High-temperature thermoelectric properties of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ ceramics

YOUJIN ZHENG^{1,*}, HUI ZHOU², TENGZHOU MA², GUIHONG ZUO¹, HONGTAO LI^{2,*},
TAICHAO SU^{3,*}, CHUNLEI WU¹, HAILIANG HUANG¹, DAN WANG¹ and LONGCHENG YIN¹

¹Department of Physics, Mudanjiang Normal College, Heilongjiang Province Key Laboratory of New Carbon-Base Functional and Superhard Material, Mudanjiang 157011, China

²Shanghai Entry–Exit Inspection and Quarantine Bureau, Shanghai 200135, China

³Institute of Materials Science and Engineering, Henan Polytechnic University, Jiaozuo 454000, China

MS received 3 April 2013; revised 21 May 2013

Abstract. Thermoelectric ceramics, $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ ($0 \leq x, y \leq 0.15$), have been prepared using a sol–gel method, followed by pressureless sintering. The phase structures and microstructures of oxides were investigated at room temperature. Thermoelectric properties including Seebeck coefficient, electrical conductivity and thermal conductivity were measured from 303 to 973 K. It was found that the samples contain nanostructured Ag phase with grain size of 100 nm. The $\text{Ag}_{0.05}\text{Y}_{0.15}\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ sample has the maximum figure of merit ($ZT \sim 0.14$ @ 973 K), which is about 27% higher than that of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$.

Keywords. Thermoelectric; $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ sol–gel.

1. Introduction

As clean energy source, environment-friendly thermoelectric materials, which can be used to convert heat energy into electrical energy directly, have attracted extensive attention (Mahan *et al* 1997). The energy conversion performance of a thermoelectric material is usually characterized by the figure of merit $Z = \sigma S^2 / \kappa$, where σ , S and κ are electrical conductivity, Seebeck coefficient and thermal conductivity, respectively. The electrical properties are determined by the power factor, defined as σS^2 or S^2 / ρ , where ρ is the electrical resistivity. A good thermoelectric material must have a large power factor and low thermal conductivity.

$\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ ceramic is considered to be a promising candidate *p*-type thermoelectric material for high-temperature power generator, which has excellent thermal and chemical stability (Wang *et al* 2010a). However, its thermoelectric performance is much lower than the state-of-the-art thermoelectric materials such as Bi_2Te_3 , PbTe and CoSb_3 (Poudel *et al* 2008; Li *et al* 2009; Biswas *et al* 2012). For practical use, their thermoelectric performance must be further improved. One approach is partial substitution for Ca or Co site by metals such as rare earth metals, Ag and transition metal (Nan *et al* 2003; Wang *et al* 2008, 2010b; Nong *et al* 2011). Recently, Nong *et al* (2011) have reported that $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ composite was

doped with Lu and Ag by solid-state reaction and spark–plasma–sintering (SPS) techniques. The maximum Z could reach 5.55×10^{-4} at 1100 K, which is the highest value reported for the polycrystalline $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ system so far. However, the feature of these materials is that they contain rare earth metal Lu, which is a scarce element in the crust of the earth. The price of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ -based thermoelectric rise sharply by doping with Lu. Compared with Lu, Y is much cheaper. It has been reported that the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ could be improved effectively by doping with Y (Wang *et al* 2010a, b) and the optimized composition ($\text{Y}_{0.2}\text{Ca}_{2.8}\text{Co}_4\text{O}_9$) is similar to that of Lu-doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ (Nong *et al* 2011).

In addition, the solid-state reaction method presents several serious drawbacks, such as high reaction temperature, large particle sizes, limited degree of chemical homogeneity and low sintering ability. Sol–gel method could conquer these drawbacks. In this method, the reactant cations are intimately mixed on an atomic scale, so the rate of the reaction will increase, leading to lower synthesis temperatures (Mathur and Shen 2002). In this paper, $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ was prepared by sol–gel method and pressureless sintering and the high-temperature thermoelectric properties were studied from room temperature to 973 K.

2. Experimental

Starting materials were standard reagents and used as commercially obtained. $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ samples for

*Authors for correspondence (lihongtao@shciq.gov.cn; youjinzheng@hotmail.com; taichao80@hotmail.com)

x and y varying from 0 to 0.15; $x + y = 0.2$, were prepared using sol-gel method as follows. The stoichiometric $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, AgNO_3 , $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and citric acid monohydrate were dissolved in distilled water and then slowly heated to 343 K with incessant stirring. The resulted uniform gel was dehydrated at 473 K for 10 h. Dry gel was ground and calcined at 1073 K for 2 h. The obtained powders were ground and pressed into pellets. Finally, these pellets were annealed at 1123 K for 8 h under O_2 atmosphere.

The collected samples were cut and polished on the surface for thermoelectric measurements. X-ray diffraction (XRD) data at room temperature were collected using the XRD diffractometer (D/MAX-RA) with $\text{CuK}\alpha$ radiation. The fracture surface morphology was carried out on a HITACHI S-4800 scanning electron microscope (SEM). The Seebeck coefficient and electrical resistivity were measured from 303 to 973 K using LRS-3 measurement system. The thermal conductivity was calculated using $\kappa = D\rho C_p$, where ρ is the sample density. The thermal diffusivity, D , and specific heat, C_p were measured by a laser flash method on a Netzsch LFA457.

3. Results and discussion

The results of XRD patterns of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ are shown in figure 1. It shows that most of the diffraction peaks can be indexed as $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ according to the JCPDS card (PDF # 21-0139). Similar to the result of $\text{Ca}_{3-x-y}\text{Ag}_x\text{Lu}_y\text{Co}_4\text{O}_{9+\delta}$ reported by Nong *et al* (2011), the second phase of the Ag peak was found with $x = 0.05$ and 0.15. In order to confirm the existence of Ag as a secondary phase, the SEM was measured.

Figure 2 shows the SEM microphotographs of fractured surface for the $\text{Ca}_{2.8}\text{Ag}_{0.05}\text{Y}_{0.15}\text{Co}_4\text{O}_{9+\delta}$ sample. As

Figure 1. XRD patterns of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$.

can be seen from the pattern, the maximum grain size is about 1–2 μm . In addition, many pores are observed in the SEM photographs of fracture surfaces for the sample, which may result in high resistivity and low thermal conductivity. Especially, an island-shaped second phase separates out and forms grains of typically 100 nm size, which are distributed on the surface of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$. According to figure 1 and the energy dispersive X-ray analysis, this nanostructured second phase is Ag. The second Ag nanophase in $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ compounds may effectively enhance phonon scattering and reduce thermal conductivity.

Figure 3 shows the dependence of electrical resistivity of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ on temperature. The resistivity for all the samples decreases with an increase in temperature, which shows semiconductor-like behaviour. The $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ sample has the highest electrical resistivity. Compared with the result of Wang *et al* (2010a,b) and Nong *et al* (2011), resistivity is much higher. The high electrical resistivity may be attributed to the low density of the samples obtained in this study. The densities of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ were measured by the Archimedes method. The densities of the samples are just about 70% of the theoretical value, which is much lower than that of sample prepared by solid-state reaction and SPS sintering reported by Nong *et al* (2011) (96%). Since the resistivity of Ag is much lower than $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$, the resistivity of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ decreases obviously with an increase in x .

According to Kobayashi *et al* (1991), the electrical conductivity of small polaron hopping conduction mechanism can be written as

$$\sigma = ne\alpha^2(A/T) \exp(-E_a/k_B T),$$

where n , e , α , E_a and A are the carrier concentration, the electron charge of carrier, the intersite distance of

Figure 2. SEM image of section plane inner of $\text{Ag}_{0.05}\text{Y}_{0.15}\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$.

hopping, the activation energy and the pre-exponential term related to the scattering mechanism, respectively. The plots of $\ln \sigma T$ vs $1000/T$ for all the samples lie on straight lines above ~ 573 K, as shown in figure 4, indicating the hopping conduction behaviour at a high temperature. The doping of Y and Ag does not change the transport mechanism, but the hopping activation energy, E_a , obtained from the slopes of the plots, is changed. The E_a decreases with an increase in x .

The Seebeck coefficient (S) of oxides $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ vs temperature is presented in figure 5. The Seebeck coefficient values are all positive, indicating p -type conduction. As can be seen from figure 5, the sample with low Ag and high Y concentrations ($x = 0.05$,

$y = 0.15$) has the largest Seebeck coefficient in the measured temperature region. $\text{Ca}_3\text{Co}_4\text{O}_9$ is a layered oxide, which consists of alternating stacks of triple rock salt-type Ca_2CoO_3 layers and single CdI_2 -type CoO_2 layers along the c axis. The edge shared CoO_2 layer was considered to be responsible for the electric conduction, whereas the rock salt-type Ca_2CoO_3 layer was regarded as a charge reservoir to supply charge carriers into the CoO_2 layer. For the $\text{Ca}_3\text{Co}_4\text{O}_9$ compound, the effective carrier is hole. The substitution of trivalent Y^{3+} for divalent Ca^{2+} would decrease the carrier concentrations and thus increase the Seebeck coefficient. In addition, the Seebeck coefficient may be increased due to the energy filtering effect of charge carrier with the nanoinclusion of Ag.

Figure 3. Electrical resistivity of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ as a function of temperature.

Figure 4. Relation between $\ln \sigma T$ and $1000/T$ for $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$.

Figure 5. Seebeck coefficient of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ as a function of temperature.

Figure 6. Thermal conductivity of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ as a function of temperature.

However, for a higher Ag concentration, i.e., the sample at $x = 0.15$ and $y = 0.05$, the high Ag content could lead to a lower Seebeck coefficient. The decrease of Seebeck coefficient may originate from the additional thermoelectric voltage of metal Ag. The total Seebeck coefficient, S of the system can be expressed as $S = S_{\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}} + S_{\text{Ag}}$. Since Seebeck coefficient of Ag in metal form is quite low and the sign is negative because of its electron carrier, the total S of composites will decrease slightly when the additional S_{Ag} is taken into account.

The thermal conductivity for $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ as a function of temperature is shown in figure 6. It can be seen that the temperature-dependent thermal conductivity behaviour of all the $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ samples is similar. The thermal conductivity for the sample with $x = 0.05$, $y = 0.15$ has the lowest value in the measured temperature

range. The thermal conductivity can generally be decomposed into two parts, one from the charge carriers (κ_e) and the other from the lattice vibration (κ_{ph}). According to Wiedemann Franz's law $\kappa_e = L\sigma T$, where L is the Lorenz number ($2.44 \times 10^{-8} \text{ W}\Omega\text{K}^{-2}$). As seen from figure 7, the thermal conductivities of samples come mainly from the contribution of the lattice vibration. Similar to the total thermal conductivity, $\text{Ag}_{0.05}\text{Y}_{0.15}\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ has the lowest value for κ_{ph} . The Y has a larger atomic mass, substitution of Y for Ca will bring large lattice disharmony and hereby decrease the thermal conductivity, which has been confirmed by Wang *et al* (2010a,b). As is well known, κ_{ph} can be depressed by the scattering effects of nanoparticles to the medium-long-wavelength phonons. The decreased thermal conductivity of $\text{Ag}_{0.05}\text{Y}_{0.15}\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ could be a partial attribute to the dispersed Ag nanophase.

The figure of merit, ZT , is calculated using experimental S , ρ and κ data measured from 303 to 973 K. The temperature dependences of figure of merit are shown in figure 8. The figure-of-merit for all the samples increases with increase of temperature. The figure of merit for non-doped $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ sample at 973 K is about 0.11, which is comparable with the result of $\text{Ca}_3\text{Co}_4\text{O}_9$, reported by Nan *et al* (2003). As can be seen from figure 7, the sample with $x = 0.05$ and $y = 0.15$ has the maximum figure of merit, and the value is about 0.14 at 973 K, which is about 27% higher than that of $\text{Ca}_3\text{Co}_4\text{O}_9$. A better thermoelectric performance of dense $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ sample can be expected by pressure-assisted sinter such as high pressure or SPS.

4. Conclusions

Nano-composite $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ has been successfully prepared by sol-gel and pressureless sintering methods. The measurement of thermoelectric properties show that the Seebeck coefficient, electrical resistivity and thermal conductivity could be modulated effectively by changing the content of Ag and Y. The maximum figure of merit Z reaches 0.14 at 973 K for the sample of $\text{Ag}_{0.05}\text{Y}_{0.15}\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$, which is about 27% higher than that of $\text{Ca}_3\text{Co}_4\text{O}_9$. These results show that doping with Y and composite with nanoinclusions of Ag could improve the thermoelectric performance of $\text{Ca}_3\text{Co}_4\text{O}_{9+\delta}$ effectively.

Acknowledgements

This work was supported by the Natural Science Foundation of Heilongjiang Province (No. E201341), the Key Advanced Research Project of National Level Innovation (Mudanjiang Normal College) (Grant no. GY201206), the Project of Science and Technology of Mudanjiang (no. G2013e1233), Open Project of Key Lab of Superhard Materials of Mudanjiang Normal College Nos 201304, 201303, the Scientific and Technological Projects under

Figure 7. Phonon and carrier thermal conductivity of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$.

Figure 8. Figure of merit of $\text{Ag}_x\text{Y}_y\text{Ca}_{2.8}\text{Co}_4\text{O}_{9+\delta}$ as a function of temperature.

Shanghai Entry–Exit Inspection and Quarantine Bureau (no. HK009-2013), China Postdoctoral Science Foundation (Grant no. 2012M521393) and the National Science Foundation of China under Grant no. 51001042.

References

- Biswas K *et al* 2012 *Nature* **489** 414
 Kobayashi T, Takizawa H and Endo T 1991 *J. Solid State Chem.* **92** 116
 Li H *et al* 2009 *Appl. Phys. Lett.* **94** 102114
 Mahan G, Sales B and Sharp J 1997 *Phys. Today* **50** 42
 Mathur S and Shen H 2002 *J. Sol.-Gel. Sci. Technol.* **25** 147
 Nan J *et al* 2003 *J. Eur. Ceram. Soc.* **23** 859
 Nong N V, Liu Chia-Jyi and Ohtakib M 2011 *J. Alloys Compd.* **509** 977
 Nong N, Pryds N and Linderöth S 2011 *Adv. Mater.* **23** 2484
 Poudel B *et al* 2008 *Science* **320** 634
 Wang Y *et al* 2008 *J. Alloys Compd.* **448** 1
 Wang Y *et al* 2010a *Appl. Phys.* **A99** 451
 Wang Y *et al* 2010b *J. Appl. Phys.* **107** 033708