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Improving the spin entropy by suppressing Co^{4+} concentration in thermoelectric $Ca_3Co_4O_{9+\delta}$

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Abstract

We report the effects of rare earth Gd doping on the spin entropy in $Ca_3Co_4O_{9+\delta}$. Magnetothermopower is found to be strongly magnetic-field dependent and increases upon Gd doping, revealing that Gd doping can improve the spin entropy of $Ca_3Co_4O_{9+\delta}$. X-ray photoemission spectroscopy (XPS) results allow us to determine the decrease in Co^{4+} concentration induced by Gd doping. Our results confirm that the spin-entropy enhancement originates from the decrease of Co^{4+} concentration. The present study suggests that we can improve the spin entropy by suppressing Co^{4+} concentration in layered cobalt oxides.

Keywords: C. Thermal properties; Layered cobalt oxide; Thermoelectric properties

1. Introduction

As a kind of clear energy-conversion system in global sustainable energy solution, thermoelectric materials have been the focus of attention [1,2]. The efficiency of a thermoelectric material is found to depend on the material properties via the dimensionless figure of merit ZT, where $ZT = S^2\sigma T/\kappa$. In this expression S, κ, and σ are the thermopower, the thermal conductivity and the electrical conductivity, respectively. Recently, layered cobalt oxide such as $Ca_3Co_4O_{9+\delta}$ has been extensively investigated as promising candidates for p-type thermoelectric material due to its thermal and chemical stability at high temperature [3–8]. The misfit-layered cobalt oxide $Ca_3Co_4O_{9+\delta}$ consists of two alternating subsystems, a CoO_2 sheet and a distorted rock-salt Ca_2CoO_3 block stacked along the *c*-axis, each fulfilling a different role in achieving prospective thermoelectric properties at high temperature. Up to now, considerable theoretical and experimental efforts [9–13] have been directed toward disclosing the mechanism of the high thermopower in layered cobalt oxide. Many authors suggested that the spin entropy plays an important role in enhancing the thermopower in layered cobalt oxides [11–17]. In particular, Wang et al. [13] found a suppression of the thermopower under a longitudinal magnetic field at low temperatures in $NaCo_2O_4$ and proposed the spin entropy as the main source for the observed high thermopower. Furthermore, a scaling behavior with both magnetic field and temperature was observed in cobalt oxides by Limelette et al. [14], providing a solid evidence for significant spin entropy contribution to thermopower.

In the high temperature limit, the spin-entropy contribution to the thermopower in the layered cobalt oxide, is suggested to be expressed by the Heikes formula $S = -(\kappa_B/e)ln\{g_3/g_4[c/(1-c)]\}$ [11,12]. In the equation, g_3 and g_4 are the spin orbital degeneracies for Co^{3+} and Co^{4+} ions respectively, c is Co^{4+} concentration and κ_B is the Boltzmann constant. It is indicated that the spin entropy contribution to the thermopower depends largely on the Co^{4+} concentration and degeneracies of Co ions. Doping with rare earth metals into Ca sites of $Ca_3Co_4O_{9+\delta}$ may be a powerful approach to change the Co^{4+} concentration or degeneracy which plays a vital role in the spin entropy. In this respect, understanding the doping effects of

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rare earth metals on the spin entropy can pave an effective way for improving the thermopower of layered cobalt oxides.

Here we report the effects of Gd doping on the spin entropy in $Ca_3Co_4O_{9+\delta}$. The magnetothermopower increases upon Gd doping, revealing that Gd doping can improve the spin entropy in the $Ca_3Co_4O_{9+\delta}$ system. X-ray photoemission spectroscopy (XPS) is carried out to determine the variation of Co^{4+} concentration. Based on analysis of XPS, we propose a suitable mechanism to explain well the spin-entropy enhancement.

2. Experiment

The starting materials were standard reagents and used as commercially obtained. $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ powders were prepared by the sol–gel method as follows: the stoichiometric $CaCO_3$, $Co(NO_3)_2 \cdot 6H_2O$, Gd_2O_3, and citric acid monohydrate were dissolved in concentrated HNO_3 and deionized water. Citrate solution was dehydrated at 353 K. The resulted uniform was crushed and heated to 473 K for 3 h to remove the moisture of gel. The obtained carbonaceous xerogel was calcined at 823 K for 3 h in air. After cooled to room temperature, the obtained powders were ground and sintered at 1173 K for 12 h, then pressed into pellets. Finally black pellets were annealed at 1173 K for 36 h under O_2 atmosphere.

X-ray diffraction (XRD) analysis was carried out using a Rigaku D/Max-gA diffractometer with Cu Kα radiation. Magnetic properties were measured by a superconducting quantum interference device (SQUID) measurement system. The thermopower measurements were performed using a commercial Quantum Design physical property measurement system (PPMS). For magnetothermopower measurements, the direction of magnetic field was parallel to the temperature gradient. X-ray photoemission spectroscopy (XPS) experiments were carried out on a BSCALB MK-II spectrometer equipped with a monochromatized Al Kα X-ray source. The overall energy resolution was 0.6 eV.

3. Results and discussion

Fig. 1 shows the XRD diffraction patterns for $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ (x=0, 0.2, 0.4 and 0.6) samples. All peaks are identical to the standard JCPDS card (No. 21-0139) of $Ca_3Co_4O_{9+\delta}$, indicating single-phase compounds are obtained [3]. Radii of ion for Ca, Co and Gd are 0.99, 0.63 and 0.94, respectively. We show the enlarged (004) diffraction peaks in the right inset of Fig. 1. It is observed that XRD peaks shift toward higher angles with increasing Gd content. The upshift of XRD peaks indicates that Gd^{3+} ions really substitute for bigger Ca^{2+} ions.

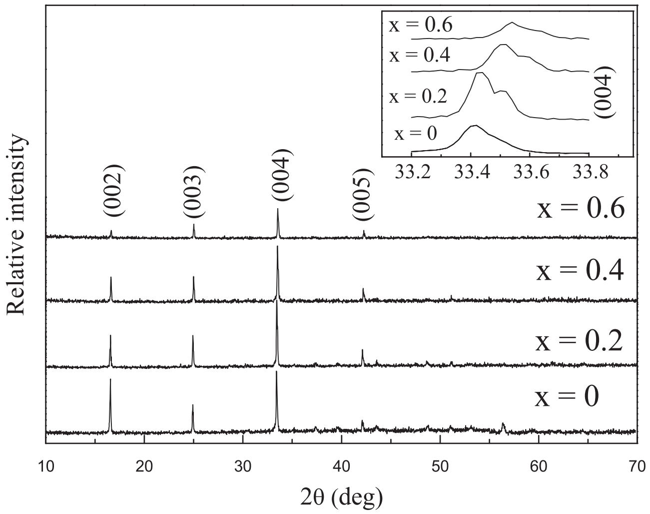

Fig. 1. XRD patterns of $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ samples.

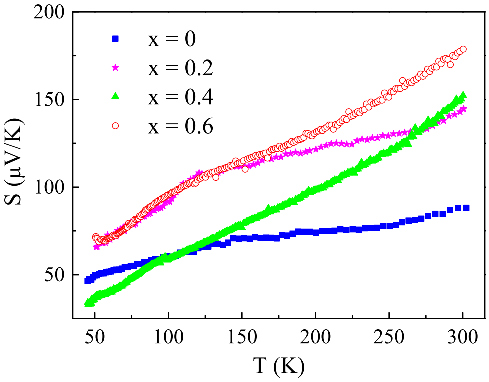

Fig. 2. Temperature dependence of thermopower for $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ samples.

Fig. 2 presents the temperature dependence of thermopower (S) for $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ (x=0, 0.2, 0.4 and 0.6) samples. S increases with increasing temperature in the investigated temperature range. The positive thermopower suggests that holes are the major charge carriers in these samples. It is found that S is obviously enhanced by Gd doping and reaches 179 μV/K at 300 K for $Ca_{2.4}Gd_{0.6}Co_4O_{9+\delta}$ material.

To investigate the effects of Gd doping on the spin entropy, we performed a series of magnetothermopower measurements on the $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ samples at 4 and 8 T, respectively. As shown in Fig. 3, a clear field-induced decrease of the thermopower is observed, which indicates a large spin entropy contribution to the thermopower. Such suppression behavior is a typical signature of a spin-entropy reduction due to the partial removal of spin degeneracy by an applied magnetic field [13]. The basic idea is that if the charge carriers retain a spin degree of freedom, it will contribute $(k_B/q)\ln 2 \approx 60$ μV/K to the thermopower [13–15]. Once the spin is forced to align with magnetic field, the spin entropy will be suppressed and hence its contribution to the thermopower decreases. From Fig. 3, we note that the thermopower is further suppressed as the applied field increases from 4 T to 8 T, implying that the spin entropy is further reduced. In fact, if the applied magnetic field is strong enough to remove the spin degeneracy of Co ions, the spin entropy will be completely suppressed and reduced to zero. To disclose the effects of

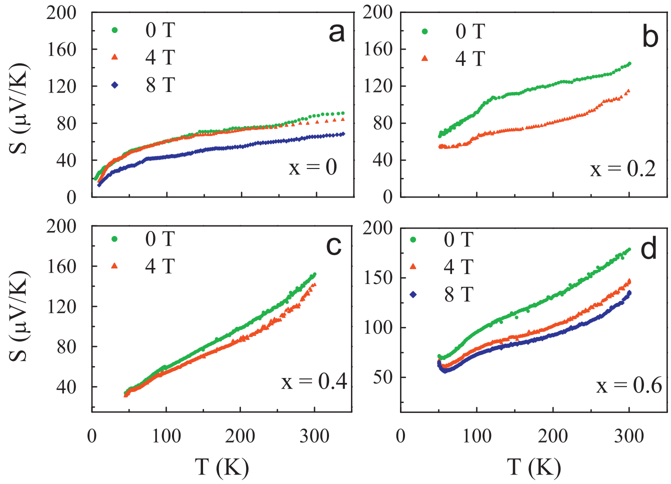

Fig. 3. Temperature dependence of thermopower for $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ at 0 and 4 T with (b) $x=0.2$ and (c) $x=0.4$; and at 0, 4 and 8 T with (a) $x=0$ and (d) $x=0.6$, respectively.

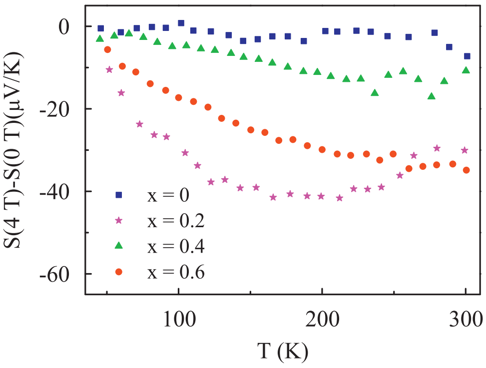

Fig. 4. Magnetothermopower, S (4 T) − S(0 T) as a function of temperature for $Ca_{3-x}Gd_xCo_4O_{9+\delta}$.

Gd doping on the spin entropy, we study the temperature dependence of magnetothermopower, $\Delta S=S(4\text{ T})-S(0\text{ T})$ (Fig. 4). It is shown that magnetothermopower at 300 K is about −7.3, −29.7, −9.3 and −34.8 μV/K for $x=0$, 0.2, 0.4 and 0.6 samples, respectively. The magnetothermopower ratios, defined as $[S(0\text{ T})-S(4\text{ T})]/S(0\text{ T})$, are calculated to be 8% for $x=0$, 15% for $x=0.2$, 7% for $x=0.4$, and 20% for $x=0.6$ at 300 K. We can find that the absolute values of magnetothermopower of doped samples are overall enhanced compared with that of undoped $Ca_3Co_4O_{9+\delta}$. The magnetothermopower results provide an experimental evidence for the spin-entropy enhancement induced by Gd doping. At low temperature, only a small fraction of spins behaves as free spins due to the onset of magnetic coupling interaction, giving rise to the rapid decrease of the spin entropy and therefore a less field-dependent thermopower [16,17], as shown in Fig. 4.

In order to understand the mechanism of spin-entropy enhancement, we performed X-ray photoemission spectroscopy (XPS) measurements to determine the variation of Co^{4+} concentration induced by Gd substitution. The Co 2p XPS spectra of $Ca_{3-x}Gd_xCo_4O_{9+\delta}$ with $x=0$, 0.4 and 0.6 are given in Fig. 5. The peaks (marked by A_1) with binding energy of ca. 780.5, 782.9 and 796 eV can be identified as Co^{4+}, similar to that reported by Dupin et al. [18]. The other peaks (marked by A_2) appearing at ca. 779.5, 787.8, and 794.6 eV can be assigned to Co^{3+} [19]. The Co 2p XPS results suggest that Co^{3+} and Co^{4+} are present in the oxides. We calculate the ratio of fitting peak area of Co^{4+} to the total Co sites and find it decreases through Gd doping. This implies that Gd doping makes the Co^{4+} concentration decrease. The Gd 4d XPS spectra for $Ca_{2.4}Gd_{0.6}Co_4O_{9+\delta}$ are presented in Fig. 6. A complex shape of Gd 4d line is caused by strong 4d–4f coulomb, exchange and spin–orbit interactions. The peaks of Gd^{3+} are in good agreement with that reported by Talik et al. [20]. The Gd 4d XPS spectra illustrate that Gd^{3+} presents in the doped samples. It can be understood that Co^{4+} concentration decreases with increasing Gd^{3+} content to balance the total valence from the standpoint of charge balance.

In the high temperature limit, the spin entropy contribution to the thermopower in the strong correlation system, can be expressed using the modified Heikes formula [11,12]

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

where g_3 and g_4 are the spin orbital degeneracies for Co^{3+} and Co^{4+} ions respectively, c is the Co^{4+} concentration and k_B is the Boltzmann constant. The valence-band XPS spectra are shown in Fig. 7. It is shown that Gd doped samples have similar structure α with undoped $Ca_3Co_4O_{9+\delta}$, demonstrating that Gd doping does not change the spin states of both Co^{4+} and Co^{3+} ions. Structure α at ~1 eV can be assigned to Co t_{2g} low-spin states [21,22]. The spin orbital degeneracies $g_3=1$ and $g_4=6$ are determined according to the low-spin states of both Co^{3+} and Co^{4+} ions. As discussed above, Co 2p XPS evinces that the Co^{4+} concentration is reduced by Gd doping. According to Eq. (1), we obviously find that Gd doping induces the spin-entropy enhancement.

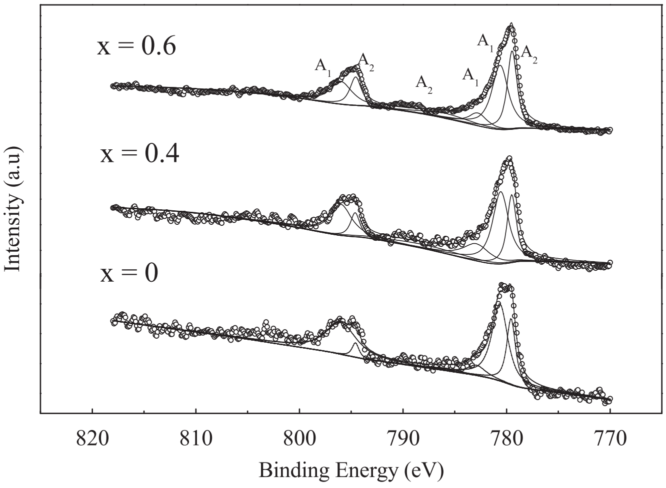

Fig. 5. Co 2p XPS spectra of $Ca_{3-x}Gd_xCo_4O_{9+\delta}$.

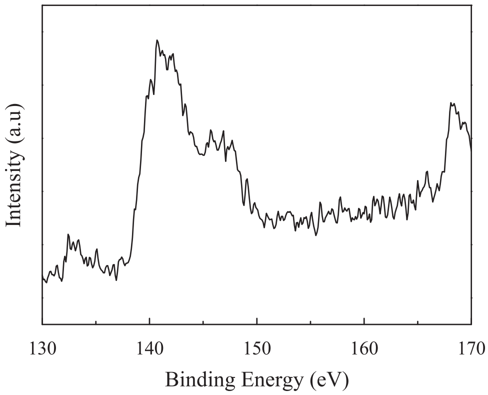

Fig. 6. XPS spectrum of Gd 4d regions for $Ca_{2.4}Gd_{0.6}Co_4O_{9+\delta}$.

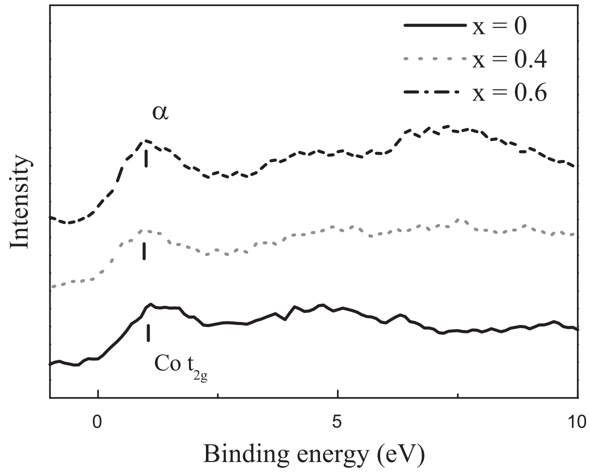

Fig. 7. Valence-band XPS spectra of $Ca_{3-x}Gd_xCo_4O_{9+\delta}$.

Suppressing Co^{4+} concentration is a promising way for improving the spin entropy of $Ca_3Co_4O_{9+\delta}$.

4. Conclusions

The effects of Gd doping on the spin entropy in $Ca_3Co_4O_{9+\delta}$ have been studied. A strong magnetic-field suppression of thermopower reveals a large spin entropy contribution. Magnetothermopower increases in all doped samples, giving evidence for spin-entropy enhancement. X-ray photoemission spectroscopy (XPS) confirms that Gd doping gives rise to the reduction of Co^{4+} concentration. This is considered to be responsible for spin-entropy enhancement. This investigation demonstrates that Gd doping can suppress Co^{4+} concentration and improve the spin entropy in $Ca_3Co_4O_{9+\delta}$. The present study suggests that we can improve the spin entropy by suppressing Co^{4+} concentration in layered cobalt oxides.

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