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High temperature thermoelectric properties of oxide $Ca_9Co_{12}O_{28}$

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The electrical conductivity, Seebeck coefficient and thermal conductivity of oxide $Ca_9Co_{12}O_{28}$ with $Ca_2Co_2O_5$-type structure are 84 S cm^{-1}, 118 μV K^{-1} and 1.73 W m^{-1} K^{-1} respectively at 700 °C, and its figure of merit is 0.67×10^{-4} K^{-1}, showing that $Ca_9Co_{12}O_{28}$ is a potential material for high temperature thermoelectric energy conversion.

In recent years, increasing attention has been given to oxides as thermoelectric materials since oxides are very suitable for long-term use in air at high temperature. Several systems have been investigated, such as $(ZnO)_5In_2O_3$,[1] $In_2O_3 \cdot MO_x$,[2] (Zn,Al)O,[3] $(Ba,Sr)PbO_3$[4] and $(Ca,Ln)MnO_3$.[5] However, the values of the figure of merit Z ($Z = S^2\sigma/\kappa$, where S, σ and κ are the Seebeck coefficient, electrical conductivity and thermal conductivity, respectively) for such oxides are smaller than for alloys and semiconductors.[6] It has been reported that $NaCo_2O_4$ has a high figure of merit (up to 8.8×10^{-4} K^{-1}), but its application is limited because of the volatility of sodium above 800 °C and its hygroscopicity in air.[7] For practical thermoelectric applications, further investigations are necessary to find new oxide systems with high thermoelectric performance.

$Ca_9Co_{12}O_{28}$ was initially synthesized in 1968,[8] but no structure analysis or physical property measurements were made. $Ca_3Co_4O_9$ was synthesized as single crystals by Woermann and Muan in 1970 and a layered structure was suggested.[9] We find that the XRD patterns of the two oxides are both very similar to that of $Ca_2Co_2O_5$ which has a layered structure with ordered oxygen vacancies.[10] We have measured the thermoelectric properties of $Ca_9Co_{12}O_{28}$, and found that it is a good thermoelectric material.

$Ca_9Co_{12}O_{28}$ was prepared from reagent grade $CaCO_3$ and Co_2O_3 powders in stoichiometric ratio (12.011 g $CaCO_3$ and 13.269 g Co_2O_3). They were thoroughly mixed by ball milling and the mixture was calcined at 900 °C in oxygen gas flow for 24 h, ground, and pressed into pellets with a diameter of 18 mm. The pellets were sintered at 920 °C in oxygen gas flow for 24 h, reground, pressed into pellets, and then sintered at 1100 °C in oxygen gas flow for another 24 h.

X-Ray powder diffraction analysis was carried out with a Rigaku diffractometer using Cu-Kα ($\lambda = 0.1506$ nm) radiation with silicon powder used as the internal standard. The specimens for the electrical measurements were rectangular bars of dimensions $5 \times 5 \times 15$ mm cut out of the sintered pellets. Two Pt–Pt/Rh thermocouples were attached to both end surfaces of the sample bar, and another two Pt electrodes were pasted between them in the standard four-wire arrangement. Electrical conductivity was measured by a dc four-probe technique. For thermoelectricmotive force measurements, the temperature gradient in the sample bar was generated by passing cool air through an alumina tube mechanically attached to one end of the sample bar. Thermoelectricmotive force measured as a function of temperature difference gave a straight line when plotted, with the slope being equal to the Seebeck coefficient. The thermal conductivity was determined from the thermal diffusivity and the specific heat capacity measured by a laser flash technique.

Fig. 1 shows the X–ray diffraction pattern of $Ca_9Co_{12}O_{28}$. All the peaks can be indexed on the basis of the $Ca_2Co_2O_5$-type structure. $Ca_9Co_{12}O_{28}$ crystallizes in the orthorhombic system with $a = 1.0893$, $b = 1.0722$ and $c = 0.7980$ nm. $Ca_9Co_{12}O_{28}$ can be written as $Ca_{1.5}Co_2O_{4.67}$ and can be considered as having the same structure as $Ca_2Co_2O_5$, but with 25% of the Ca sites vacant.

The graph of electrical resistivity *vs.* 1/temperature in range 20–700 °C is shown in Fig. 2. The electrical conductivity increases slightly with temperature and its value is 83.4 S cm^{-1} at 700 °C. The relationship between log ρ and $1/T$ is not linear in the measured temperature range, and the excitation energies change with temperature, indicating a weakly localized system.

Fig. 3 presents the absolute values of Seebeck coefficients, S, *vs.* temperature for $Ca_9Co_{12}O_{28}$. The oxide has positive values of S, indicating p-type conduction. The absolute values of S increase with increasing temperature, and reach 118 μV K^{-1} at 700 °C. The power factor, $S^2\sigma$, increases with increasing temperature in the measured temperature range, and its value reaches 1.16×10^{-4} W K^{-2} m^{-1} at 700 °C.

Fig. 4 shows the temperature dependence of thermal conductivity of $Ca_9Co_{12}O_{28}$. The value at 300 K is 1.93 W K^{-1} m^{-1} which is similar to other transition metal oxides with perovskite structures. However, the thermal conductivity decreases with increasing temperature up to 600 °C, where its value is 1.70 W m^{-1} K^{-1}. At 700 °C, the thermal conductivity is 1.73 W m^{-1} K^{-1} which is only slightly larger than that at

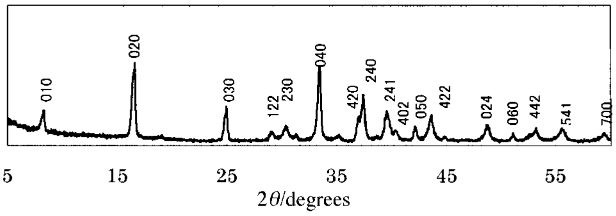

Fig. 1 X-ray diffraction pattern of $Ca_9Co_{12}O_{28}$.

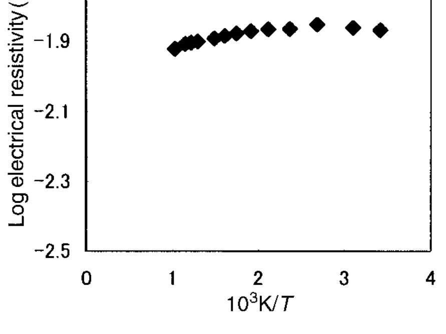

Fig. 2 Log electrical resistivity *vs.* 1/temperature for $Ca_9Co_{12}O_{28}$.

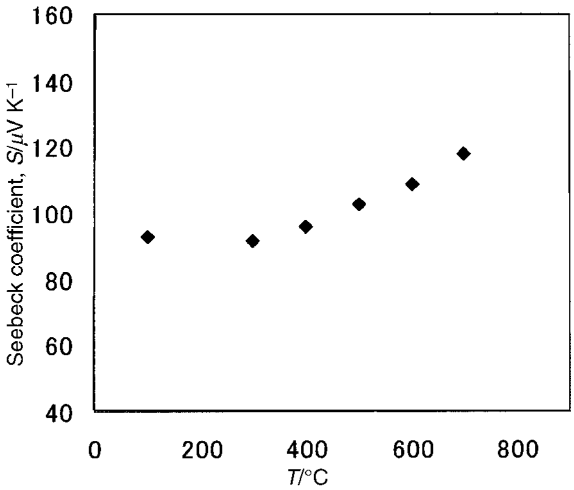

Fig. 3 Seebeck coefficients *vs.* temperature for $Ca_9Co_{12}O_{28}$.

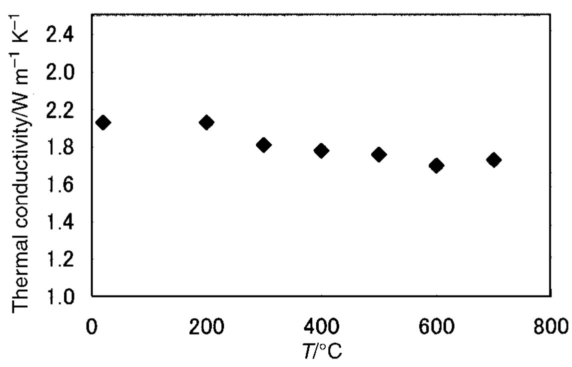

Fig. 4 Thermal conductivity *vs.* temperature for $Ca_9Co_{12}O_{28}$.

600 °C. The thermal conductivity can be expressed by the sum of a lattice component (κ_l) and an electronic component (κ_e) as $\kappa=\kappa_l+\kappa_e$.[4] Because $\kappa_e=L\sigma T$, where L is the Lorenz number, κ_e of the oxide increases with temperature. Hence the decrease in thermal conductivity of $Ca_9Co_{12}O_{28}$ with temperature results from the decrease of the lattice component κ_l which is due to an increase in phonon scattering.

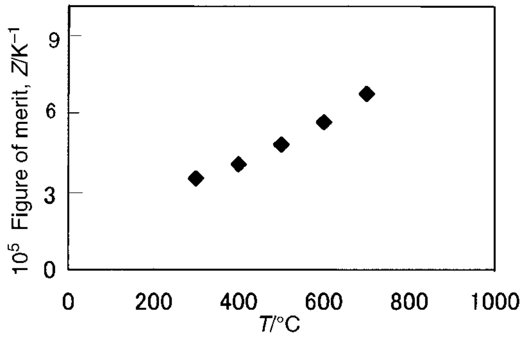

Fig. 5 Figure of merit Z *vs.* temperature for $Ca_9Co_{12}O_{28}$.

The graph of the figure of merit Z of $Ca_9Co_{12}O_{28}$ *vs.* temperature is presented in Fig. 5. The value of Z increases with temperature over the measured temperature range, reaching 0.67×10^{-4} K^{-1} at 700 °C, at which stage it is still increasing. According to Fig. 5, the value of Z would reach 1.0×10^{-4} K^{-1} at 900–1000 °C.

It can be concluded from our results that the oxide $Ca_9Co_{12}O_{28}$ is a potential material for high temperature thermoelectric energy conversion. Substitution of Ca or Co by other elements is in progress in an attempt to improve the value of Z.

References

1 M. Kazeoka, H. Hiramatsu, W. Seo and K. Koumoto, *J. Mater. Res.*, 1998, **13**, 523.
2 M. Ohtaki, D. Ogura, K. Eguchi and H. Arai, *Mater. Chem.*, 1994, **4**, 653.
3 M. Ohtaki, D. Ogura, K. Eguchi and H. Arai, *J. Appl. Phys.*, 1996, **79**, 1816.
4 M. Yasukawa and N. Murayama, *J. Mater. Sci. Lett.*, 1997, **16**, 1731.
5 M. Ohtaki, D. Ogura, K. Eguchi and H. Arai, *J. Solid State Chem.*, 1995, **120**, 105.
6 T. Kobayashi, H. Takizawa, T. Endo, T. Sato and M. Shimada, *J. Solid State Chem.*, 1991, **92**, 116.
7 T. Itoh, T. Kawata, T. Kitajima and I. Terasaki, *Phys. Rev. B*, 1997, **56**, 12685.
8 JCPDS Card, 21–139.
9 E. Woermann and A. Muan, *J. Inorg. Nucl. Chem.*, 1970, **32**, 1455.
10 K. Vidyasagar, J. Gopalakrishnan and C. N. R. Rao, *Inorg. Chem.*, 1984, **23**, 1206.

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