Transactions of the Materials Research Society of Japan 30[2] 519-522 (2005)

Preparation and thermoelectric properties of textured $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics by spark plasma sintering method

T.Yoshimura[1], K.Nishio[2], K.Takahashi[1], K.Tokiwa[1], T.Kineri[3], A.Yasumori[2] and T.Watanabe[1]
[1]Department of Applied Electronics
[2]Department of Materials Science and Technology
Tokyo University of Science. 2641 Yamazaki Noda-shi Chiba 278-8510, Japan
j8103654@ed.noda.tus.ac.jp
[3]Department of Materials Science & Environmental Engineering
Tokyo University of Science Yamaguchi. 1-1-1 Daigakudoori Onoda-shi Yamaguchi 756-0884

The preparation of highly textured $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics and their thermoelectric properties have been reported. Plate-like $(Ca_2CoO_3)_{0.62}CoO_2$ particles were synthesized from a solution consisting of metal salts, citric acid, organic solvents, and H_2O. $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics were prepared by a spark plasma sintering (SPS) process, which is a new type of sintering method for this material. Plate-like pure phase $(Ca_2CoO_3)_{0.62}CoO_2$ was obtained by heat treatment at 1173 K for 3 hr in air. The average diameter and thickness of an obtained plate-like particle was 2 and 0.5 μm, respectively. The grains were oriented easily by applying uni-axial pressure. Ceramics of a high density (4.6814 g/cm^3) and orientation (Lotgering factor of 35%) were obtained using the SPS method at 1073 K (SPS temperature) for 2 min at 29.4 MPa (uniaxial pressure) in an Ar atmosphere (atmospheric pressure). These ceramics showed major anisotropic and high performance in thermoelectric properties, including along the in-plain (*a-b* plain) direction resistivity of 9.6 mΩcm, Seebeck coefficient of 138.3 μV/K, and power factor of 1.99 μW/cmK^2, as well as along the out-of-plain direction resistivity of 22.5 mΩcm, Seebeck coefficient of 132.9 μV/K, and power factor of 0.78 μW/cmK^2.
Key words: $(Ca_2CoO_3)_{0.62}CoO_2$, thermoelectric properties, highly oriented, spark plasma sintering process, modified Pechini process

Introduction

Thermoelectric materials having the properties of large thermo-power, low resistivity, and low thermal conductivity were investigated. Layered cobalt oxides, i.e., Na-Co-O and Ca-Co-O have been used by many researchers because they show low resistivity and low thermal conductivity [1-7].

$(Ca_2CoO_3)_{0.62}CoO_2$ consists of Ca_2CoO_3 triple rock-salt layers and CoO_2 layers alternately stacked along the *c*-axis to form a misfit-layered structure. Thus, the physical properties are highly two-dimensional compared with *a* or *b*-axis direction. $(Ca_2CoO_3)_{0.62}CoO_2$ has a large Seebeck coefficient in spite of low resistivity and relatively low thermal conductivity. However, a large single crystal is difficult to obtain, and thermoelectric properties of $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics are inferior to that of single crystal [7].

The spark plasma sintering (SPS) process is easy, cost effective, and requires no previous sintering experience. And, it allows metal compounds, ceramics, polymers, and thermoelectric semiconductors to be synthesized. SPS is an effective method to prepare ceramics with superior density and to reduce grain growth [8-10]. When compared with the conventional powder sintering method, SPS allows preparing ceramics at low temperatures and at a shorter duration by charging the intervals between powder particles with electrical energy and by efficiently and momentarily applying a highly energized spark electrical discharge. The relatively low temperature and short sintering duration of the SPS process would be advantageous in keeping in check the exaggerated grain growth.

In this study, we prepared textured $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics with major anisotropic and high thermoelectric properties. A plate-like $(Ca_2CoO_3)_{0.62}CoO_2$ precursor powder was prepared using a modified Pechini method. The powder was sintered by SPS with an application of uni-axis pressure for an obtained one axis-oriented $(Ca_2CoO_3)_{0.62}CoO_2$ ceramic.

Experimental procedure

$(Ca_2CoO_3)_{0.62}CoO_2$ powders were prepared using the modified Pechini method. Pechini's method [11] is well known as a simple method for preparing metal oxide powders where polymeric precursors are made from metal salts, ethylene glycol, and citric acid using a low temperature heat-treatment. This method allows the metal cations to be mixed at a molecular level and stoichiometric compositions to be achieved by chelating the metal ions in solution with citric acid. Many studies using this method have been reported [12-15]. Furthermore, this process offers several advantages in

fabricating ceramic thin films, including low cost, homogeneous compositions, high purity, and low heat-treatment temperatures. In this study, we prepared a precursor solution with metal salts ($Ca(NO_3)_2{\cdot}4H_2O$ and $Co(NO_3)_2{\cdot}6H_2O$), citric acid, and ethylene glycol monomethyl ether. These metal salts were dissolved with a solution consisting of citric acid and ethylene glycol monomethyl ether. The solution was refluxed at 333 K for 1 hr. The precursor solution was heated at 723 K for 2 hr after drying at 388 K. To obtain the plate-like precursor powder, the dried powder was heat treated at 1173 K in air for 3 hr.

Spark plasma sintering (SPS) was carried out using a spark plasma sintering system (DR. SINTER LAB 515S, Sumitomo Coal Mining Company, Ltd., Japan). For the SPS, the precursor powder was placed in a graphite die, and it was heat-treated up to 1073 K at a rate of 100 K/min and then kept at that temperature for 2 min under a pressure of 29.4 MPa in an Ar atmosphere (1013 hPa). After reaching and holding the sintering temperature in the SPS process, the electric power was turned off at 1073 K, and the sample was cooled to room temperature in the SPS chamber.

The relative densities of the samples were measured using Archimedes' method. An investigation was carried out using an SEM-5800LV system (JEOL Ltd., Japan). The surface of the sample was removed by using HCl (1 mol/L) to observe the fine structure of the sample clearly. XRD patterns of powders and ceramics were measured using a Rint-1000 system (Rigaku Co., Japan) and X-ray diffractometer model CN4148 (Rigaku Co., Japan). The electrical properties were measured using a PPMS-6000 system (Quantum Design Japan).

The Seebeck coefficient and electrical resistivity were measured using the standard four-probe method (ULVAC-RIKO, ZEM-2) in a flowing He atmosphere at a temperature range of 300 to 773 K along the in-plane and out-of-plane directions, respectively.

Results and discussion

The homogeneous precursor solution was obtained using the modified Pechini method with ethylene glycol monomethyl ether. Figure 1 shows a SEM image of the $(Ca_2CoO_3)_{0.62}CoO_2$ powders prepared using the modified Pechini method. The plate-like $(Ca_2CoO_3)_{0.62}CoO_2$ particles were easily obtained. The average diameter and thickness of the obtained plate-like particle were 2 and 0.5 μm, respectively. The shape of the crystal grains prepared from the solution was thought to be influenced more from that method's crystal structure than the one of the other method. It was thought that the plate-like particles were easily aligned by applying uni-axial pressure.

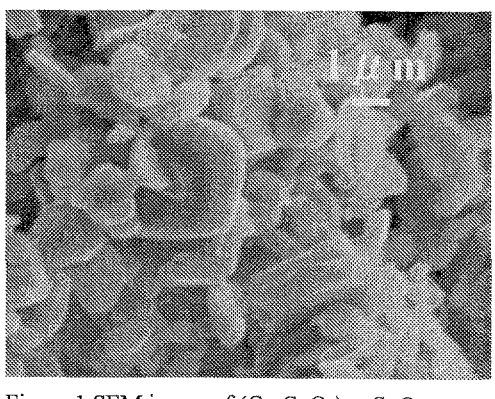

Figure 1 SEM image of $(Ca_2CoO_3)_{0.62}CoO_2$ precursor powders.

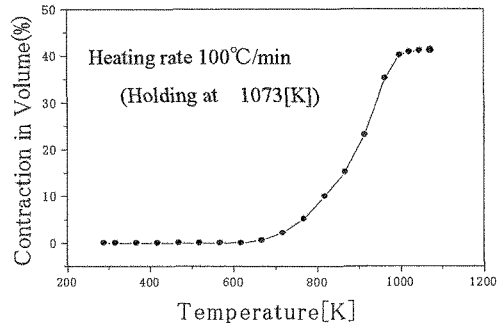

Figure 2 Sintering temperature dependence of contribution in volume of $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics.

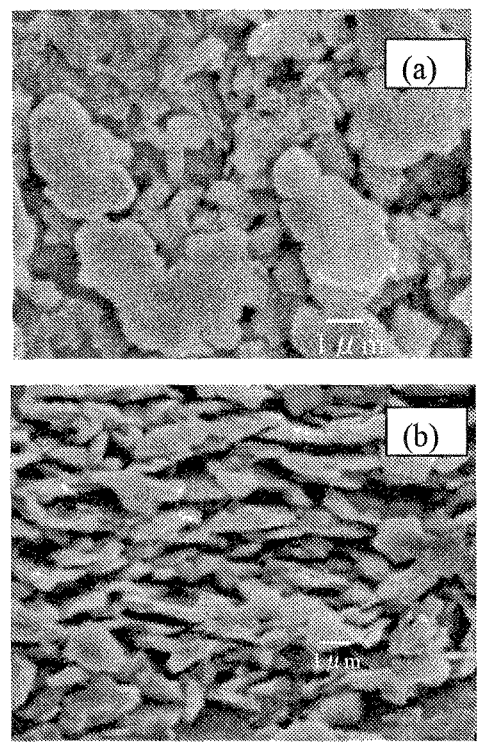

Figure 3 SEM images of $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics, in-plane (a) and out-of-plane (b).

Figure 2 shows shrinkage as a function of the heat treatment temperature for $(Ca_2CoO_3)_{0.62}CoO_2$ powder. Uni-axial pressure (29.4 MPa) was applied to the sample during treatment in the SPS chamber. Shrinkage of the sample occurred within a narrow temperature range over a short time. The obtained ceramic had a high bulk density (density: 4.6814 g/cm^3). In an SEM observation, the densification was investigated, but the grain growth was not investigated in the sample (see figure 3). From these results, the shrinkage mechanism of the sample was thought to not be normal sintering, but a heat treatment or Joule's heat treatment. It may involve

another mechanism in the SPS sintering. Furthermore, figure 3 shows major anisotropic properties (compare (a) with (b)).

Figure 4 shows XRD patterns of $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics obtained with the platelet powder synthesized using the modified Pechini method measured for the in-plane (a) and out-of-plane (b) directions and that prepared from a powder synthesized by a conventional solid-state reaction measured for the in-plane (c), respectively. Figure 4 (a) shows that peaks of *00l* phases are more intense than those of other phases in diffraction patterns of figure 4 (b) and (c). Figure 4 shows that the *c*-axis of prepared $(Ca_2CoO_3)_{0.62}CoO_2$ ceramic seems to align perpendicularly for a uni-axis pressure direction. From these results, plate-like grains were aligned in a *c*-axis direction by applying uni-axis pressure.

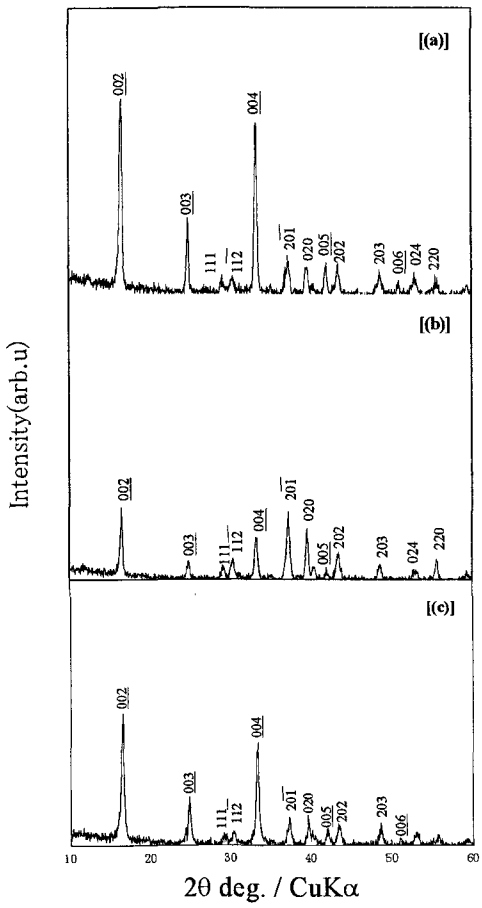

Figure 4 XRD patterns of $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics obtained with the platelet powder synthesized by modified Pechini method measured for along in-plane (a) and out-of-plane (b), and that prepared from a powder synthesized by conventional solid-state reaction measured for along in-plane (c).

The degree of texture was evaluated in terms of the Lotgering factor [7],

$$f=(p-p_0)/(1-p_0), \qquad (1)$$

where

$$p=\Sigma I_{(00l)}/\Sigma I_{(hkl)} \qquad (2)$$

for the diffraction pattern of the sample, and $p_0 = p$ for a randomly oriented powder diffraction pattern from reference. A Lotgering factor of the sample along an in-plane direction shows the value above 35%. From these results, we found that the ceramic samples were obtained as oriented ceramic. $(Ca_2CoO_3)_{0.62}CoO_2$ consisted of Ca_2CoO_3 triple rock-salt layers and CoO_2 layers alternately stacked along the *c*-axis to form a misfit-layered structure. The obtained sample was expected to show major anisotropic and high thermoelectric and electric properties.

Figure 5 shows the temperature dependent Seebeck coefficient (S), resistivity (Ω) (a), and power factor (S^2/Ω) (b) of the oriented $(Ca_2CoO_3)_{0.62}CoO_2$ ceramic along the in-plane and out-of plain directions, respectively. These results indicate that these ceramics showed major anisotropic and high performance in thermoelectric properties. In this study, $(Ca_2CoO_3)_{0.62}CoO_2$ dense ceramic was obtained using a short treatment in SPS sintering. And highly textured ceramic was obtained by using plate-like particles prepared with the modified Pechini method. The $(Ca_2CoO_3)_{0.62}CoO_2$ ceramic showed major anisotropic and high performance in thermoelectric properties, including along the in-plain direction resistivity of 9.6 mΩcm, Seebeck coefficient of 138.3 μV/K, and power factor of 1.99 μW/cmK^2, as well as along the out-of-plain direction resistivity of 22.5 mΩcm, Seebeck coefficient of 132.9 μV/K, and power factor of 0.78 μW/cmK^2.

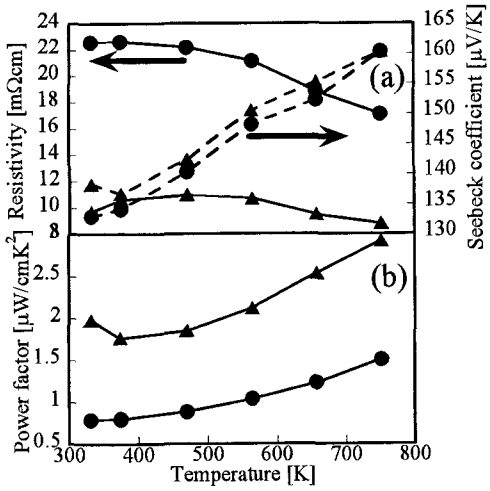

Figure 5 Electrical resistivity, Seebeck coefficient (a) and Power factor (S^2/Ω) (b) , $(Ca_2CoO_3)_{0.62}CoO_2$ ceramics along in-plane (▲) and those of out-of-plane (●) direction, respectively.

Conclusions

Highly textured $(Ca_2CoO_3)_{0.62}CoO_2$ ceramic for thermoelectric material was obtained using a spark plasma sintering method with a plate-like precursor powder. Plate-like $(Ca_2CoO_3)_{0.62}CoO_2$ particles were synthesized from a solution consisting of metal salts, citric acid, organic solvents, and H_2O. Plate-like pure phase $(Ca_2CoO_3)_{0.62}CoO_2$ was obtained by a heat treatment at 1173 K for 3 hr in air. The average diameter

and thickness of the obtained plate-like particle was 2 and 0.5 μm, respectively. The grains were oriented easily by applying uni-axial pressure. Ceramics of a high density (density: 4.6814 g/cm^3) and orientation (Lotgering factor: 35%) were obtained using the SPS method at 1073 K (SPS temperature) for 2 min at 29.4 MPa (uni-axial pressure) in an Ar atmosphere (atmospheric pressure). These ceramics showed major anisotropic and high performance in thermoelectric properties, including along the in-plain direction resistivity of 9.6 mΩcm, Seebeck coefficient of 138.3 μV/K, and power factor of 1.99 μW/cmK^2, as well as along the out-of-plain direction resistivity of 22.5 mΩcm, Seebeck coefficient of 132.9 μV/K, and power factor of 0.78 μW/cmK^2.

Reference

1) I. Terasaki, Y. Sasago, K. Uchinokura, Phys. Rev. B 56 (1997) R12685-R12687
2) H. Yakabe, K. Kikuchi, I. Terasaki, Y. Sasago, K. Uchinokura, Proceedings of the 16th International Conference on Thermoelectrics, (1997) 523-527
3) T. Itoh, T. Kawata, T. Kitajima, I. Terasaki, Proceedings of the 17th International Conference on Thermoelectrics, (1998) 567-569
4) I.Terasaki, Proceedings of the 19th International Conference on Thermoelectrics, (2000) 20-24
5) S. Li, R. Funahashi, I. Matsubara, K. Ueno, S. Sodeoka, H. Yamada, J. Mter. Chem., 9 (1999) 1659-1660
6) S. Li, R. Funahashi, I. Matsubara, K. Ueno, S. Sodeoka, H. Yamada, Chem. Mater., 12 (2000) 2424-2427
7) A. Masset, C. Michel, A. Maignan, M. Hervieu, et al., Phys. Rev B 62 (2000) 166.
8) Y. W. Gu, K. A. Khor, P. Cheang, Biomater., 25, (2004) 4127-4134
9) Dongli Wang, Lidong Chen, Qin Yao, Jianguo Li, Solid State Com., (2004) 615-618
10) L. G. Yu, K. A. Khor, H. Li, P. Cheang, Biomater. 24 (2003) 2695-2705
11) M. P. Pechini, US Patent (1967) 3330697
12) M. S. G. Baythoun, F. R. Sale, J. Materials Science 17 (1982) 2757-2769
13) L. W. Tai, P. A. Lessing, J.Mater. Res., 7 (1992) 502-510
14) S. Roy, W. Sigmund and F. Aldinger, J. Mater. Res. 14 (1999) 1524-1531
15) Ch. L. Robert, F. Ansart, C. Deloget, M. Gaudon, A. Rousset, Mater. Res. Bull. 36 (2001) 2083-2101

(Received December 23, 2004; Accepted February 15, 2005)