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Preparation and transport properties of aqueous sol-gel synthesized $NaCo_2O_{4-\delta}$

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We have successfully prepared thermoelectric materials $NaCo_2O_{4-\delta}$ at lower temperature (700°C) using aqueous sol-gel methods. We find that the electrical resistivity and thermopower of $NaCo_2O_{4-\delta}$ depend strongly on the sintering temperature and partial pressure of oxygen. The oxygen content of $NaCo_2O_{4-\delta}$ is found to decrease with increasing sintering temperature. The sample prepared at the combination of 700°C and pure flowing oxygen exhibits the highest value of power factor.

1. Introduction

Thermoelectric materials can be used for generating electricity for power source and pumping heat for refrigeration. An ideal thermoelectric material should have good electrical conductivity (σ) to avoid Joule heat, large thermopower (S) to convert energy more powerful, and low thermal conductivity (κ) to hold temperature difference between heat sink and heat source. These three transport parameters are embodied as thermoelectric figure of merit $Z = \sigma S^2/\kappa$, where σS^2 is the power factor strongly depending on the Fermi level, namely, a function of the carrier concentration and the temperature. Terasaki *et al.* [1] have recently shown that hexagonal layered oxide $NaCo_2O_4$ exhibits a large thermopower (~100 μV/K at 300 K), a low resistivity (~0.2 mΩ-cm at 300 K) and a low thermal conductivity (~20 mW/cm K) [2]. This three combined thermoelectric parameters make this material an attractive candidate for thermoelectric applications.

Sol-gel method provides the advantage of mixing the constituting precursors at the molecular level and gives more homogeneous cations stoichiometry. As a result, the sol-gel method avoids the necessity of the intermediate grindings which are required to overcome the diffusion problem encountered in the solid state reaction. In addition, the sol-gel method has been used to prepare a wide variety of ultra-fine and high-purity powders, monolith, fibers, thin films, and composites. Most of the sol-gel routes use costly metal alkoxides which involve complex laboratory skills, particularly in the synthesis of multicomponent systems. In this paper, we report the preparation of $NaCo_2O_{4-\delta}$ using a simple aqueous sol-gel method [3] at the temperature as low as 700°C and present the temperature dependence of electrical resistivity and thermopower as a function of temperature for $NaCo_2O_{4-\delta}$ sintered at different combinations of temperature and partial pressure of oxygen.

2. Experimental procedure

The stock solutions of constituent metal nitrates were separately prepared by dissolving $NaNO_3$ and $Co(NO_3)_3$ in deionized water. The concentrations of the resulting solutions were determined using ICP chemical analysis. An aqueous solution was obtained by quantitatively mixing urea and metal nitrates of known assay with desired atomic ratios of Na and Co (Na : Co = 1.15:2). The reason for using the excess Na is to compensate the loss of Na during the calcination procedure. The mixed solution is then heated at ~100–135°C until a gel is formed, followed by the heating at 250–300°C to remove the remaining organics in the gel. The resulting gel powders were then subject to heat treatments at desired combinations of calcination temperature and partial pressure of oxygen at a total pressure of 1 atm of a N_2-based gas mixture for 12 h. The as-calcined powders were examined using a powder X-ray diffractometer Shimadzu XRD-6000 equipped with Fe K_α radiation. Electrical resistivity was measured in an Oxford closed cycle cooler cryostat by a standard linear four-probe method using a quasi-DC technique between 10 and 300 K. The electrical probes of the samples were sputter-coated with palladium before the silver paste was applied to make the contacts. Thermopower was measured using steady-state techniques between 80 and 300 K. The temperature of the sample and the temperature gradient across the Seebeck probes were monitored by a Cernox sensor and two type-E thermocouples connected in a differential mode. The thermally generated Seebeck voltage across the

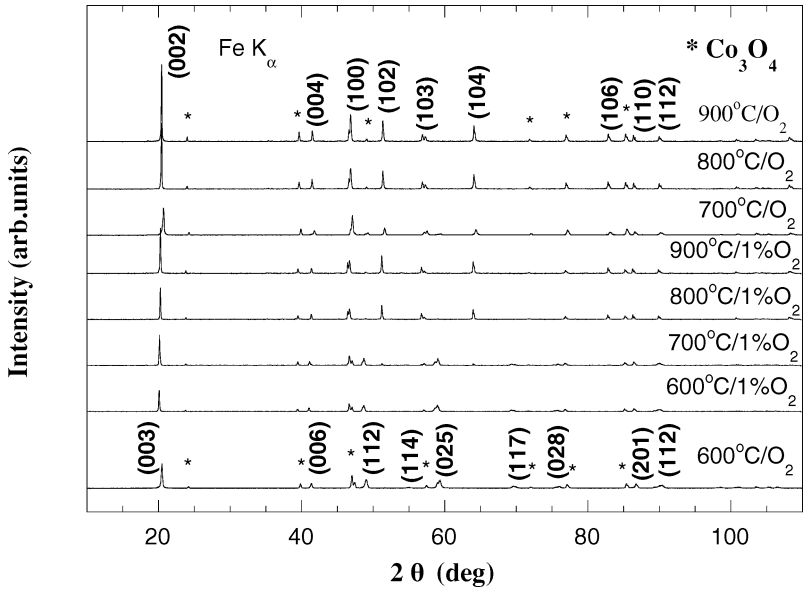

Figure 1 The XRD patterns of $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen.

sample was measured using a Keithley 182 nanovoltmeter. The detailed experimental apparatus and procedure are described elsewhere [4, 5]. The thermopower of the sample was obtained by subtracting the thermopower of Cu Seebeck probes, which were calibrated against high-purity Pb by comparing with Robert's data [6]. Thermogravimetric analyses (TGA) were carried out using a Perkin Elmer Pyris 1 thermogravimetric analyzer. The oxygen content and valence state of cobalt were determined using the iodometric titration method.

3. Results and discussion

Fig. 1 shows the XRD patterns of the powders calcined at different combinations of temperature and partial pressure of oxygen. Orthorhombic phase of β-$Na_{0.6}CoO_2$ (ICDD diffraction data card 30-1181) [7] is obtained as the gel powder is calcined at the conditions of 600–700°C in 1% partial pressure of oxygen or 600°C in pure oxygen, whereas hexagonal phase of $NaCo_2O_4$ (ICDD diffraction data card 27-0682) is obtained as the powder is calcined at the conditions of 700–900°C in pure oxygen or 800–900°C in 1% partial pressure of oxygen. It is worth noting that hexagonal $NaCo_2O_4$ is normally obtained at 860–920°C using the solid-state reaction [8]. Fig. 1 also shows the assigned miller indices for the hexagonal $NaCo_2O_{4-\delta}$ with the space group $P6_322$ and the orthorhombic β-$Na_{0.6}CoO_2$, respectively. Table I summarizes the refined lattice parameters for $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen.

We now turn to the transport property measurements on the samples treated at different combinations of temperature and partial pressure of oxygen. Fig. 2 shows the temperature dependence of the resistivity for samples prepared at different combinations of temperature and partial pressure of oxygen. All the samples show metal-like temperature dependence down to 10 K without indication of carrier localization despite the presence of disorder in the Na layers [9]. One can readily see that the resistivity of the title material varies with the sintering conditions with the lowest resistivity occurring at the combination of 700°C and pure flowing oxygen and with the highest resistivity at the sintering temperature of 900°C. The variation of resistivity with the combination of sintering temperature and partial pressure of oxygen suggests that the electrical conductivity is associated with the oxygen content in the sample, which in turn would affect the carrier concentration of the materials. Based on our TGA curve (Fig. 3), it indicates that the title material tends to lose oxygen beginning at 800°C, followed by a bigger loss of oxygen at 915°C. As a result, the hole concentration is reduced for materials sintered at higher temperatures. Table I shows the oxygen deficiency and the average valence state of Co

TABLE I The refined lattice constants for $NaCo_2O_{4-\delta}$ heated at different combinations of temperatures and partial pressure of oxygen

Heating temperature/Partial pressure of oxygen	a (Å)	c (Å)	V (Å)^3	δ[a]	Average valence of Co
700°C/100%	2.8348 (1)	10.9637 (4)	75.955 (5)	−0.10	+3.60
800°C/100%	2.8321 (0)	10.9660 (2)	75.872 (2)	0.16	+3.34
900°C/100%	2.8331 (0)	10.9607 (2)	75.885 (2)	0.21	+3.29
800°C/1%	2.8270 (0)	10.9341 (2)	75.675 (2)	–	–
900°C/1%	2.8274 (0)	10.9279 (4)	75.658 (4)	–	–

[a]The values of δ and the average valence state of Co are determined by averaging the results of three runs of titration and assuming the Na content is stoichiometric.

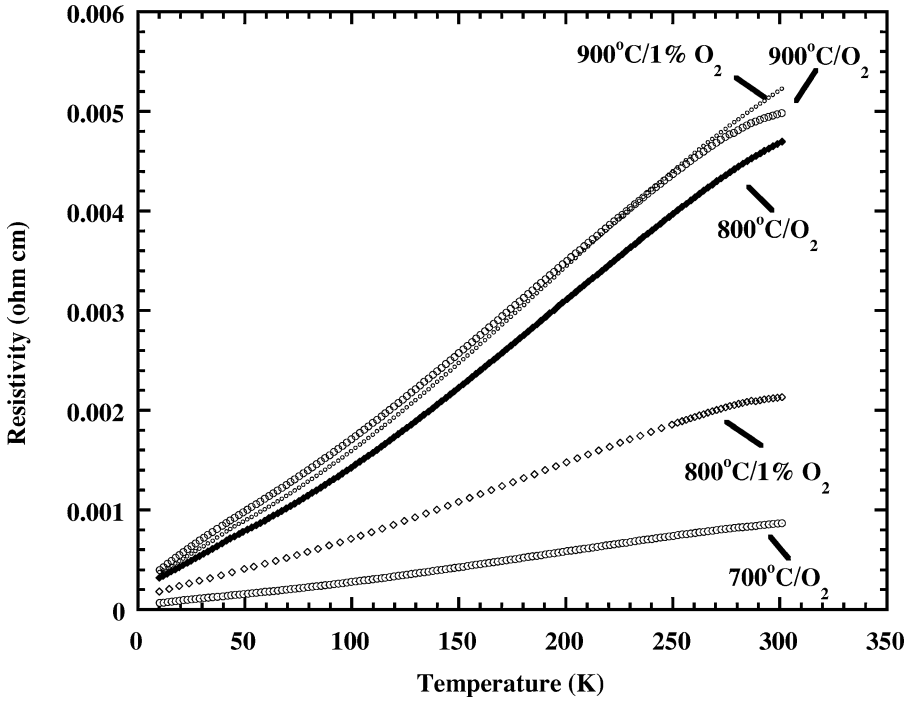

Figure 2 Temperature dependence of electrical resistivity for $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen.

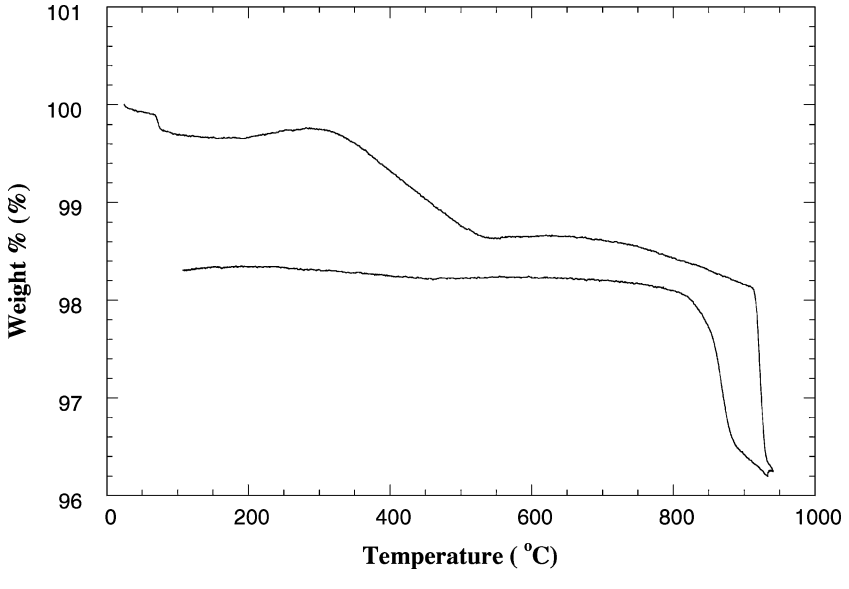

Figure 3 Thermogravimetric curve for $NaCo_2O_{4-\delta}$ heated from 30 to 950°C at the rate of 10.0°C/min. in flowing oxygen.

for samples prepared at various temperatures in pure flowing oxygen using the iodometric titration. These results indicate that the oxygen deficiency (the average valence of Co) increases (decreases) with increasing sintering temperature, which correlate well with the higher resistivity (lower carrier concentration) for the material sintered at 900°C in pure oxygen.

Thermopower is a sensitive probe of the topology of the Fermi surface and the energy dependence of the electron relaxation processes. Thermopower measurements are also a complementary and powerful tool to resistivity measurements in understanding the transport mechanism of materials. In general, the thermopower can provide two pieces information, i.e., the sign of carriers and the characteristic energy associated with the dominant charge carriers. The diffusion thermopower for metals can be expressed by the Mott formula [10],

$$S = \frac{\pi^2}{3}\frac{k_B^2}{e}T\left[\frac{d\ln\sigma(E)}{dE}\right]_{E=E_F}, \qquad (1)$$

where $\sigma(E)$ is the conductivity-like function, k_B the Boltzmann constant. Since the conduction of a metal is occurring in the vicinity of Fermi level, the average energy of electron with respect to the Fermi level is small. As a result, the bare diffusion thermopower is small and linear with temperature. In practice, the linearity of thermopower is scarcely observed, which could be caused by the phonon-drag effects [11], electron-phonon interaction enhancement [12] or strong Coulomb correlation

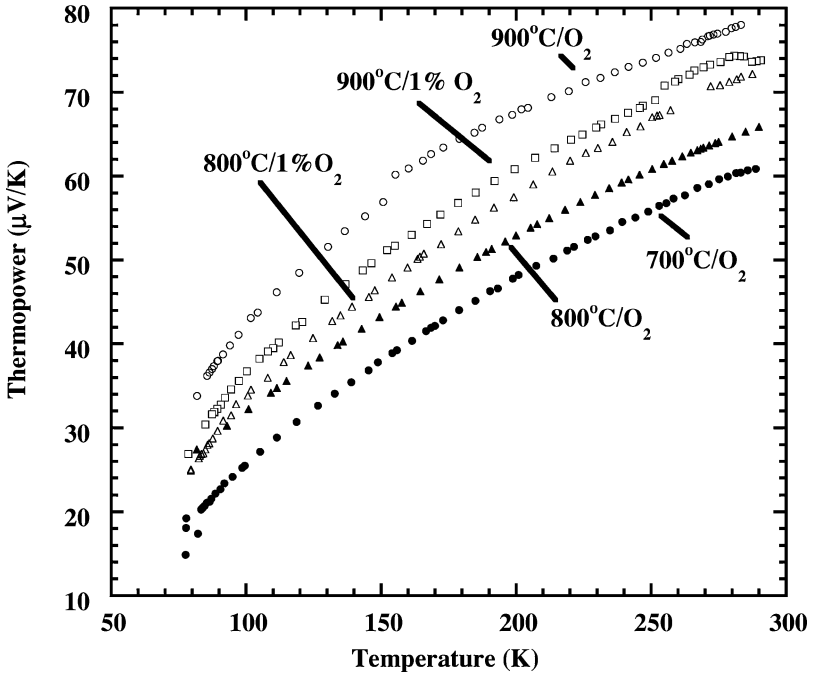

Figure 4 Temperature dependence of thermopower for $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen.

of electrons [13]. As shown in Fig. 4, the thermopower of all samples decreases with decreasing temperature and shows nonlinear behavior with respect to temperature. Specific-heat measurements suggest that $NaCo_2O_{4-\delta}$ is a strongly correlated system [14]. A theoretical calculation using the numerical diagonalization method indicates that the large value of thermopower is enhanced by the spin and orbital degrees of freedom which require a strong Coulomb correlation [15]. These theoretical and experimental studies seem to suggest that nonlinear behavior of thermopower is a consequence of strong electron correlation in $NaCo_2O_{4-\delta}$. In Fig. 4, the thermopower also shows little change in the shape of the temperature dependence, indicating little change of electronic structure of $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen. In cuprate superconductors [16, 17], the thermopower tends to increase as the oxygen deficiency (carrier concentration) increases (decreases). The title material $NaCo_2O_{4-\delta}$ shows similar correlation of thermopower and oxygen deficiency for the materials sintered at different

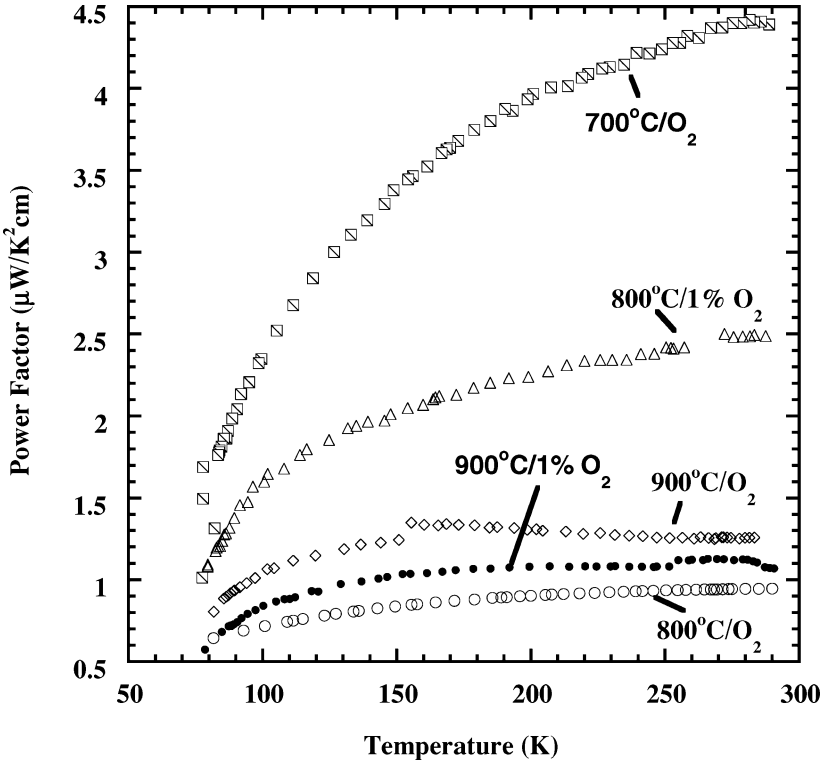

Figure 5 Temperature dependence of power factor for $NaCo_2O_{4-\delta}$ prepared at different combinations of temperature and partial pressure of oxygen.

temperature in pure oxygen flow. Both of the thermopower and resistivity increases as the material is sintered at higher temperature which resulting in higher oxygen deficiency (Table I). The calculated power factors of the materials are shown in Fig. 5. We find that $NaCo_2O_{4-\delta}$ prepared at 700°C in pure flowing oxygen exhibits the highest value of power factor.

4. Conclusions

We have prepared $NaCo_2O_{4-\delta}$ at temperature as low as 700°C using aqueous sol-gel methods and find that the electrical resistivity and thermopower varies with the sintering conditions. The higher resistivity and thermopower are observed for the material with higher oxygen deficiency. The sample prepared at the combination of 700°C and pure flowing oxygen exhibits the largest power factor. Further work is in progress to investigate the effects of the sodium content on the transport properties using the rapid heat-up techniques [18] for controlling the sodium content when calcining the sol-gel precursor powders.

Acknowledgments

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