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Technical note

A new process for lamellar texturing of thermoelectric $Ca_3Co_4O_9$ oxides by spark plasma sintering

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Abstract

Processing of textured $Ca_3Co_4O_9$ (Ca349) thermoelectric ceramics with a good platelet orientation by spark plasma sintering (SPS) consolidation is reported. Two configurations wherein: (i) the oxide powder, being directly introduced into the graphite mould and (ii) placing a compact pellet prepared from the oxide powder in the centre of the mould have been investigated. The free deformation configuration route is found to improve the microstructure and transport properties of $Ca_3Co_4O_9$ TE oxides. The material prepared exhibited a better performance than the sample obtained by conventional SPS way.

Keywords: Shaping; Grain growth; Electrical properties; Spark plasma sintering

1. Introduction

The last decade has seen a big surge in research[1–13] on thermoelectric (TE) oxide materials, with primary focus on discovering new compounds with high Seebeck coefficient, and in improving the TE properties of the existing materials. For any practical application, the existing properties (Seebeck coefficient, electrical and thermal conductivity) of TE materials must be improved at least by two or three orders of magnitude more than those typically seen in bulk polycrystalline samples prepared by conventional sintering. Because ρ is highly anisotropic, particularly in the popular $Ca_3Co_4O_9$ (Ca349) TE oxide single crystal,[3] there has been considerable interest in developing methods of preparing these oxides with a good crystallographic alignment. Several efforts has been reported to produce bulk dense and textured TE oxides by hot pressing (HP),[11,14,15] spark plasma sintering (SPS)[16–18] or processing external magnetic field[18] as developed for the lamellar Bi2223 superconducting materials.[19] Using HP, the materials can be processed with a good texture; however, this technique is limited to very thin samples.[11,15] The low temperature and rapid processing using SPS offer an interesting route for the preparation of thick and highly dense materials,[9,16,17] but with a reduced texture. The open question is how to combine the enhancement of the sample density in SPS technique with a good platelet-alignment of Ca349 grains. In this work, a novel configuration is proposed to consolidate the oxide powder by SPS into a highly textured and dense lamellar $Ca_3Co_4O_9$, by inducing a free deformation into the sample preform.

2. Experimental procedure

The $Ca_3Co_4O_9$ TE ceramic powders were prepared by first calcining a stoichiometric mixture of commercially available, Co_3O_4 oxide and $CaCO_3$ at 900 °C for 12 h. The powder was then reground, shaped into pellets with a diameter of 13 mm by pressing uniaxially at 30 MPa. The shaped pellets were presintered at 920 °C, for 2 h and placed (Fig. 1(a)) at the center of a graphite die of 20 mm diameter with an aim to ensure the free deformation and texturation of the sample. In another configuration, Ca349 powder was directly introduced into the graphite (Fig. 1(b)) mould as reported elsewhere.[16–18] The final processing was carried out using the spark plasma sintering system (model: Dr. Sinter SPS 2080, Sumitomo Coal Mining Co., Ltd., Japan) at the "*Plate-forme Nationale de Frittage Flash, CNRS, Toulouse, France*". The pulsed electric current (2000 A, 4 V) was passed through the sample under vacuum (10^{-3} bar)

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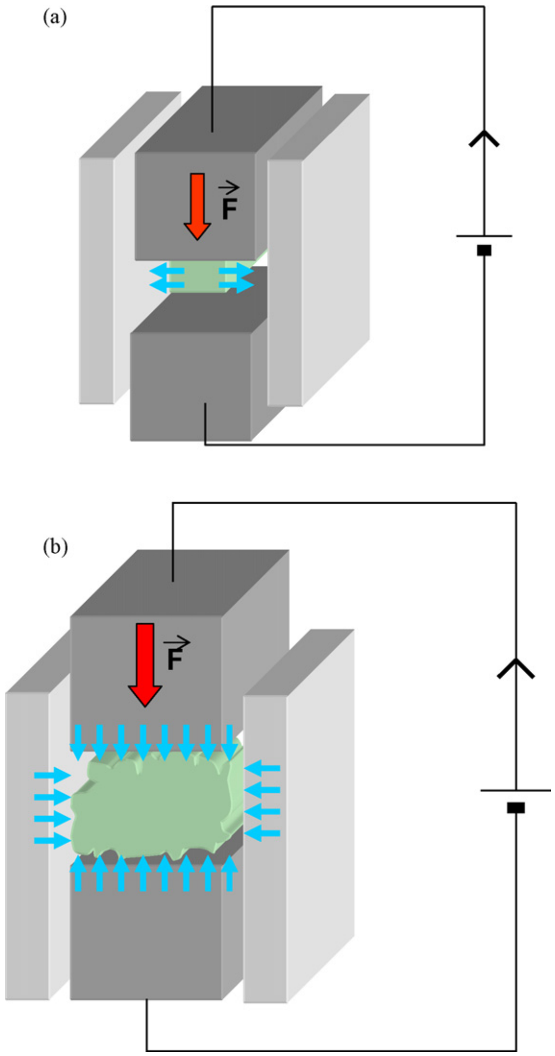

Fig. 1. Schematic diagram of the two configurations using during SPS processing: (a) free deformation configuration and (b) conventional SPS.

under an uniaxial pressure of 50–75 MPa. Samples were heated for comparison at three different temperatures, 800, 850 and 900 °C, while a load of 15 or 25 kN was applied for 2 min. The temperature was controlled using thermocouple put into the die close to the sample. For comparative studies, the starting powder was directly introduced into the graphite mould and sintered under similar conditions using SPS. The as-prepared thick samples were polished to remove the graphite foil used during processing. We will call here after the SPS samples processed from powder and pellet, "powder series" and "pellet series", respectively.

Diffraction experiments were first carried out at room temperature using a Philips θ–2θ diffractometer and the monochromatic Cu Kα radiation for the phase identification. The microstructures of the samples after processing were investigated at 300 K using the high resolution Carl Zeiss (Supra 55, Oberkochen, Germany) scanning electron microscope (SEM). The electrical resistivity and Seebeck coefficient were measured simultaneously by the dc four-probe method using ZEM-3 (ULVAC-RIKO, Inc., Japan) from room temperature to 550 °C.

3. Results and discussion

The density of all sintered samples evaluated from the mass over sample size is 98% of the theoretical density.[3] Fig. 2 presents a comparison of microstructures of samples consolidated by SPS at different sintering temperatures and pressures. From the fractured surface, grains with platelet like morphology can be distinguished easily. The grains size increases with applied pressure during SPS process as compared to conventional (Fig. 2(a)) sintering microstructure. The SEM images showing the SPS process at 800–900 °C for a few minutes were effective in obtaining dense $Ca_3Co_4O_9$ ceramics. The two samples prepared from powders 50 and 75 MPa, also revealed similar microstructures (Fig. 2(b) and (c)). The microstructural analyses show that the samples processed by SPS from powder, although they are dense, results in bulks with randomly oriented grains. This result shows that when the powder is directly introduced into the graphite mould, during the process, in addition to the uniaxial force applied through the plunger, an additional horizontal force from the mould walls (Fig. 1(b)) are also acting on the sample. In this configuration, the pressure around the sample seems like a hydrostatic pressure leading to the dense ceramic but with randomly grain orientation. Similar results are obtained in the literature[16–18] using SPS technique, where the powder was directly introduce into the mould for processing. Fig. 2((d)–(f)) shows the microstructures of the configuration where the sample pellet was free deformed during processing. Basically, the deformation is a change in shape due to an applied force. Under the load due to the empty space around the pellet (Fig. 1(a)) the sample shape changed gradually into the pancake. The final diameter and thickness are 20 and 1.5 mm compare to initial size of 13 and 5 mm, respectively. This deformation is also favoured by the platelet shape of the grains where the growth rate of in-plane is higher than the out-of-the plane one. But, the sample prepared at 800 °C (Fig. 2(d)) shows the random orientation of the grains compared to those of Fig. 2(e) and (f) processed at 850 and 900 °C, respectively. The high temperatures seem to be favourable to induce the better alignment of platelets.

The bulk ceramic shows well-aligned grains perpendicular to the applied pressure direction. The SPS process allows the control of grain alignment according to the starting processing configuration, i.e. either from powder or pellet. It is clear that alignment and texture are maintained through the bulk sample as evidenced by the stacking of platelets. In addition to morphological texture (Fig. 2(f)) seen in SEM, X-ray diffraction (XRD) also reveals a clear crystallographic texture (Fig. 2(g)) and serves as another signature of grain alignment. The XRD recorded on the surface perpendicular to the applied pressure direction indicates that the preferred growth direction is $\{0\,0\,\ell\}$. This result can be compared to other textured samples[9,15] or to the conventional sintering sample where all peaks are indexed.[9,11]

Fig. 3(a) shows the electrical resistivity versus temperature response for conventional sintered (CS) and SPS samples at various temperatures and applied pressures during processing. It is clear that the SPS leads to decrease in resistivity ($\rho \approx 6$–$9\,\mathrm{m\Omega\,cm}$) values as compared to CS sample ($\rho \approx 40\,\mathrm{m\Omega\,cm}$). On the other hand, all curves show a transition

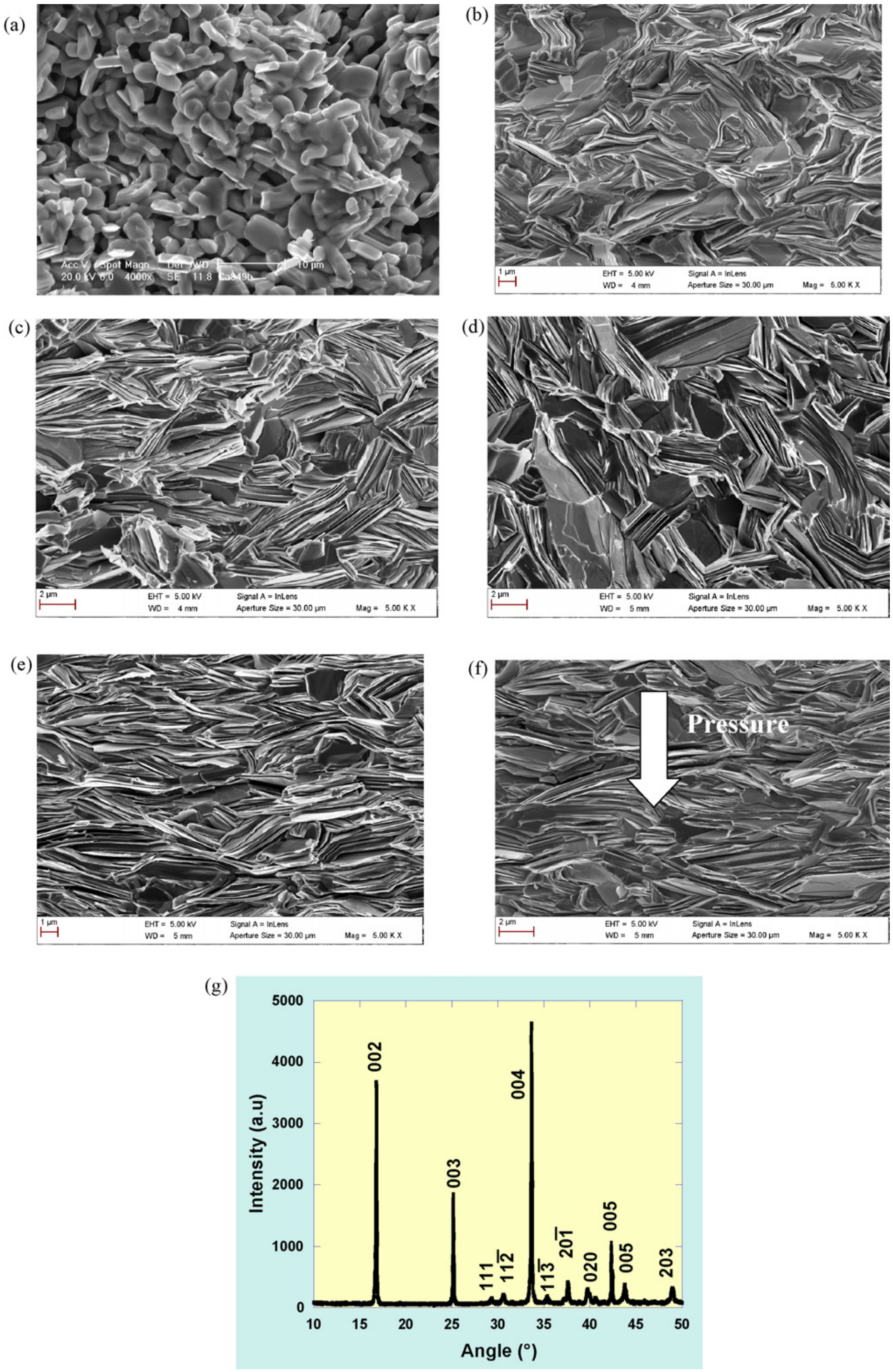

Fig. 2. SEM microstructure of the samples: (a) conventional sintering, 920 °C, 24 h; (b) SPS-powder, 900 °C/50 MPa; (c) SPS-powder, 900 °C/75 MPa; (d) SPS-pellet, 800 °C/50 MPa; (e) SPS-pellet, 850 °C/50 MPa; (f) SPS-pellet, 900 °C/50 MPa; (g) XRD of the surface perpendicular to the applied pressure.

around $T^* = 250\,^\circ\mathrm{C}$. This transition is attributed to the magnetic transition,[3] or structural transition reported by Muguerra et al.[20] But at T^*, the $\rho(T)$ of CS sample shows the metallic behaviour where probably, the resistivity component along the *c*-axis is higher. Regarding the two series of SPS samples, the $\rho(T)$ curves show a semi-conducting behaviour after T^*. One can also note that, the resistivity curves of the samples prepared from powder are above the series processed from pellets. The different resistivities can be clearly correlated to the microstructure observations (Fig. 2) where the powder series are randomly oriented with respect to pellet samples, where the platelets are stacked and aligned. For the powder series the two samples prepared at

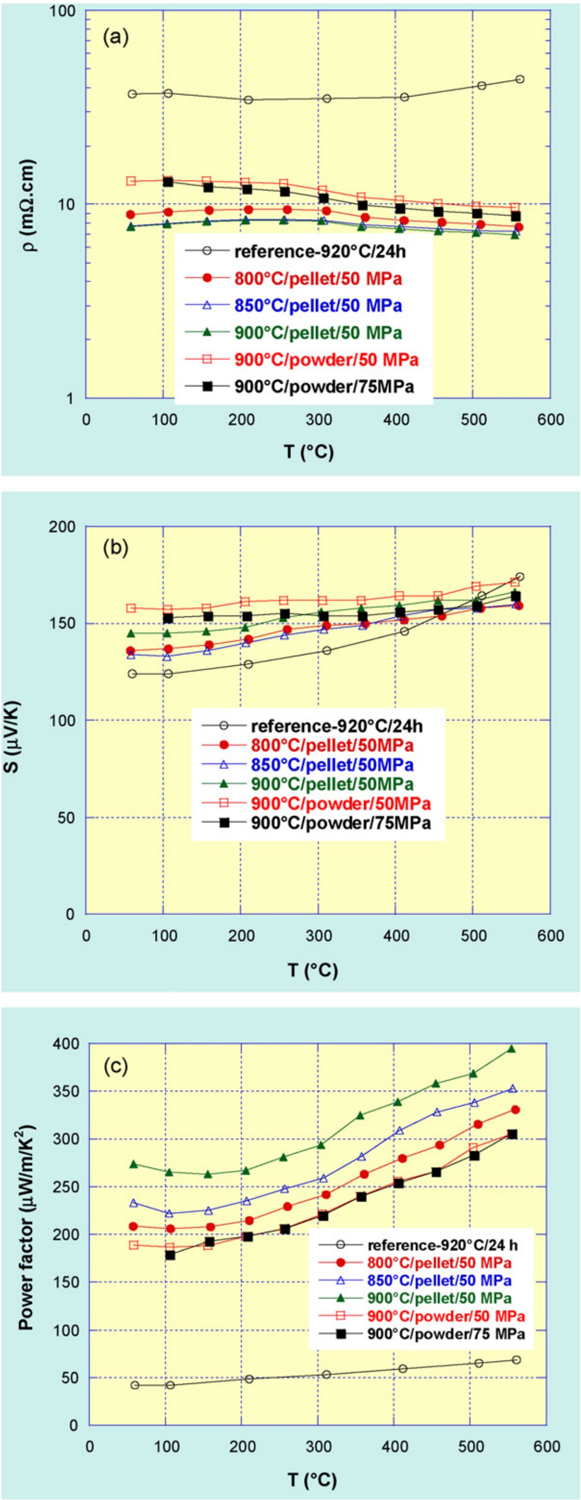

Fig. 3. (a) Resistivity, (b) Seebeck coefficient and (c) power factor vs. temperature dependencies of polycrystalline Ca349 sample and the two series of SPS samples.

900 °C under 50 and 75 MPa have rather closer resistivity values comparable to other reported works.[9,16] The three pellet series processed at 800, 850 and 900 °C at 50 MPa also shows similar ρ values, but the resistivity of the sample prepared at 800 °C is a little bit higher due to the low grain alignment as observed in Fig. 2(d). The results show that starting with the pellet during SPS process is an interesting way to induce a good grain alignment and consequently decrease the electrical resistivity. The Seebeck coefficients of all samples are positive within a narrow range (Fig. 3(b)), indicating that Seebeck coefficient is insensitive to the microstructure alignment of the samples as reported.[9,16]

The temperature dependence of the power factor ($\mathrm{PF} = S^2/\rho$) of Ca349 calculated from the thermoelectric power and resistivity data is plotted in Fig. 3(c). The samples processed from pellet as a starting material show the largest power factor than the powder series one. This is clearly linked to the lowest resistivity values obtained for the pellet series samples. The power factor is improved as compared to the reported values[9,16] by using conventional SPS process.

The value of 395 μW/(m K^2) obtained at 550 °C can be compared to 66 μW/(m K^2) for conventional sintering material and 200 or 309 μW/(m K^2) reported elsewhere[9,16] for dense ceramics.

Further studies are underway in order to increase the thickness of textured TE ceramics. The individual monolayer samples are hot-stacked as previously developed[21] for the lamellar Bi2223 superconductor. The thermal conductivity of these samples will be investigated and the figure of merit ZT discussed.

4. Conclusion

By combining rapid SPS and free deformation configuration, it is possible to produce oriented and lamellar grain structured $Ca_3Co_4O_9$ thermoelectric ceramics. It is demonstrated that, the free deformation configuration is a useful route to improve the microstructure and transport properties of $Ca_3Co_4O_9$TE oxides. The material prepared by this technique exhibited a better performance than the sample obtained by conventional SPS way. Details of the volume texture using neutron diffraction will be reported elsewhere and a further anisotropy study of thermal conductivity is still needed to estimate the ZT value.

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