Effect of micro-structure on electrical transport properties in Ca$_3$Co$_4$O$_9$ ceramics

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Abstract
The different Ca$_3$Co$_4$O$_9$ powders were obtained by the solid reaction and the polyacrylamide gel method. The synthesized temperature of Ca$_3$Co$_4$O$_9$ was reduced to 933 K by the polyacrylamide gel method. The electrical properties can be effectively improved by combining polyacrylamide gel method and Spark Plasma Sintering. There are little change of resistivities with gain size changing, but resistivity is obviously influenced by oxygen stoichiometry. The phenomenon results from small polaron hopping conductive mechanism. The hopping activation energy reduce in oxygen rich atmosphere due to smaller hopping distance.

Keywords: microstructure; polyacrylamide gel method; electrical properties; vacancies

1. Introduction
Thermoelectric generator converts thermal energy directly to electrical energy by thermoelectric materials. The performance of materials is evaluated by the dimensionless figure of merit \( ZT \) (\( ZT = \alpha^2 \sigma T / \kappa \)), where, \( \alpha \), \( \sigma \), \( \kappa \) and \( T \) are the Seebeck coefficient, electrical conductivity, thermal conductivity and the absolute temperature, respectively. The conversion efficiency of the materials can be improved by increasing the operation temperature and temperature difference. So bulk high temperature thermoelectric materials are appealed for thermoelectric generators.

In recent years, increasing attention has been given to oxide thermoelectric materials since oxides are very suitable for long-term use at high temperatures in air. Terasaki et al. have reported a high Seebeck coefficient (100 \( \mu \)V/K at 300 K) and a low electrical resistivity (0.2 m\( \Omega \) cm at 300 K) for a NaCo$_2$O$_4$ single crystal [1]. These data indicate that some semiconducting oxides are potential for thermoelectric applications. Because of the volatility of sodium above 1073 K and hygroscopicity in air, the practical application of NaCo$_2$O$_4$ is quite limited. It is necessary to find other stable oxide systems with good thermoelectric properties. Among Co-based oxides, the crystal structure and physical properties of Ca$_3$Co$_4$O$_9$ have been reported in detail [2]. This compound is thought to be a misfit-layered oxide consisting of two monoclinic subsystems, namely Ca$_2$CoO$_3$ layer and CoO$_2$ layer. The CoO$_2$ layer plays an important on the Seebeck coefficient and electrical conductivity [3]. The value of \( ZT \) for single crystals of [Ca$_2$CoO$_3$)$_{1-y}$][CoO$_2$] is nearly 0.83, so Ca$_3$Co$_4$O$_9$$_{1-y}$ will be a potential material for practical use due to its no-tonicity, low cost and high thermoelectric properties [4]. The current researches of Ca$_3$Co$_4$O$_9$$_{1-y}$ are mainly focused on improving processes and properties [5-6]. The relationship between properties and micro-structure is scarcely reported. In this paper, the effect of micro-structures, oxygen stoichiometry and crystal structure on electrical transport properties were discussed in detail.

2. Experimental
The powders of Ca$_3$Co$_3$O$_9$$_{1-y}$ were synthesized by the polyacrylamide gel method and solid state reactions respectively. The details of solid state reaction method were similar to other report [7-8], while the polyacrylamide gel method was narrated as follows. The stoichiometric Ca(CH$_3$COOH)$_2$H$_2$O, Co(CH$_3$COOH)$_2$4H$_2$O and EDTA were dissolved in distilled water. The value of pH was controlled at about 6 by NH$_4$OH. After completely dissolved, Acrylamide (monomer) and N,N’-methylene-bisacrylamide (crosslinked agent) were added into the solution. The uniform gel was rapidly gained after the initiator was added at 348 K. The moisture of gel was quickly disposed in a microwave oven. The powders of Ca$_3$Co$_3$O$_9$$_{1-y}$ were gained after dry gel were calcined at about 933 K.
973 K for 3 h. Ca$_3$Co$_4$O$_{9+\delta}$ ceramics were gained by press-less sintering and Spark plasma sintering respectively. The densities of all ceramics were evaluated by the Archimedes method. Micro-structures of Ca$_3$Co$_4$O$_{9+\delta}$ ceramics were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The resistivities of samples prepared by different processes were measured by DC four-probe method in different oxygen pressures. The anisotropic electrical transport nature of Ca$_3$Co$_4$O$_{9+\delta}$ ceramics was characterized and confirmed by electric force microscopy (EFM). In order to express expediency, the symbols of samples for different processes or test condition were listed in Table 1.

Table 1. Preparation process and test condition of S1, S2, S3, S4 and S5 samples

<table>
<thead>
<tr>
<th>Symbol of sample</th>
<th>Composition</th>
<th>The process of powder</th>
<th>The process of sinter</th>
<th>Annealing temperature and times</th>
<th>Test condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Ca$_3$Co$<em>4$O$</em>{9+\delta}$</td>
<td>Solid reaction</td>
<td>pressureless sintering</td>
<td>973 K (8 h)</td>
<td>$P_{O2}$=0.21 atm</td>
</tr>
<tr>
<td>S2</td>
<td>Ca$_3$Co$<em>4$O$</em>{9+\delta}$</td>
<td>Solid reaction</td>
<td>SPS sintering</td>
<td>973 K (8 h)</td>
<td>$P_{O2}$=0.21 atm</td>
</tr>
<tr>
<td>S3</td>
<td>Ca$_3$Co$<em>4$O$</em>{9+\delta}$</td>
<td>Polyacrylamide gel method</td>
<td>SPS sintering</td>
<td>973 K (8 h)</td>
<td>$P_{O2}$=0.21 atm</td>
</tr>
<tr>
<td>S4</td>
<td>Ca$_3$Co$<em>4$O$</em>{9+\delta}$</td>
<td>Polyacrylamide gel method</td>
<td>SPS sintering</td>
<td>1123 K (8 h)</td>
<td>$P_{O2}$=0.21 atm</td>
</tr>
<tr>
<td>S5</td>
<td>Ca$_3$Co$<em>4$O$</em>{9+\delta}$</td>
<td>Polyacrylamide gel method</td>
<td>SPS sintering</td>
<td>973 K (8 h)</td>
<td>$P_{O2}$=1.00 atm</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Characterization of phase and synthesis process

Fig. 1 shows the XRD patterns of Ca$_3$Co$_4$O$_{9+\delta}$ powders prepared by different processes. Almost all XRD patterns are identical to the standard JCPDS card of 21-0139. The single-phase is shown for the powders prepared by the polyacrylamide gel method, while there is a little impurity for the powders prepared by the solid reaction.

Fig. 2 shows DTA and TG curve of dry gel powder. The exothermic peaks of the gel sample occurring at 637 and 739 K correspond to the decomposed temperature of polyacrylamide. The large loss of weight occurs before 800 K, which attributes to decomposition of organic substance.

In the inset of Fig. 2, the crystal peak and decomposed peak of Ca$_3$Co$_4$O$_{9+\delta}$ are shown at about 933 and 1213 K respectively. The synthesized temperature of powder is lower than that (1047 K) of other method, while the decomposed temperature of Ca$_3$Co$_4$O$_{9+\delta}$ is coincident with the result from E. Woermann [9].

Fig. 3 shows SEM images of the samples annealed at different temperatures. All grains of samples are shown in the form of sheet. For the sample annealed at 973 K, the size of sheet-like grain is about 1 um. The grain size becomes bigger with increasing temperature, while C-axis alignment is more obvious at higher annealing temperature.

3.2. Electrical properties analysis

According to the results from the Archimedes method, the relative densities of S1, S2, S3 samples are 75%, 97%, 98% respectively. In order to eliminate the surface carbon introduced in SPS process, all SPS ceramics were annealed at certain temperature.

Fig. 4 shows the temperature dependence of electrical resistivity of different samples. All samples exhibit semiconductor characteristic, the electrical resistivity of S3 sample is the lowest due to purity and high density. The electric resistivity of poly-crystal bulk materials depends greatly on microstructure, such as porosity, purity, grain orientation and size.