Textured $Ca_3Co_4O_9$ thermoelectric oxides by thermo-forging process

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Abstract

Dense $Ca_3Co_4O_9$ (Co349) thermoelectric oxides have been successfully formed by thermo-forging process. The various parameters influencing the formation of the Co349 textured material have been investigated. The electrical transport measurements show an anisotropy of the resistivity up to ρ^c/ρ^{ab}~4, in good agreement with scanning electron microscopy observations. Texture was evidenced by X-ray diffraction patterns and neutron measurements. The details of processing and characterization are highlighted.

Introduction

Much effort has been devoted in the last decade to the development of processing bulk thermoelectric oxides and the research of new compounds [1-6] with high figure of merit. Besides these oxides themselves, their preparation with satisfactory structural homogeneity, material density and grain alignment are essential for the design of practical systems suited for application like power generator. Especially, the optimization of platelet orientation is one of the main problems to overcome. Weak links at grain boundaries and low sample density, which affect the resistivity and consequently the figure of merit is one reason for improving the texturing technique [7]. The figure of merit is defined as $ZT = S^2T/\rho\kappa$ (S is Seebeck coefficient, T temperature, ρ electrical resistivity and κ the thermal conductivity) varying by six orders of magnitude. These differences are assumed to be related to the microstructures resulting from the use of different types of process: i) conventional or spark plasma sintering [8], ii) reactive templated grain growth [6], iii) hot-pressing [7, 9] and iv) magnetic texturation [10].

In this paper, we report the preliminary results obtained on the polycrystalline $Ca_3Co_4O_9$ thermoelectric oxide processed by thermo-forging. The correlation between the microstructures and electrical properties has been investigated. In addition, the texture development is evidenced by X-ray and neutron texture measurements.

Experimental

The $Ca_3Co_4O_9$ powder was prepared by conventional solid-state reaction. Pure Co_3O_4 oxide and $CaCO_3$ carbonate were mixed, calcined (900°C, 12 hrs) and pressed uniaxially (30 MPa) into pellets. The samples were processed into the versatile set-up using the thermo-mechanical schedule described in more detail elsewhere [11]. Briefly, the pellet is heated at 920°C during 24 hrs under various stress (0-16 MPa) in air. For the microstructural analysis of the non-pressed and hot-forged samples, scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used. The chemical specimen composition after processing and the texture of the samples were investigated using XRD measurements on Philips apparatus with CuK_α radiation and neutron diffraction using the D1B set-up (Institut Laue-Langevin, Grenoble-France). Electrical resistivities were measured using a dc four probe method with the physical property measurement system-PPMS (Quantum design). The measurement were performed in the temperature range from 5 to 400 K in self field.

Results and discussion

Figure 1 shows SEM micrographs of cross section of the samples processed at 0, 7 and 16 MPa. The microstructure of the hot-pressed dense samples shows homogeneously distributed needle-shaped (> 15 μm) grains in contrast to the non-pressed sample where one can clearly observe some voids and platelet-shaped grains (5 μm). It can be seen that with increasing applied stress from 0 to 16 MPa, the grains size increased from 5 to >15 μm. Crystallites growth has been favoured by hot forging as illustrated on the microstructures. In order words, crystallite growing is easier at larger stresses that improve grain contacts. These observations are correlated to the sample densities obtained from mass and volume determination. The density increases from 3.10 g/cm^3 for non-pressed sample to 4.65 g/cm^3 (with respect to the theoretical value of 4.92 g/cm^3) for the sample prepared at 16 MPa.

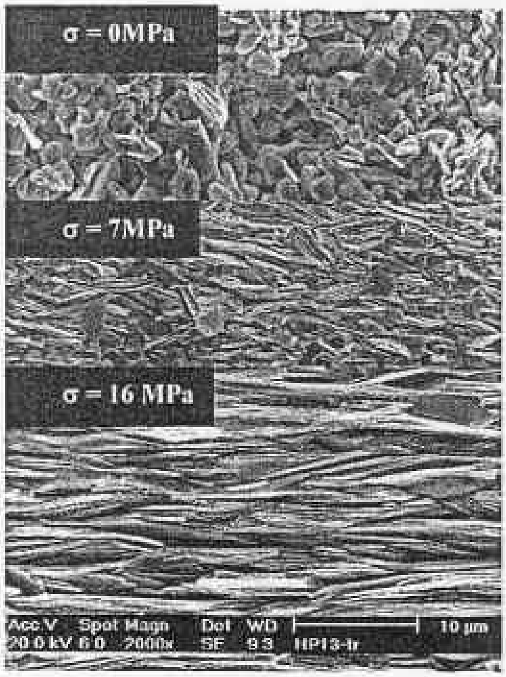

Figure.1: SEM-images of the cross-section of the samples processed at various mechanical pressures.

The temperature (T) dependence of the resistivity (ρ) for the reference $Ca_3Co_4O_9$ sample (σ = 0 MPa), and the samples processed under 7 and 16 MPa respectively is showed in figure 2. For the thermo-forged samples, the current was injected perpendicular to the processed stress direction, in this way the current flow essentially in ab-planes as seen in the high magnification microstructure (figure 1, σ = 16 MPa). The ρ(T) curves show similar behaviour, corresponding to the metal to semiconducting transition from high (400 K) to low temperature (5 K). This is in agreement with earlier reports [2, 5] on the thermoelectric oxides. These curves shows that the room temperature resistivity of the non-pressed sample is 27.19 mΩ.cm as compared to 17.92 and 5.12 mΩ.cm for the samples processed under 7 and 16 MPa. The decrease in resistivity values can be argued as due to the densification of the material under hot-pressing and good alignment between platelets. The signature of the grain boundary component to the resistivity seems to be low for the hot forged samples. In the other hand, the resistivity (ρ) of anisotropic sample is studied by using the Montgomery method [12]. According to the sample geometry, the resistivity can be measured by injecting the current and measuring the voltage between various configurations of the contacts (figure 3a). Figure 3b shows the temperature dependence of the resistivity following the direction perpendicular and parallel to the stress applied during the thermo-forging. From these measurements, we can clearly observe the transition around 50 K between the semi-conducting behaviour at low temperature and metallic state at high temperature. One can also deduce an anisotropy of 4 at room temperature, corresponding to the ratio of resistivities measured parallel ($\rho^{//}$ or ρ^{ab}) and perpendicular ($\rho^{\perp}$ or ρ^{c}) to the current flow directions respectively. The comparison with the sample processed without applied stress using the same thermal conditions shows that, at room temperature, the resistivity value lies between in-plane and out of plane configurations, but closer to the out of plane value in agreement with the statistical random distribution of the crystallites.

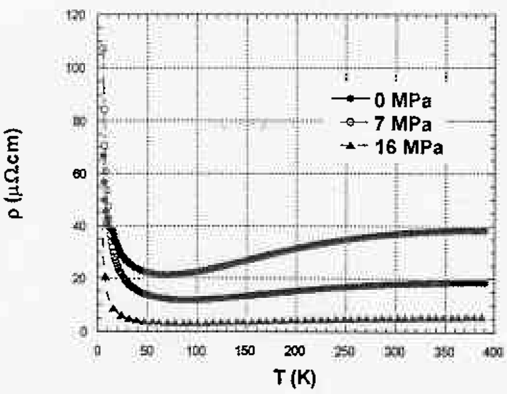

Figure.2: Effect of synthesis stress (σ) on the room temperature resistivity.

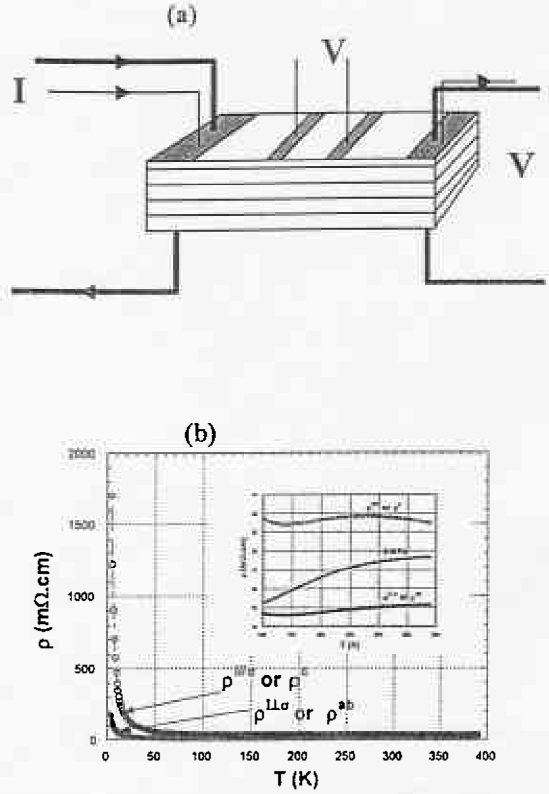

Figure.3: (a) Sketch of the geometry used for measuring resistivity. (b) Temperature dependence of the resistivity, ρ, for current applied parallel (o) and perpendicular (●) to the stress (σ = 16 MPa) axis. (Inset) high magnification above room temperature showing the non-textured sample (σ) between both configurations.

The ρ value obtained for the non-forged sample is comparable with the values reported [2] of $Ca_3Co_4O_9$ prepared by conventional solid state techniques.

The temperature dependence of the Seebeck coefficient for the in-plane hot-forged (σ = 16 MPa) samples is illustrated on figure 4. We can notice the positive values confirming the p-type conductor behaviour. At room temperature the large magnitude of 140 μV/K obtained can be compared with data reported in the literature [5, 6, 10]. Shortly, we will perform the thermal conductivity in order to determine the figure-of-merit (ZT) of our highly dense textured specimen.

Quantitative texture analysis of the anisotropic sample has been investigated using XRD and neutron measurements. The XRD pattern of the top surface of the sample processed at 16 MPa, exhibits strongly dominant {00ℓ} peaks indicating the presence of a strong texture (figure 5) with respect to the non-textured sample [13] where all the peak intensities are indexed. The combined analysis of the neutron data [14] indicated that the {00ℓ} orientation is the unique component of texture as reported by Guilmeau et al. [7], with comparable texture strengths.

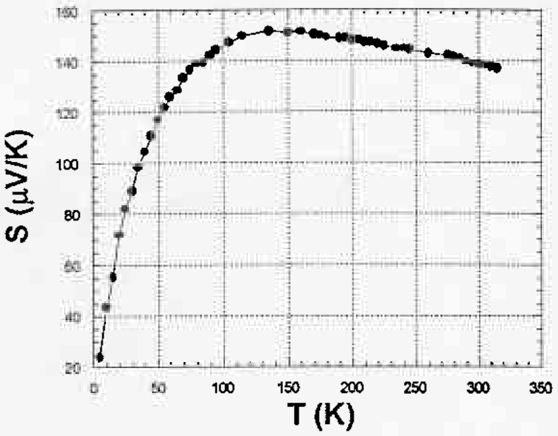

Figure.4: Seebeck coefficient vs. temperature for the hot-forged (σ = 16 MPa) sample.

The texture is axially symmetric around the stress axis giving rise to the {00ℓ} cyclic fibre texture. Figure 6 illustrates the achieved texture degrees at the intermediate (7 MPa) and largest applied pressure (16 MPa) using {004} pole figures. The maximum orientation density on these figures is around 3.9 m.r.d. (multiple random distribution) and 16.8 m.r.d. with 23 % and 33 % of the volume randomly oriented, respectively.

A quantitative correlation between anisotropic electrical resistivity, Seebeck coefficient, thermoelectric power, figure of merit and texture strength is now under examination in order to estimate potentialities of the thermo-forging technique for the elaboration of these thermoelectric compounds.

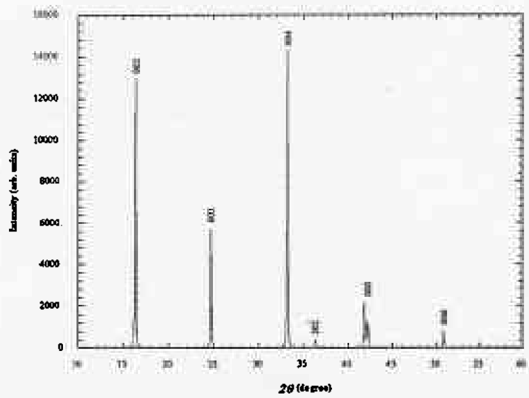

Figure.5: XRD patterns of hot-forged $Ca_3Co_4O_9$ bulk sample, the surface parallel to the applied stress (σ = 16 MPa) during the process.

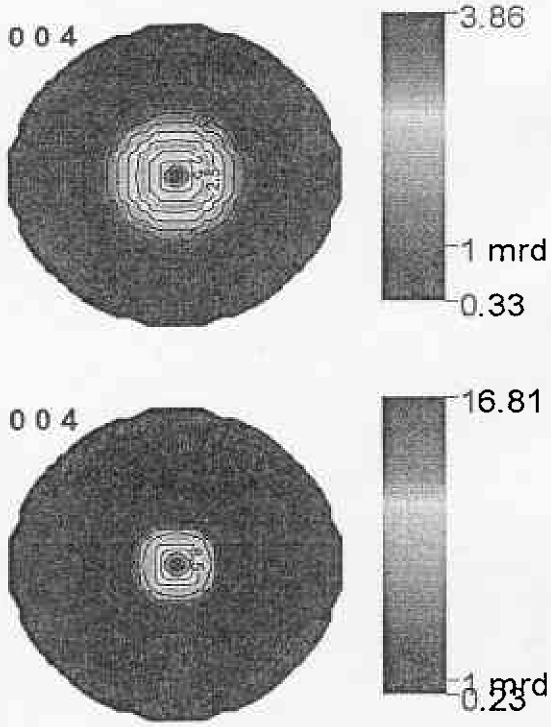

Figure.6: {004} Pole figures for the samples processed at 7 and 16 MPa, top and bottom respectively.

Conclusions

In summary, the thermoelectric oxide $Ca_3Co_4O_9$ bulks have been processed using thermo-forging technique. The pellets obtained are highly dense and strongly oriented with the mean c-axis parallel to the stress direction applied during the heat treatment. Crystallite alignment of the bulk sample is confirmed by the strong texture as seen from the neutron diffraction measurements and corresponds to the grain orientation as seen by SEM measurements. The thermoelectric power of 140μV/K is promising and the figure-of–merit will be investigated soon.

Acknowledgments

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