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Ceramics International 33 (2007) 1305–1308
CERAMICS INTERNATIONAL
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Synthesis of highly textured $Ca_3Co_4O_9$ ceramics by spark plasma sintering

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Received 1 February 2006; received in revised form 16 February 2006; accepted 15 April 2006
Available online 12 September 2006

Abstract

Highly textured $Ca_3Co_4O_9$ ceramics were successfully prepared by spark plasma sintering using plate-like $Ca_3Co_4O_9$ particles synthesized by the citrate sol–gel method. The microstructure and electrical properties of the samples were investigated. The results show that spark plasma sintering is an effective technology to prepare textured $Ca_3Co_4O_9$ ceramics and that the electrical conductivity of the textured $Ca_3Co_4O_9$ ceramics is anisotropic in various directions. At 700 °C, the electrical resistivity of the sample parallel to the press direction is 6.13×10^{-5} Ω m, which is a very low value reported so far.

Keywords: C. Electrical properties; $Ca_3Co_4O_9$ ceramics; Spark plasma sintering

1. Introduction

In recent years, increasing attention has been given to oxides as high temperature thermoelectric materials for power generation because of their high thermal stability, oxidation resistance and weak-toxicity. Several systems have been investigated, such as NiO, $(Zn_{1-x}Al_x)O$, $(ZnO)_5In_2O_3$, $(Ca_{0.9}M_{0.1})MnO_3$ and Fe_2O_3 [1–6]. However, the values of figure-of-merit, Z ($Z = S^2\sigma/\kappa$, where S, σ and κ are Seebeck coefficient, electrical conductivity and thermal conductivity, respectively), of such oxides are smaller than those of alloys and semiconductors. As a result, the optimum thermoelectric material should simultaneously exhibit large S, large σ and small κ. In order to obtain large ZT, we therefore need to increase S and σ without increasing κ.

Recently, misfit layered $Ca_3Co_4O_9$ was reported to exhibit metallic conductivity, extraordinary large s value and low κ value [7–12]. $Ca_3Co_4O_9$ has a layered structure in which two different kinds of Co–O layers alternate in the direction of the *c*-axis. In one of the layers, Co atom is surrounded by six O atoms in an octahedral configuration and the octahedral are edge-shared (CoO_2 layers). In the other layers, Ca, Co and O form triple rock-salt ($Ca_2CoO_{3+\delta}$) layers. Crystals with a layered structure can be considered as natural superlattices, which consist of conducting and insulating layers stacked alternately and should offer higher thermoelectric performance. Considering of the anisotropic electrical transport properties $Ca_3Co_4O_9$ textured polycrystals are needed for the application in the thermoelectric field. However, it is difficult to prepare textured $Ca_3Co_4O_9$ ceramics by conventional solid-state method and ordinary sintering technique [7–9]. Masuda et al. recently reported the fabrication of textured $Ca_3Co_4O_9$ ceramics by combining the templated grain growth technique (TGG) with hot pressing (HP) to improve the thermoelectric properties [13]. Tani et al. utilized the reactive templated grain growth (RTGG) technique to prepare C-aligned thermoelectric layered cobaltites [14]. And the results show the obtained C-aligned $Ca_3Co_4O_9$ ceramics exhibit much higher electrical conductivity than that of randomly oriented ceramics [13,14].

In this paper, textured $Ca_3Co_4O_9$ ceramics were fabricated using spark plasma sintering (SPS) process in combination with plate-like $Ca_3Co_4O_9$ particles prepared by citrate sol–gel method. The grain orientation in the SPS process and the electrical properties of the textured $Ca_3Co_4O_9$ ceramics were investigated. To date, to our knowledge, no similar work has been reported.

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0272-8842/$32.00
doi:10.1016/j.ceramint.2006.04.011

2. Experimental procedures

2.1. Preparation of plate-like $Ca_3Co_4O_9$

In a typical procedure, stoichiometric of hydrous calcium and cobalt nitrates were dissolved in an aqueous solution of citrate acid. The resulting solution was heated at 80 °C with magic stirring in order to obtain the gel. The gel was dried initially at 120 °C for 12 h and further heat treated at 800 °C for 2 h in a muffle furnace at an increasing temperature rate of 5 °C/min.

2.2. SPS sintering and characterization

The powders were placed into a graphite die (20 mm in diameter), and an electric current of 400–1000 A was applied under a pressure of 30 MPa. During this procedure, the temperature increased to 700, 750, 800 and 850 °C at a rate of 100 °C/min. The powders were maintained at the desired temperature for 5 min, and then the electric current was switched off, the pressure was released, the sample was cooled to room temperature.

The phase identification of the obtained samples was made by X-ray diffraction on a Japan Rigaku D/max-3c. The microstructure of the powder was examined by scanning electron microscopy on a Hitachi SEM-570. The microstructure of the sintered sample was examined using field emission scanning electron microscopy on a JEOL JSM-6500F. To investigate the electrical properties, samples perpendicular and parallel to the pressing direction were cut from the sintered pellets as shown schematically in Fig. 1. The Seebeck coefficient and the electrical resistivity were measured simultaneously using ULVAC ZEM-2 in the helium atmosphere. The densities of the sintered samples were measured using Archimedes method.

3. Results and discussion

Fig. 2 shows the SEM micrograph of the $Ca_3Co_4O_9$ particles synthesized by citrate sol–gel method. Plate-like particles are about 0.3 μm in length and 0.2 μm in thickness. The XRD pattern shows all the peaks are the diffraction peaks from $Ca_3Co_4O_9$.

Fig. 3 shows XRD patterns of as sintered samples for the surfaces perpendicular and parallel to the press direction.

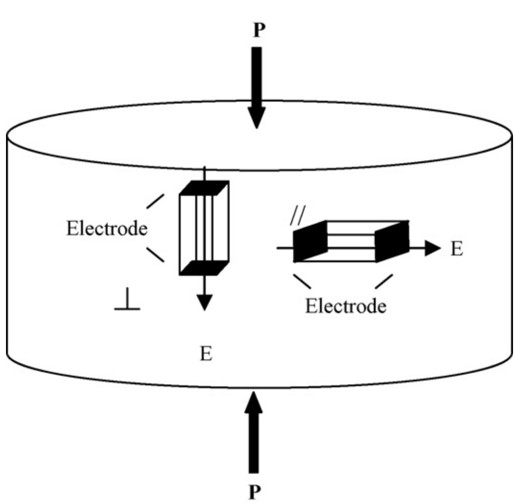


Fig. 1. The schematic of the sample cut from the sintered pellets along the direction parallel and perpendicular to the pressing direction.

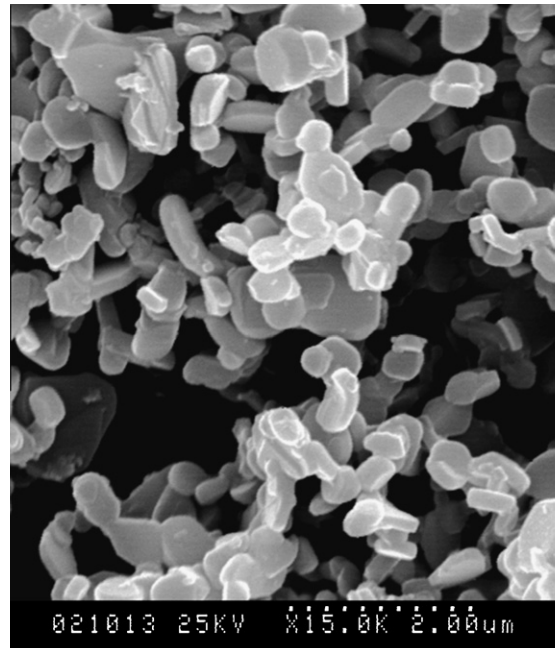


Fig. 2. SEM micrograph of the $Ca_3Co_4O_9$ particles synthesized by citrate sol–gel method.

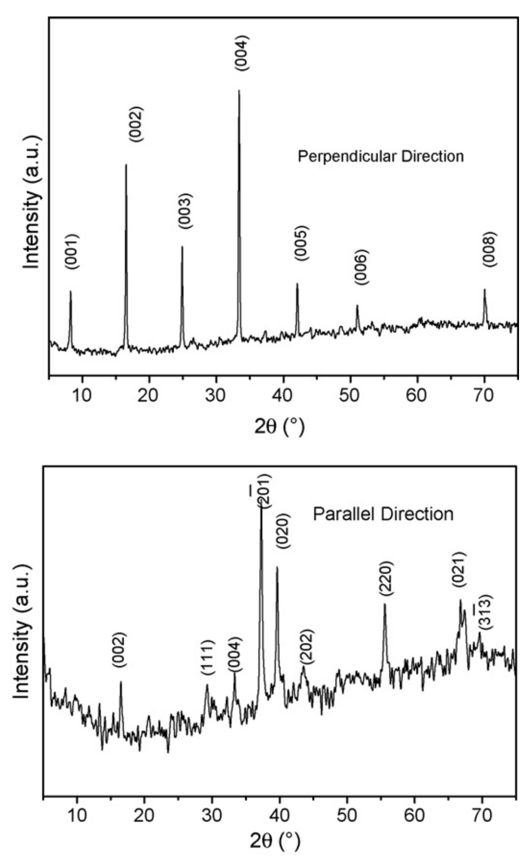
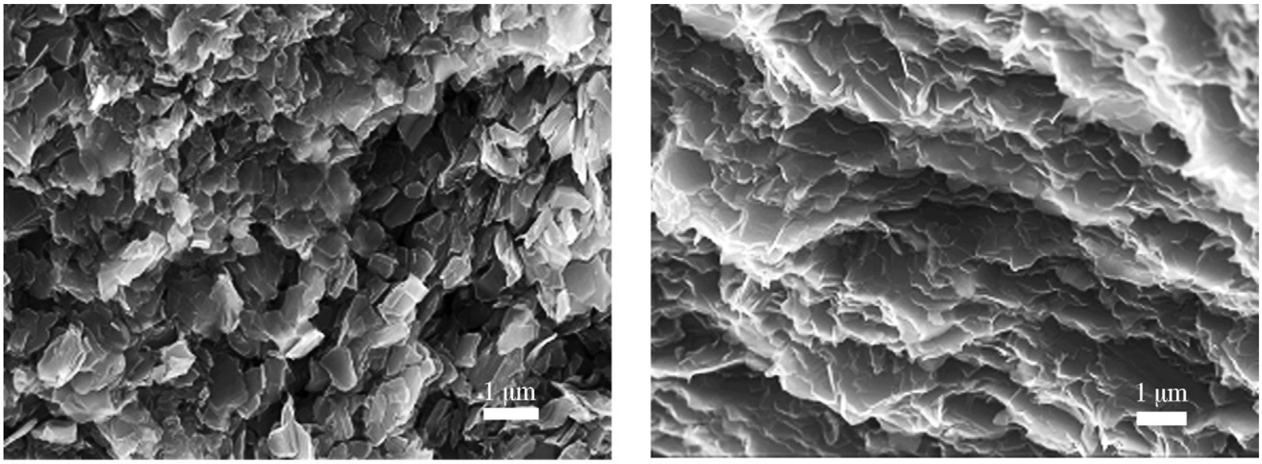


Fig. 3. XRD patterns of the SPS sample in parallel and perpendicular directions.



(a) (b)

Fig. 4. SEM micrograph of SPS sample: (a) perpendicular and (b) parallel to the press direction.

The perpendicular surface exhibits intense diffractions from [0 0 l] planes but little diffraction from other crystal planes, while the parallel surfaces exhibits almost no diffraction from [0 0 l] planes, indicating that the *c*-axis, which is perpendicular to the sublattice layer, is preferentially oriented. The degree of orientation of the SPS sample reached nearly one, which is much higher than that of the sample prepared by the solid state method and SPS technique [15]. Nan et al. reported the preparation of $Ca_3Co_4O_9$ ceramics by citrate sol–gel method and ordinary pressless sintering. However, the XRD pattern and SEM micrograph presents no preferred orientation [16]. Matsubara et al. reported the synthesis of $Ca_3Co_4O_9$ ceramics by solid-state reaction and SPS [17]. The XRD pattern and microstructure also show no grain alignment. Hao et al. prepared textured bismuth titanate ceramics by SPS using plate-like bismuth titanate particles [18]. In order to confirm that grain alignment was really induced by SPS, we sintered $Ca_3Co_4O_9$ ceramics at 800 °C for 2 h by conventional pressless sintering method using the plate-like powders synthesized by the citrate sol–gel method in a muffle furnace for comparison. The XRD pattern as-prepared sample exhibits not only [0 0 l] peaks but also other peaks and shows no preferred orientation. This indicates that SPS is an effective technique for grain alignment. Hence, the reasons of the preparation textured $Ca_3Co_4O_9$ ceramics may be explained from two aspects. First, the morphology of $Ca_3Co_4O_9$ particles by citrate sol–gel method are regular plate-like. However, it is difficult to obtain the powders with uniform morphology by solid-state method. Secondly, SPS is an effective sintering technology to prepare textured ceramics due to its special sintering mechanism. During the sintering process, spark discharges occur between powder particles, and intense heating of the contact zones of the powder take place, which leads to melting on the contact surfaces of the particles in a very short time. With an increase of the liquid phase, the plastic yielding value decrease, and plastic deformation occurs throughout the particles under the press used in the sintering process. Hence, the particles rearrangement occurs and orientation of the particles takes place [18].

Fig. 4(a) presents a SEM micrograph of the surface perpendicular to the press direction; Fig. 4(b) shows a SEM micrograph of the surface parallel to the press direction. All the samples were sintered at 800 °C for 5 min under a pressure of 30 MPa. The micrographs show a highly textured $Ca_3Co_4O_9$ ceramics.

The densities of the SPS samples sintered at different temperature are given in Fig. 5. It can be seen from Fig. 5 the densities increased with increasing sintering temperature. Although the sintering temperature is low and the sintering time is short, a dense bulk with a density of >95% of its theoretical density was obtained using SPS.

The electrical resistivity of the SPS sample sintered at 800 °C for 5 min has been measured in the parallel and perpendicular directions. Temperature dependence of the electrical resistivity is shown in Fig. 6. As suspected, the data of electrical resistively exhibit anisotropy properties and the value of the perpendicular-cut sample is greater than the parallel-cut sample. This result is consistent with Masuda and Tani reported [13,14]. The electrical resistively in both directions decrease with increasing the measured temperature. At 700 °C, the electrical resistivity of the sample parallel to the press direction is $6.13 \times 10^{-5}\ \Omega$ m, which is a very low value reported so far.

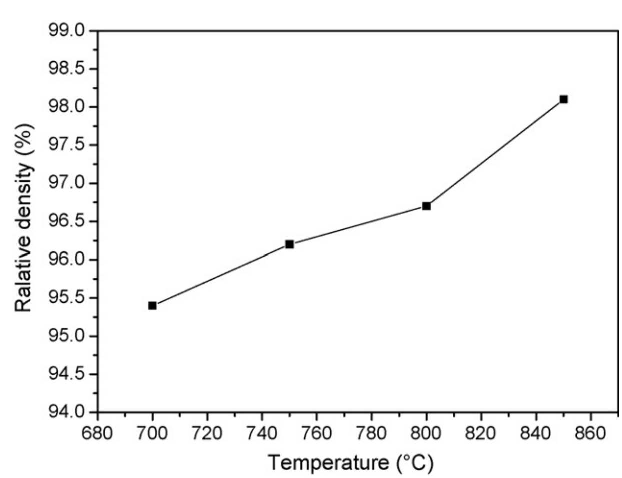


Fig. 5. Relationship between relative density and sintering temperature by SPS.

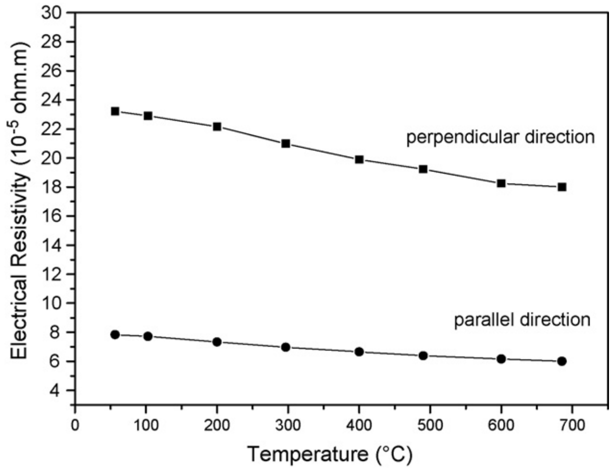


Fig. 6. Temperature dependence of the electrical resistivity of sample in parallel and perpendicular directions.

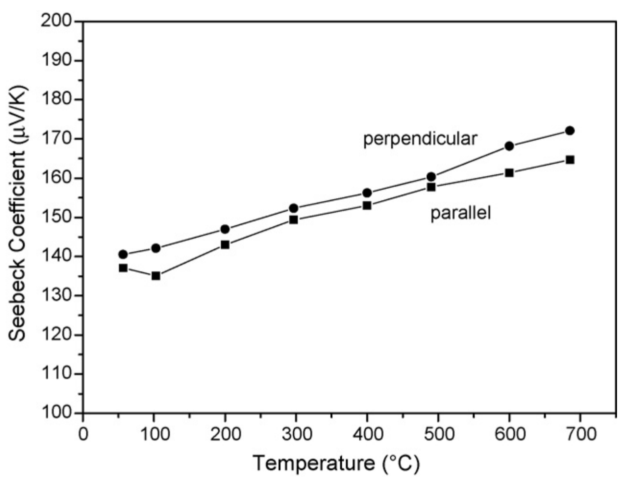


Fig. 7. Temperature dependence of the Seebeck coefficient of sample in parallel and perpendicular directions.

Temperature dependence of the Seebeck coefficient is shown in Fig. 7. It can be seen from Fig. 7 the Seebeck coefficient increase with increasing the measured temperature .The Seebeck coefficient values of the sample in both direction are nearly equal, indicating that the Seebeck coefficient is insensitive to orientation and micro-texture. This result is consistent with that of Tani reported [14].

4. Conclusions

Dense and highly textured $Ca_3Co_4O_9$ ceramics have been obtained by combining the sol–gel method with spark plasma sintering. The phase composition, microstructure and electrical properties were investigated. The sample shows grain alignment and anisotropic electrical resistivity in the directions parallel and perpendicular to the press direction. SPS is an effective sintering method to prepare textured, dense $Ca_3Co_4O_9$ ceramics at a low temperature and in a short time. At 700 °C, the electrical resistivity of the sample parallel to the press direction is $6.13 \times 10^{-5}\ \Omega$ m, which is a very low value reported so far. And the results show that the Seebeck coefficient is insensitive to orientation and micro-texture. Hence, SPS technique is helpful to improve the electrical properties of $Ca_3Co_4O_9$ ceramics.

Acknowledgements

We are grateful for the support of National Natural Science Foundation of China under grant number 50271001 and Beijing Municipal Education Commission under contract No. KZ200310005001.

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