The peaks at 290 and 700 cm^{-1} corresponded to the O atom vibration in Ca–O and Co–O of $[\text{Ca}_2\text{CoO}_3]$ rock-salt layer [30], respectively. The assignments of Raman peaks in CCO

Table 1 f of the pure, Sr- and Ti-doped CCO samples

Sample	Nominal composition	f
CCO	$\text{Ca}_3\text{Co}_{3.92}\text{O}_9$	0.77
Sr-0.05	$\text{Ca}_{2.95}\text{Sr}_{0.05}\text{Co}_{3.92}\text{O}_9$	0.79
Sr-0.1	$\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Co}_{3.92}\text{O}_9$	0.75
Sr-0.2	$\text{Ca}_{2.8}\text{Sr}_{0.2}\text{Co}_{3.92}\text{O}_9$	0.80
Ti-0.05	$\text{Ca}_3\text{Co}_{3.87}\text{Ti}_{0.05}\text{O}_9$	0.76
Ti-0.1	$\text{Ca}_3\text{Co}_{3.82}\text{Ti}_{0.1}\text{O}_9$	0.74
Ti-0.2	$\text{Ca}_3\text{Co}_{3.72}\text{Ti}_{0.2}\text{O}_9$	0.82

Fig. 2 Raman spectra for (a) Sr-doped CCO samples and (b–e) the dependent peak positions of P1, P2, P3, and P4 on different Sr doping concentrations.

were well-studied by combined experimental and computational studies [31–33]. Therefore, it is reasonable to assign P2 (~ 473 cm⁻¹) and P3 (~ 600 cm⁻¹) to in-plane E_{1g} and out-of-plane A_{1g} mode of $[\text{CoO}_2]$ layer and the P1 (~ 275 cm⁻¹) and P4 (~ 662 cm⁻¹) are attributed to $[\text{Ca}_2\text{CoO}_3]$ rock-salt layer, respectively. Figures 2(b)–2(e) also present the peak positions of P1, P2, P3, and P4 as a function of Sr doping content. P1 and P4 shift towards lower frequencies whereas P2 and P3 are almost unaffected with increasing doping content. This indicates that the incorporation of Sr ions affects the $[\text{Ca}_2\text{CoO}_3]$ rock-salt layer. According to the equation of harmonic oscillator approximation [30]: $\omega = (k / \mu)^{1/2}$, where ω is the wavenumber, k is the force constant, and μ is the mass, respectively. The heavy atoms like Ca or Co in CCO system are expected to vibrate at low wavenumber region whereas the light O atom will vibrate at high wavenumber region. Therefore, the incorporation of Sr ions theoretically leads to the shifting of P1 towards lower wavenumber with increasing Sr doping level due to the larger mass of Sr. In addition, the variation of ionic radii Ca or Co induces the lattice distortion by doping at Ca sites and further affects the Ca–O and Co–O vibration of $[\text{Ca}_2\text{CoO}_3]$ rock-salt layer. Hence, the high wavenumber (P4) was also shifted. For Ti-doped CCO samples, the dominant peaks remained almost unchanged at P1 (~ 277 cm⁻¹), P2 (~ 483 cm⁻¹), P3 (~ 600 cm⁻¹),

and P4 (~ 660 cm⁻¹), as shown in Fig. 3(a). Figures 3(b)–3(e) also present the evolution of P1, P2, P3, and P4 as a function of the Ti doping content. The P2 and P3 peaks were shifted to lower positions with increasing Ti concentration whereas the P1 and P4 peaks were almost unaffected, indicating the substitution of Ti affects the $[\text{CoO}_2]$ layer instead of $[\text{Ca}_2\text{CoO}_3]$ layer. Figure 3(f) shows the different doping sites of Sr and Ti in two sublayers in CCO system: The Sr dopant atoms prefer to occupy the Ca site of $[\text{Ca}_2\text{CoO}_3]$ layer whereas the doped Ti atoms occupy Co site of $[\text{CoO}_2]$ layer.

To understand the morphology and structure characteristics of SPS sintered undoped CCO and Sr-/Ti-doped CCO samples, SEM was employed to study the morphology of the polished surfaces of all samples. As shown in Fig. 4(a), the pristine undoped CCO sample exhibits the homogenous structure. The average grain sizes of Sr- or Ti-doped CCO samples are 2–5 μm . Whereas Sr-doped CCO samples have elongated plate-like grains along a – b crystal planes of CCO, showing significant aspect ratios with large grain size along with these two directions. A similar observation was also made in La-doped CCO [23], which is related to their layered crystalline structures. On the other hand, Ti-doped CCO samples ($x = 0.05$ and 0.1) showed randomly shaped and crystallized grains, as presented in Figs. 4(e)–4(g).

Fig. 3 (a) Raman spectra for Ti-doped CCO samples and (b–e) the dependent peak positions of P1, P2, P3, and P4 on different Ti doping concentrations. (f) The doping mechanism of Sr or Ti in CCO crystal structure.

Fig. 4 SEM images of (a) pristine CCO, (b–d) Sr doped CCO with $x = 0.05$, 0.1 , and 0.2 , respectively, and (e–g) Ti doped CCO with $x = 0.05$, 0.1 , and 0.2 , respectively.

To understand the effects of Sr and Ti doping in SPS-sintered CCO, σ , S , PF , and κ were measured and calculated from room temperature to 973 K. Figure 5(a) shows the temperature dependence of σ of the pure CCO and Sr-doped CCO samples. It can be seen that the undoped CCO and Sr-doped CCO show different electrical transport behaviors: the semiconductor behavior for pure samples, typical metallic behavior below 500 K, and semiconductor behavior above 500 K for Sr-doped CCO samples. Compared to pure CCO, σ is significantly increased with various Sr doping contents particularly at room temperature. The Sr-doped CCO sample with $x = 0.1$ shows the best σ with the highest of the values measured in this study at 957 K. However, σ decreased when the Sr doping was increased to $x = 0.2$ because the random grains could hinder the efficiency of charge carrier transportation. Similarly, the phonon transport could also be affected, and thus reduce the σ of the Sr-doped sample. From the temperature dependencies of S shown in Fig. 5(b), it can be seen that p-type carrier is dominant in both undoped CCO and Sr-doped CCO. The enhancement of σ and S after Sr substitution leads to the remarkably higher PF values of Sr-doped CCO samples compared

to pure CCO in Fig. 5(c). The highest reported PF value of $0.475 \text{ mW}/(\text{m}\cdot\text{K}^2)$ was obtained from the 10% Sr-doped CCO sample. Figure 5(d) shows the temperature dependence of κ in Sr-doped CCO compared to pure CCO and the lowest κ was obtained in Sr-doped sample ($x = 0.1$). The combination of the highest PF and lowest κ of 10% Sr-doped CCO sample resulted in the highest ZT of 0.38 at 957 K, as shown in Fig. 1(a). Figure 5 shows the temperature dependence of σ , S , PF , and κ of the pure CCO and Ti-doped CCO samples. The σ is surprisingly decreased with increasing Ti concentration though it increased in the 0.2 Ti sample (Fig. 6(a)). The temperature dependence S values of Ti-doped samples exhibited a similar trend as compared to Sr-doped CCO samples in Fig. 6(b). The S values are positive and increase with increasing temperature, implying the hole carriers in Ti-doped CCO samples. Therefore, the PF values in Fig. 6(c) present the same trend as the σ curves of Ti-doped CCO samples. Figure 6(d) shows the temperature dependence of the total κ of pure and Ti-doped CCO. The κ was found to decrease with increasing temperature in Sr- and Ti-doped CCO pellets. For all doped samples, the significant reduction of κ was observed with increasing Sr and Ti

Fig. 5 Temperature dependence of (a) σ , (b) S , (c) PF , and (d) κ of the pure CCO and Sr-doped CCO samples.

Fig. 6 Temperature dependence of (a) σ , (b) S , (c) PF , and (d) κ of the pure CCO and Ti-doped CCO samples.

concentration to 0.1 then increased with further increasing Sr and Ti concentration to 0.2. The lowest κ of $\sim 1.18 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ was obtained from Sr-doped CCO sample with $x = 0.1$ and $\sim 1.45 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$ for the Ti-doped CCO sample with $x = 0.1$ at 957 K. The combined PF and κ result in a slight increase ZT with Ti substitution compared to pure CCO sample, as shown in Fig. 1(a).

To investigate the simultaneous increase of σ and S obtained in Sr- and Ti-doped CCO pellets, we further measured carrier concentration (n) and mobility (μ) of all SPS-sintered pellets using Hall measurement. Figure 7 shows the measured n and μ as the function of Sr- and Ti-doping concentrations. It can be seen that Sr substitution increased n , resulting in increased σ . Low concentration of Sr substitution ($x = 0.05$ and 0.1) significantly enhanced μ to $2.75 \text{ cm}^2/\text{Vs}$, which is almost three-fold times than the pure CCO sample. However, further increase in the sample of Sr concentration ($x = 0.2$) greatly decreased μ to almost the same as the undoped CCO since the enhanced carrier scattering induced by the increased n results in the lower μ . Therefore, the σ of Sr-doped CCO peaked at Sr concentration of 0.1 (Fig. 5(a)). On the other hand, Ti substitution of CCO decreased n slightly when $x =$

0.05 and 0.1 and increased n when $x = 0.05$ and 0.1. In addition, μ of Ti-doped CCO samples were observed to be nearly constant, suggesting that σ was mainly affected by n rather than μ as shown in Fig. 6(a): The σ in Ti-doped CCO showed a minimum at $x = 0.05$ and 0.1 then increased in Ti-doped CCO ($x = 0.2$). The room temperature σ values of pure, Sr-, and Ti-doped CCO samples are listed in Table 2. The S could be explained by the equation for degenerate semiconductors [1]:

$$S = \frac{8\pi^2 \kappa_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3} \quad (1)$$

where κ_B is the Boltzmann constant, e is the electronic charge, h is the Planck constant, T is the temperature, n is the carrier concentration, and m^* is the effective mass. Equation. (1) shows the relationship between n and S that S can be enhanced by reducing n . Increasing temperature can also increase S . According to Eq. (1), S should be decreased with n increasing. However, the increased n after Sr doping should result in decreased S , which did not follow the S trend of Fig. 5(b). Moreover, the n of Ti-doped CCO first decreased and then increased with increasing Ti content, resulting in the decrease of S for Ti-doped CCO ($x = 0.2$). Thus, the monotonically increased S values in all Sr- and Ti-doped CCO samples

Fig. 7 Measured (a) n and (b) μ of all SPS-sintered pellets.

Table 2 Summary of the concentration and binding energies of Co^{3+} and Co^{4+} from the fitted XPS spectra for pure CCO, Sr-doped CCO ($x = 0.1$), and Ti-doped CCO ($x = 0.2$)

Sample	Binding energy (eV)		Concentration
	Co 2p _{3/2}	Co 2p _{1/2}	
CCO			
Co ³⁺	779.2	794.1	33.1%
Co ⁴⁺	780.1	795.4	66.9%
Sr-0.1			
Co ³⁺	779.3	794.2	51.7%
Co ⁴⁺	780.5	795.8	48.3%
Ti-0.2			
Co ³⁺	779.5	794.7	53.1%
Co ⁴⁺	781.2	796.6	46.9%

at high temperatures could be understood by the spin-entropy contribution of Co ions, which is determined by the ratio between Co^{3+} and Co^{4+} ions [14,34,35]. The S of strongly correlated systems can be expressed by the modified Heikes formula [36]:

$$S = -\frac{k_B}{e} \ln \left[\frac{g_3}{g_4} \left(\frac{c}{1-c} \right) \right] \quad (2)$$

where g_3 and g_4 are the spin-orbital degeneracy of Co^{3+} and Co^{4+} , respectively, and c is the concentration of Co^{4+} . Equation (2) implies that S could be increased by the decreased concentration of Co^{4+} .

To confirm the spin-entropy induced by Sr and Ti doping in CCO samples, chemical states of Co were performed by XPS analysis. Figure 8 displays the high-resolution XPS scans of Co 2p from pure CCO, $\text{Ca}_{2.9}\text{Sr}_{0.1}\text{Co}_{3.92}\text{O}_9$, and $\text{Ca}_3\text{Co}_{3.72}\text{Ti}_{0.2}\text{O}_9$ samples. The Co 2p spectrum of three samples represented by the two main peaks of Co 2p_{3/2} at ~779.5 eV and Co 2p_{1/2} at ~794.5 eV, respectively. The satellite peaks of Co 2p_{3/2} for three samples appearing at ~779.5 eV

Fig. 8 Co 2p XPS spectra for CCO, Sr doped CCO ($x = 0.1$), and Ti doped CCO ($x = 0.2$).

correspond to Co^{3+} species, which are in agreement with Ref. [10]. It is well accepted that the $[\text{CoO}_2]$ layer contains both Co^{3+} and Co^{4+} species whereas the insulating $[\text{Ca}_2\text{CoO}_3]$ layer only contains Co^{3+} species [13,19]. Based on XRD and Raman results, the Sr and Ti occupy the different sites in $[\text{Ca}_2\text{CoO}_3]$ and $[\text{CoO}_2]$ layer of CCO. To illustrate the Sr and Ti doping effects on spin-entropy of Co, the peak positions of Co^{3+} and Co^{4+} were firstly determined by peak fitting of two main peaks (Co 2p_{3/2} and Co 2p_{1/2}). The concentrations of Co^{3+} and Co^{4+} were calculated by the ratio areas of the fitted peaks for Co^{3+} and Co^{4+} to the total area of Co 2p. The binding energies of Co^{3+} and Co^{4+} together with their calculated concentrations are listed in Table 2. Compared to the pristine CCO, the concentrations of Co^{3+} significantly increased to ~51.7% for Sr-doped CCO ($x = 0.1$) and ~53.1% for Ti-doped CCO ($x = 0.2$) samples. Therefore, the concentration of Co^{4+} greatly decreased to keep the total charge-balanced. It is evident that both the Sr and Ti doping effects depressed the concentration of Co^{4+} and had a contribution to the spin-entropy of the CCO system, which is consistent

with the previous reported CCO based materials [10,34,35,37]. Thus, it can be concluded that the enhancement of S values in Sr- and Ti-doped CCO samples was induced by the spin-entropy enhancement through suppressing Co^{4+} concentration.

To understand the low κ in Sr- and Ti-doped CCO pellets, the electrical thermal conductivity (κ_e) and lattice thermal conductivity (κ_l) were investigated. The κ_e was calculated using Wiedemann–Franz law [1,38] by $\kappa_e = L\sigma T$ and $\kappa_l = \kappa - \kappa_e$, where L is the Lorenz number and $L \approx 1.5 \times 10^{-8} \text{ V}^2 \cdot \text{K}^{-2}$. Figures 9(a) and 9(b) show the temperature dependence of calculated κ_e for both Sr- and Ti-doped CCO samples, in which the measured σ is shown in Figs. 5(a) and 6(a) were used for determining κ_e . The obtained κ_e values of Sr- and Ti-doped CCO samples have a similar increasing trend with the σ since κ_e comes from the electrons or holes transporting heat and is proportional to σ according to Wiedemann–Franz law [1]. Figures 9(c) and 9(d) show the temperature dependence of κ_l for Sr- and Ti-doped CCO samples, where the κ_l showed an overall reduced trend because of the enhanced phonon scattering at higher-temperature region. The doping elements tend to reduce the κ contribution from lattice vibration, especially for the substitution of Ca with Sr. Figures

10(a) and 10(b) show the plots of κ_l as a function of $1000/T$ of all pellets. The linear relationship indicates that the phonon scattering is dominated by Umklapp phonon scattering [39,40] in all samples. Furthermore, as shown in Figs. 10(c) and 10(d), the κ_l/κ ratio values of all samples were calculated to be greater than 80% in the whole temperature range, confirming the dominant transport is phonon transport (κ_l) for κ , rather than κ_e [41]. Such a reduction of κ_l in both doped samples could be explained by the doping effects. Considering the atomic mass of Sr is much heavier than Ca, the substitution of Sr at Ca site increases the phonon scattering, which will dramatically reduce the κ_l of Sr-doped CCO samples. In addition, the Sr doped CCO with $x = 0.05$ and 0.1 show more oriented elongated grains from SEM images, which could significantly decrease the grain boundary scattering to reduce κ_l . The κ_l of Sr-doped CCO increases due to the formation of random arrayed grains with Sr content up to 0.2. Therefore, the electronic contribution κ_e of Sr-doped CCO with $x = 0.2$ slightly increases. For Ti-doped CCO samples, the atomic mass of Ti is very close to the Co, thereby the substitution of Ti has almost unaffected the κ_l in theory. However, based on the analysis of XRD and SEM results, the substitution

Fig. 9 Plots of thermal properties as a function of T for (a, b) κ_e , and (c, d) κ_l for Sr- and Ti-doped CCO pellets.

Fig. 10 (a, b) Plots of κ_1 as a function of $1000/T$ for Sr- and Ti-doped CCO pellets. (c, d) κ_1/κ ratio values as a function of T for Sr- and Ti-doped CCO pellets.

of Ti in CCO leads to the formation of Co_3O_4 secondary phase with increasing Ti doping content. It is well-accepted that impurity segregation preferentially at the grain boundaries remarkably improves the grain boundary scattering [42], which results in the lower κ_1 in Ti-doped CCO samples.

4 Conclusions

A series of pure, Sr- and Ti-doped CCO samples were fabricated by solid-state sintered followed with SPS method. Our study demonstrates that doping sites could greatly affect the TE performance of CCO material. The Raman spectra indicate that the Sr replaces the Ca site of $[\text{Ca}_2\text{CoO}_3]$ layer whereas Ti occupies the Co site of $[\text{CoO}_2]$ layer. The Sr substitution of Ca site results in the improvement of spin-entropy accompanied by decreasing Co^{4+} . For Sr-doped CCO samples, the highest PF and lowest κ can be obtained with Sr dopant level of 0.1, leading to the highest ZT of 0.38 at 957 K. Moreover, the enhancement of ZT is not evident when incorporated with different Ti concentrations.

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