Synthesis of $Ca_3Co_4O_9$ ceramics by polymerized complex and hydrothermal hot-pressing processes and the investigation of its thermoelectric properties

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Abstract $Ca_3Co_4O_9$ ceramic powders were synthesized by the polymerized complex (PC) method and consolidated by the hydrothermal hot-pressing (HHP) technique. Observation by scanning electron microscope indicated that the form of powders by the PC process was fine and flaky. The density of the sintered body increased with an increase of the operating temperature and pressure during the HHP process. The electrical resistivity was greatly reduced with an increase of the operating pressure, but the thermal conductivity is prone to increase with an increase of the operating temperature and pressure. The Seebeck coefficient was hardly affected by the HHP condition. As a result, the sample treated by the HHP process under the condition of 573 K, 200 MPa, and 1 h showed a maximum ZT of about 0.29 at 1,073 K.

Introduction

Recently metal oxides have attracted much attention from many researchers as high-temperature thermoelectric materials because of their stability to heat and low toxicity. $Ca_3Co_4O_9$ is a layered oxide composed of an electrically conductive CoO_2 layer and an insulating Ca_2CoO_3 layer which are aligned along the c-axis. The electrical resistivity of this phase exhibits significant anisotropy due to its crystal structure; the electrical resistivity along the c-axis is considerably higher than that along the ab-plane [1–4].

The $Ca_3Co_4O_9$ sintered body is generally synthesized by the conventional solid-state reaction method from the metal carbonate and oxide powders [5, 6], or the sol–gel method from the metal-citrate complexes [4, 7]. The polymerized complex (PC) method, which is a kind of sol–gel process, is considered to be useful for obtaining a homogeneous and fine powder precursor. This method is based on the stable formation of metal-citrate complexes and the following polymerization between ethylene glycol and citric acid complexed with constituent metals [8]. Heating of the resultant polymeric product in air causes a breakdown of the polymer, which allows the fabrication of metal oxide precursors. The obtained powder precursors are generally very fine, and the main advantage of this technique is the escape from possible phase segregation during the process of solvent removal [9].

On the other hand, the hydrothermal hot-pressing (HHP) technique is a method by which hard solid bodies of powders can be produced in a short time and at a relatively low temperature under the saturated vapor pressure [10, 11]. The following sintering of the solid bodies prepared by the HHP process may produce the solid sintered body resulting in the low electrical resistivity.

It is generally considered that the homogeneous phase with free segregation and fine crystal grains can contribute to the increase of the Seebeck coefficient [12] and the decrease of the thermal conductivity of materials [13, 14]. On the other hand, the fine crystal grains may cause the increase of the electrical resistivity [14]. The combination of the PC and HHP processes may be efficient for the synthesis of $Ca_3Co_4O_9$ ceramics with large Seebeck coefficient, low electrical resistivity, and low thermal conductivity. The objective of this study is the synthesis of the solid sintered body of $Ca_3Co_4O_9$ with fine crystal grains by the PC and HHP processes, and the investigation of their microscopic structure and thermoelectric properties.

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Experimental procedure

$Ca_3Co_4O_9$ ceramics were synthesized by the PC method and HHP technique as summarized in Fig. 1. Citric acid and stoichiometric amounts of calcium acetate hydrate and cobalt acetate hydrate were dissolved in ethylene glycol by heating and stirring the solution until complete dissolution. At first, the solution was heated at 433 K to remove most of the water from the solution. After the completion of the decomposition of acetate ions, the temperature of the solution was gradually increased to 523 K. During this heating process, the formation of the polymer between ethylene glycol and metal-citrate complexes was promoted. As the solution was condensed, it became viscous, and this viscous product was decomposed to a fine powder at 723 K. The obtained powder precursor was ground and calcined at 973 K for 12 h in air to remove a residual organic matter completely. The calcined powder was compressed by the hydrothermal hot-pressing technique similar to that reported in our previous studies [15, 16]. The calcined powder was kneaded with 0.05 M NaOH solution (10 mass% for the powder) to be set in the cylinder of an autoclave for the hydrothermal hot pressing (HHP). Figure 2 shows the schematic drawing of the autoclave used in this experiment. The autoclave has a cylinder made of stainless steel with an inside diameter of 20 mm and the sample is compressed by the piston in the cylinder from the top and bottom. The sample was first compressed at the
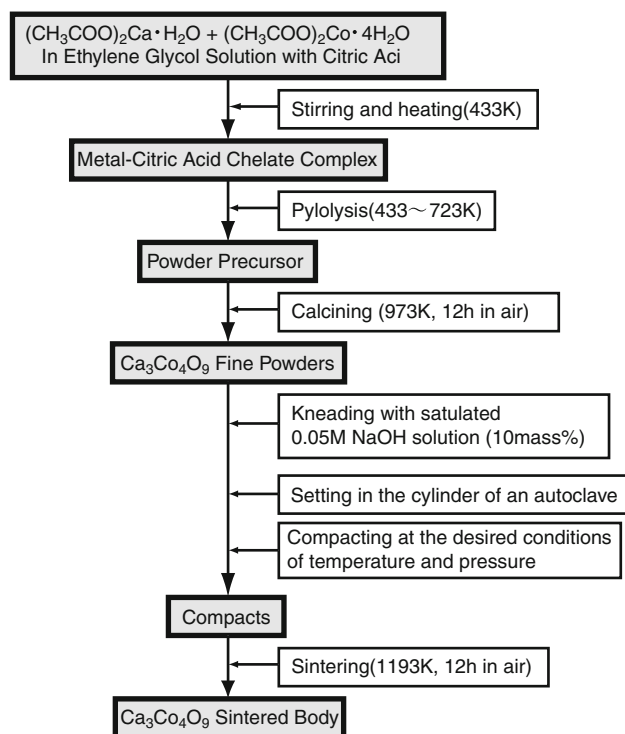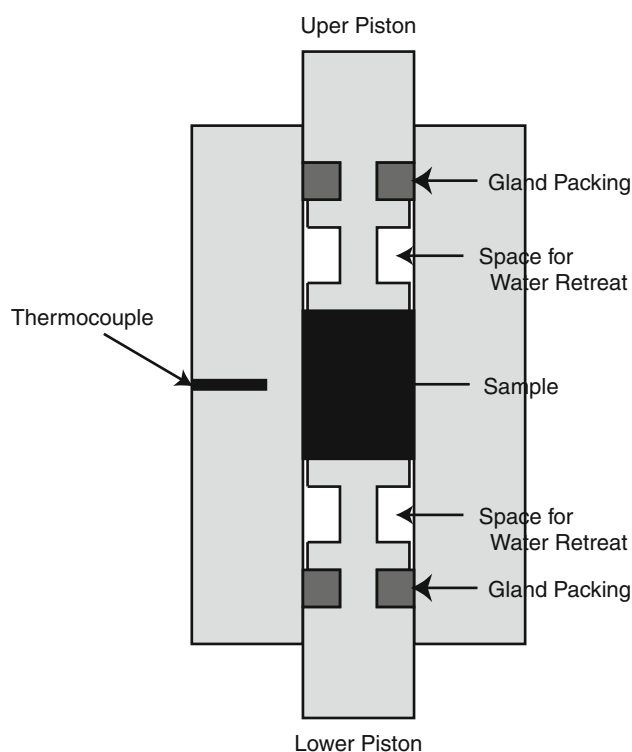

Fig. 2 Schematic drawing of the autoclave for the hydrothermal hot pressing

ambient temperature and the desired pressure (50–200 MPa). Then it was heated at a rate of 10 K min^{-1} to the desired temperature (373–573 K), and kept for a desired time (1–5 h) at each temperature. The rectangular prism with about $18 \times 7 \times 2$ mm was cut off from the obtained compacts. The cut off compacts were sintered at 1193 K for 12 h in air. As a reference, the sample by the conventional solid-state reaction method was also prepared; a mixture of $CaCO_3$ and Co_3O_4 powders was pressed into a pellet under a pressure of 560 MPa for 30 s at room temperature, calcined at 1,173 K for 12 h in air, ground, again pressed into a pellet, and then sintered at 1,193 K for 12 h in air.

The phase identification of the obtained samples was made by X-ray diffraction at room temperature. The microscopic structure of the samples was examined using a scanning electron microscope (SEM). The density D of the samples was measured by the Archimedes method. The Seebeck coefficient S and electrical resistivity ρ were simultaneously measured by the standard four-probe dc method in air in the temperature range from room temperature to 1,173 K using the sintered samples shaped in the rectangular prism. The measurement was carried out along the pressed plane. The thermal diffusibility λ and specific heat C_p were measured by the laser flash method. The measurement of λ was carried out along the pressing direction, i.e., perpendicular to the pressed plane. The

Fig. 1 Flow chart of the sample preparation

thermal conductivity κ of the samples was calculated from the measured λ, C_p, and D using $\kappa = \lambda C_p D$.

Results and discussion

From the result of the X-ray diffraction, it was found that the calcined powder precursor was composed of $Ca_3Co_4O_9$ phase without any impurity phase. Figure 3 shows the SEM photograph for the cross-section of powder precursors plowed in the resin prepared by the PC process. As shown in the photograph, the somewhat flaky powders with a length of about 0.5–1 μm and a thickness of about 0.2 μm, reflecting the crystal structure of $Ca_3Co_4O_9$, are obtained.

As a preliminary experiment, we have examined the effect of the operating time during the HHP process on the phase stability and thermoelectric properties of the sintered samples. The sintered samples ultimately obtained were generally composed of $Ca_3Co_4O_9$ phase with almost no impurity phase, but impurity phases such as CoO and Co_3O_4 were detected in the samples treated under longer operating period beyond 1 h of HHP by the X-ray diffraction, and ZT of the samples decreased with an increase of the operating time. It seems that the treatment of HHP over a long period is not so good for the phase stability of $Ca_3Co_4O_9$. And so, we have determined that the optimum operating time during the HHP process is 1 h.

The relative density D/D_0 of the sintered samples, where D_0 is the theoretical density calculated from the X-ray diffraction data, tends to increase with an increase of the operating temperature and pressure, but it is 80% at most, and somewhat porous sintered samples were obtained. The degree of the crystallographic orientation of the samples can be estimated from the intensity of the (hkl) peaks, $I(hkl)$, in the X-ray diffraction patterns using the Lotgering
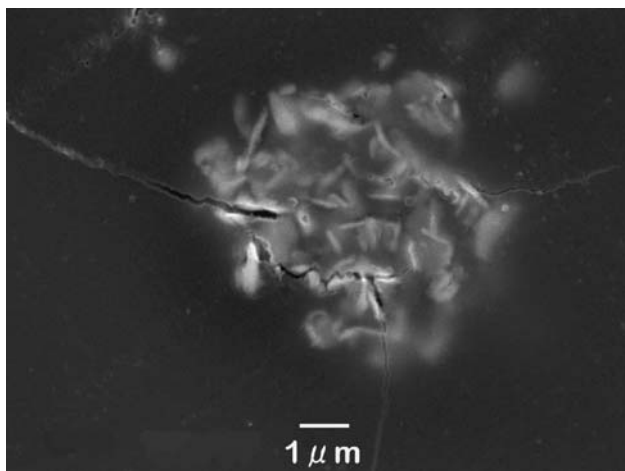

Fig. 3 SEM photograph for $Ca_3Co_4O_9$ powder precursors prepared by the polymerized complex method

factor, $f = (P - P_0)/(1 - P_0)$ [17]. When estimating the degree of the orientation along the c-axis, P is defined as $\Sigma I(00l)/\Sigma I(hkl)$; $P = P_0$ for a crystallographically isotropic (randomly orientated) sample. For the sample with the c-axis completely aligned along the pressing direction, the f-value is calculated to be 1. When the X-ray is irradiated to the sintered samples along the pressing direction, the f-value generally increases with an increase of the operating temperature and pressure, but it is about 0.35–0.6, and so the obtained samples were somewhat orientated along the c-axis.

Previously, we had synthesized the $Ca_3Co_4O_9$ ceramics by the combination of the citric acid complex (CAC) and HHP processes [16]. The CAC process is similar to the PC process; in the CAC process, the polymerization process between metal-citrate complexes and ethylene glycol is omitted. In the CAC process, the flaky powder is also obtained, but the size of the powder is somewhat larger; length and thickness of the powder is about 2 and 0.3 μm, respectively. The powder obtained by the PC process is generally much finer. In the PC process, metal cations such as Ca and Co are separately located as chelate complexes on the long chain of the polymer, and so during the process of the breakdown of the polymer by heating, the crystal growth of $Ca_3Co_4O_9$ is suppressed and the resultant $Ca_3Co_4O_9$ powder may become fine. Similar behavior is reported by Zhang et al. [7] on the synthesis of $Ca_3Co_4O_9$ particles by citric sol–gel method, where they used the polyethylene glycol as a dispersant. The f-value of the sintered samples by the CAC and HHP processes is about 0.4–0.6, which is almost the same value of the samples by the PC and HHP processes. The density of the sintered samples by the CAC and HHP processes is about 75–90%, which is generally larger than that by the PC and HHP processes.

First, we have examined the effect of the operating temperature during the HHP process on the Seebeck coefficient, electrical resistivity, and thermal conductivity of the sintered samples. Figure 4a–c shows the temperature dependence of the Seebeck coefficient, electrical resistivity, and thermal conductivity for the samples treated by the PC and HHP processes under the individual operating temperature during the HHP process, respectively. The operating pressure and time are fixed as 100 MPa and 1 h, respectively. As already mentioned, the measurement of the Seebeck coefficient and electrical resistivity was carried out along the pressed plane, while the measurement of the thermal conductivity was carried out along the pressing direction. The Seebeck coefficient gradually increases with temperature, while the electrical resistivity is almost constant independent of temperature. It is reported that the electrical resistivity in the ab-plane of the single crystal increases with temperature while that along the c-axis decreases [3]. On the other hand, it is reported that the
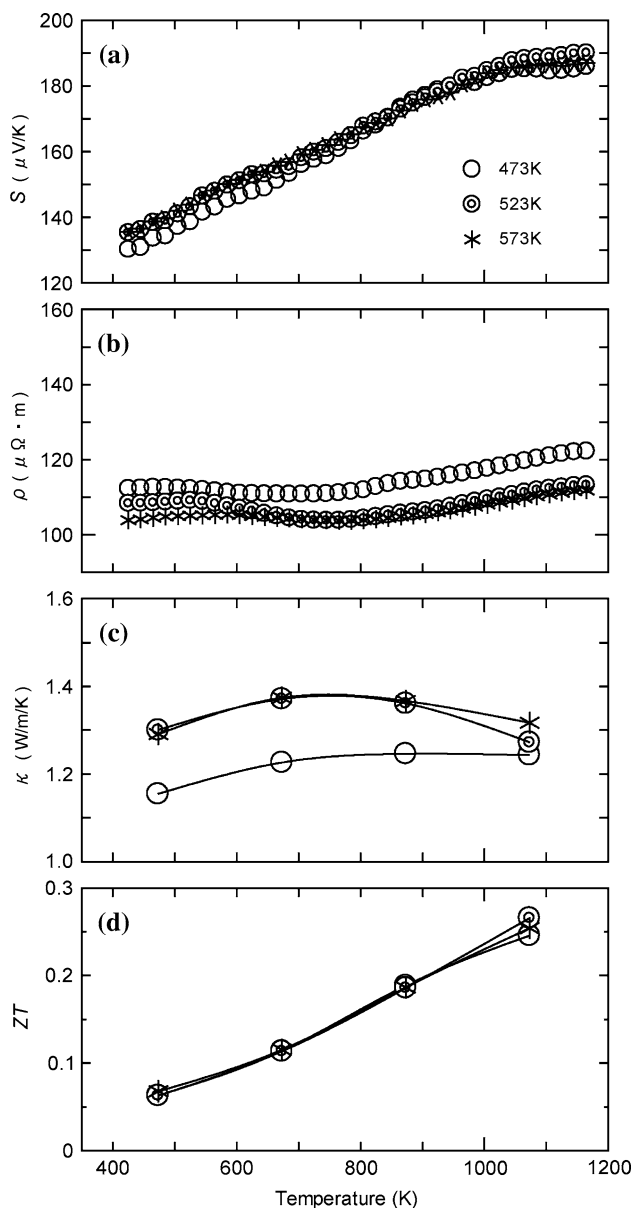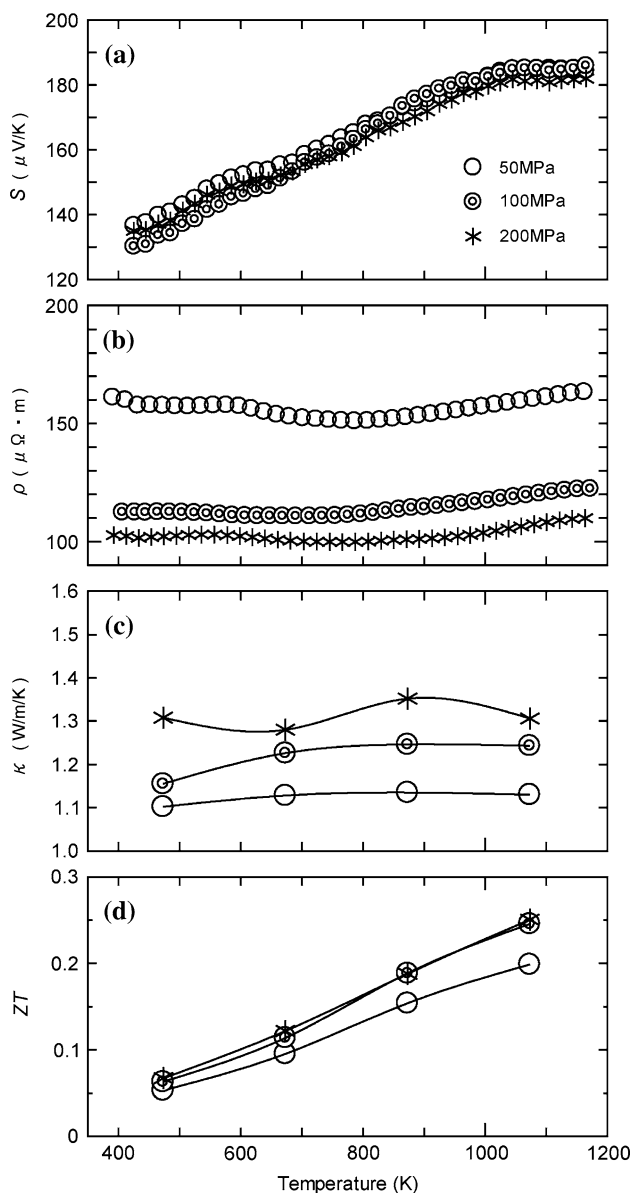
Fig. 4 Temperature dependence of the (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity, and (d) ZT for the samples prepared by the PC and HHP processes under the individual operating temperature

Seebeck coefficient in the *ab*-plane increases with temperature [3, 18], and there is almost no isotropy on the Seebeck coefficient [18, 19]. The temperature dependence of the electrical resistivity observed in our samples shows an intermediate behavior of that reported on the *ab*-plane and *c*-axis of the single crystal, and it is similar to the data for ceramics reported by Li et al. [19]. This is perhaps because our sintered samples are somewhat orientated, but not so highly orientated along the *c*-axis. The Seebeck coefficient is almost independent of the operating temperature during the HHP process, which shows that carrier density of the samples is almost the same among these

samples. With an increase of the operating temperature during the HHP process, the electrical resistivity generally decreases, while the thermal conductivity is apt to increase. Here, the measurement of the thermal conductivity was done along the pressing direction, i.e., perpendicular to the measured direction of the Seebeck coefficient and electrical resistivity. In order to estimate the ZT value of the samples with crystallographic orientation, the Seebeck coefficient, electrical resistivity, and thermal conductivity must be measured along the same direction in the sintered body. As mentioned above, the Lotgering factor *f* of our samples is 0.35–0.6, and it is somewhat orientated. We have estimated ZT of the samples from the measured Seebeck coefficient, electrical resistivity, and thermal conductivity, although thus estimated ZT values are reference ones. Figure 4d shows the temperature dependence of the corresponding ZT for the samples. There is almost no difference in ZT among these samples.

Next, we have examined the effect of the operating pressure during the HHP process on the thermoelectric properties of the samples, which is shown in Fig. 5. The operating temperature and time during the HHP process are fixed as 473 K and 1 h, respectively. The Seebeck coefficient is almost independent of the operating pressure similarly as observed in Fig. 4a. The electrical resistivity is much reduced with an increase of the operating pressure, while the thermal conductivity increases. As a result, the ZT of the samples increases with an increase of the operating pressure, which is mainly ascribed to the reduction of the electrical resistivity. From the above result, thermoelectric properties, especially the electrical resistivity, of the samples are greatly affected by the magnitude of the pressure during the HHP process.

When a single sign of charge carrier is predominant, the thermal conductivity κ of a material can be written as

$$\kappa = \kappa_{car} + \kappa_{ph}$$

where κ_{car} is the carrier contribution and κ_{ph} is the lattice contribution. κ_{car} can be calculated using the Wiedemann–Franz relationship $\kappa_{car} = L\sigma T$, where L is the Lorentz number, σ is the electrical conductivity, and T is the absolute temperature. The Lorentz number is calculated using the reduced Fermi energy, which can be estimated from the Seebeck coefficient and the Fermi-Dirac integral [20]. The lattice contribution κ_{ph} can be obtained by subtracting κ_{car} from κ. The operating pressure dependence of κ_{car} and κ_{ph} for the samples is shown in Fig. 6. The value of κ_{ph} is much larger than that of κ_{car}. With an increase of the operating pressure, κ_{car} and κ_{ph} generally increase, but κ_{ph} is more enhanced. The greater enhancement of κ_{ph} seems to show that the connection between crystal grains becomes stronger with an increase of the operating pressure during the HHP process.

Fig. 5 Temperature dependence of the (**a**) Seebeck coefficient, (**b**) electrical resistivity, (**c**) thermal conductivity, and (**d**) ZT for the samples prepared by the PC and HHP processes under the individual operating pressure

Fig. 6 Temperature dependence of κ_{car} and κ_{ph} for the samples prepared by the PC and HHP processes under the individual operating pressure

obtained by higher operating pressure during the HHP process. The smaller electrical resistivity and higher thermal conductivity of the sample treated under higher pressure seem to be ascribed to the solid connection between crystal grains. As one of other densification processes, hot forging is well known. Prevel et al. [21] prepared the highly textured $Ca_3Co_4O_9$ ceramics by the hot-forging process. The crystal grain size and relative density of their samples are 5–15 μm and 95% respectively, which are larger than those of our samples. On the other hand, the electrical resistivity following the direction perpendicular to the stress applied during the hot forging of their samples is almost 150 μΩ m at room temperature, which is generally larger than the electrical resistivity of our samples. These results seem to indicate that the hydrothermal hot-pressing process is more efficient for obtaining samples with solid connection between crystal grains.

From the above results, we have determined that the optimum temperature and pressure during the HHP process are 573 K and 200 MPa, respectively. Figure 8a–d shows the temperature dependence of the Seebeck coefficient, electrical resistivity, thermal conductivity, and ZT for the sample treated by the PC and HHP processes under the optimum condition, respectively. The data of the sample by the conventional solid-state reaction (SSR) method are also shown in the figure. The Seebeck coefficient of the sample by the PC and HHP processes is somewhat larger than that of the

Figure 7a, b shows the SEM photographs for the cross-section perpendicular to the pressed plane of the sintered samples whose operating pressures are 100 and 200 MPa, respectively. The plate-like grains are packed and somewhat aligned along the pressed plane. In the sample whose operating pressure is 100 MPa, more pores are observed and the boundaries between crystal grains can be more easily detected, but in the sample whose operating pressure is 200 MPa, the boundaries are generally hard to detect. The relative densities of the samples whose operating pressure is 100 and 200 MPa are 77.8 and 79.5%, respectively. These results show that a denser and more solid sample can be
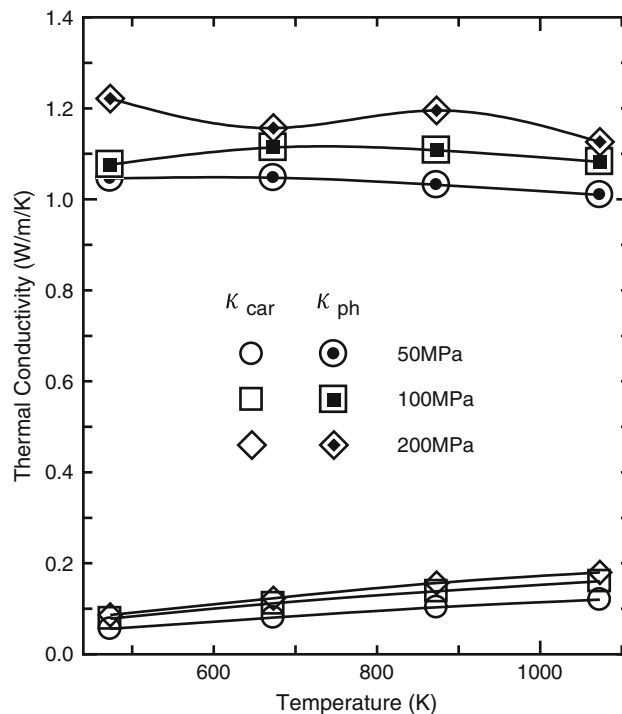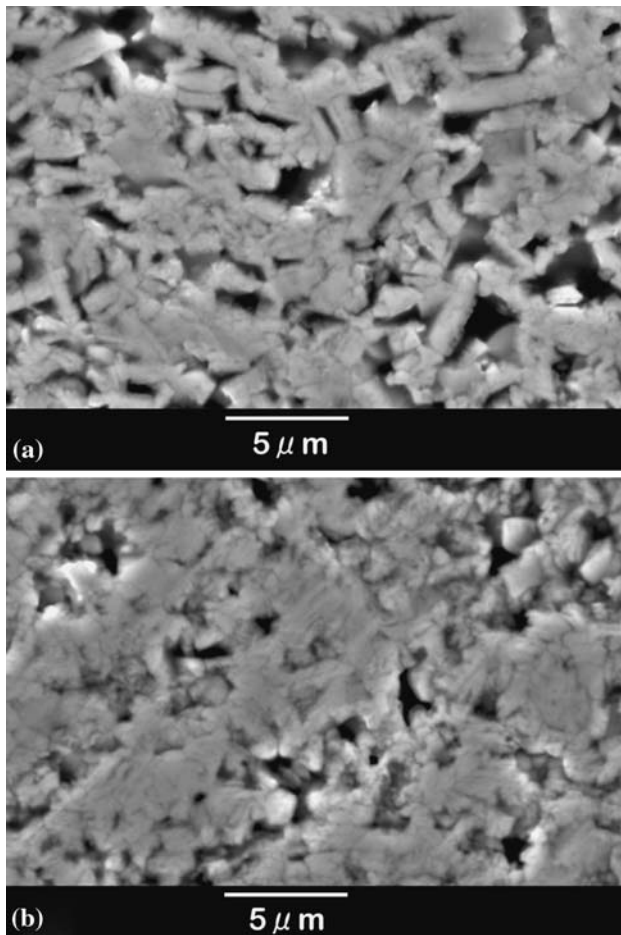
Fig. 7 SEM photographs for the cross-sections perpendicular to the pressed plane for the samples prepared by the PC and HHP processes. The operating pressure during the HHP process is (**a**) 100 MPa and (**b**) 200 MPa

Fig. 8 Temperature dependence of the (**a**) Seebeck coefficient, (**b**) electrical resistivity, (**c**) thermal conductivity, and (**d**) ZT for the samples prepared by the PC and HHP processes, and SSR method

sample by the SSR method. The larger Seebeck coefficient of the sample by the PC and HHP processes is considered to be ascribed to the better homogeneity of the sample. The electrical resistivity of the sample by the PC and HHP processes is smaller than that of the sample by the SSR method, and the calculated power factor, S^2/ρ, of the sample by the PC and HHP processes is 400 μW m^{-1} K^{-2} at 1,073 K, which is larger than that of the sample by the SSR method, 330 μW m^{-1} K^{-2} at 1,073 K. As already mentioned, the PC process is efficient for preparing fine homogeneous powders. The fine crystal grains in the sintered bodies are apt to increase the electrical resistivity of the material, while the HHP process is a process by which hard solid bodies of powders can be produced. The power factor of the sample by the PC and HHP processes is also larger than that of the sample by the CAC and HHP processes, which was previously reported [16]. The combination of the PC and HHP processes can be more efficient for the synthesis of Ca$_3$Co$_4$O$_9$ ceramics with the large Seebeck coefficient and low electrical resistivity, which can produce the large power
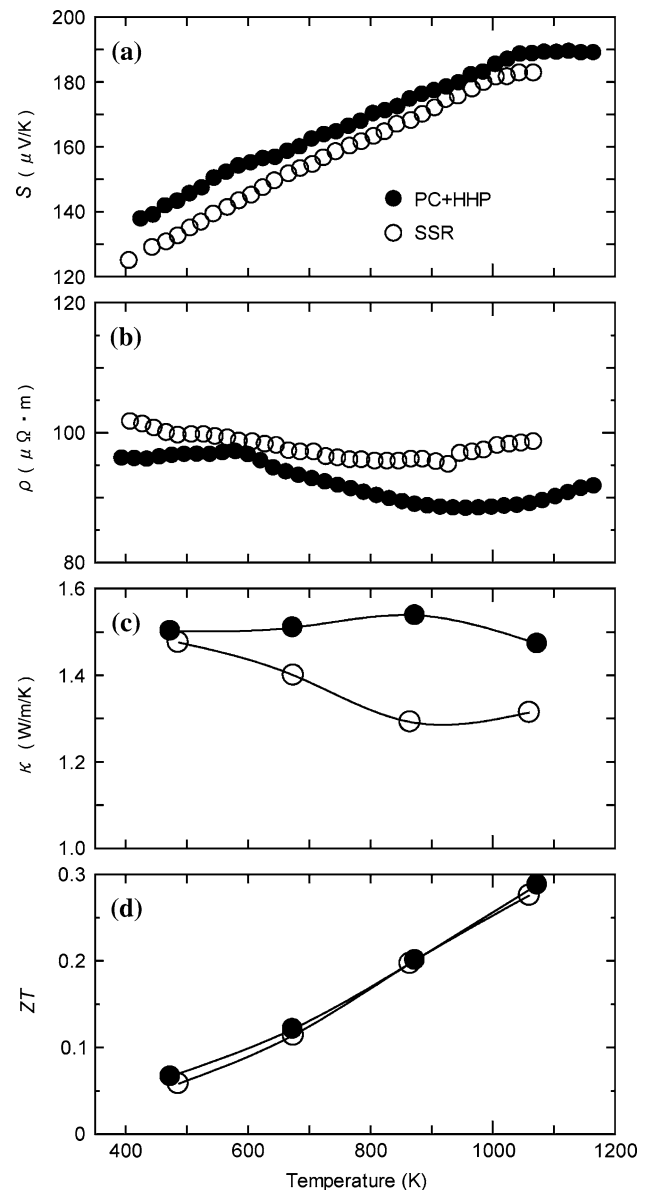
factor. The decrease of the electrical resistivity in the sample by the PC and HHP processes seems to be due to the solid connection between crystal grains. On the other hand, this solid connection can enhance the thermal conductivity of the sample simultaneously. As a result, there is almost no difference in the obtained ZT between the samples by the PC and SSR processes; the obtained maximum ZT is about 0.29 at 1,073 K.

Conclusion

We have prepared Ca$_3$Co$_4$O$_9$ ceramics by the PC and HHP processes, and examined their microscopic structure

and thermoelectric properties. The PC method is useful for preparing a fine and flaky powder, and the HHP technique is a method by which hard solid bodies can be produced from powders at a relatively low temperature under the saturated vapor pressure. The Seebeck coefficient of the samples is hardly affected by the conditions of the HHP process. With an increase of the operating temperature and pressure during the HHP process, the electrical resistivity of the samples generally decreases but the thermal conductivity is apt to increase. The optimum temperature and pressure for ZT during the HHP process is 573 K and 200 MPa, respectively. The electrical resistivity of the samples by the PC and HHP processes is smaller than that of the sample by the SSR method, and the power factor of the former is larger than that of the latter. On the other hand, the thermal conductivity of the former is larger than that of the latter. The smaller electrical resistivity and larger thermal conductivity of the samples by the PC and HHP processes seem to be ascribed to the solid connection between crystal grains. The obtained maximum ZT is about 0.29 at 1,073 K, which is almost the same as that of the sample by the SSR method.

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