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ScienceDirect

Ceramics International 41 (2015) 10897–10903

CERAMICS INTERNATIONAL

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Effect of Na doping on the $Ca_3Co_4O_9$ thermoelectric performance

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Received 23 March 2015; received in revised form 20 April 2015; accepted 6 May 2015
Available online 14 May 2015

Abstract

$Ca_{3-x}Na_xCo_4O_9$ polycrystalline thermoelectric ceramics with small amounts of Na ($x=0$, 0.01, 0.03, 0.05, 0.07, and 0.10) have been prepared using the classical solid state method. Microstructural characterization has shown that Na has been incorporated into the $Ca_3Co_4O_9$ phase and that no Na-based secondary phases have been produced. It has also been found that Na addition promotes grain growth and favours sintering due to the formation of a small amount of liquid phase. Electrical resistivity decreases when Na content increases until 0.07Na addition while Seebeck coefficient is maintained practically unchanged. The improvement in electrical resistivity leads to higher power factor values than the usually obtained in samples prepared by more complex and expensive techniques.

Keywords: A. Sintering; C. Electrical properties; Doping; Seebeck coefficient

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1. Introduction

Thermoelectric (TE) materials are characterized by their ability to directly transform a temperature gradient to electrical power due to the Seebeck effect. The conversion efficiency of such materials is usually quantified by the dimensionless figure of merit ZT, $TS^2/\rho\kappa$ (where the electrical part S^2/ρ is also called power factor, PF), where S, ρ, κ, and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively [1]. This characteristic has attracted attention to this type of materials for applications in waste heat recovery devices or solar thermoelectric generators [2–4].

Considering the ZT expression, a high performance thermoelectric material should possess a large Seebeck coefficient together with low electrical resistivity and thermal conductivity. The low electrical resistivity is necessary to avoid Joule heating while the low thermal conductivity is required to maintain a large temperature gradient in the thermoelectric device.

Nowadays, TE devices are based on intermetallic materials, such as Bi_2Te_3 or $CoSb_3$, with high ZT values [5–7], and can be industrially used at relatively low temperatures, e.g. in vehicles exhaust. On the other hand, these intermetallic materials show some important drawbacks, as their scarcity in earth's crust [8] or their degradation and/or liberation of heavy elements at high temperatures under air [4]. These problems lead to the limitation of their working temperatures constraining their effective performances. These temperature limitations were surpassed by the discovery, in 1997, of attractive thermoelectric properties in $Na_2Co_2O_4$ ceramics [9], which have higher chemical stability at high temperatures. Moreover, they are composed of cheaper, more environmentally friendly, and abundant elements than the intermetallic ones. This discovery boosted the search for new ceramic materials with high thermoelectric performance. Nowadays, different thermoelectric ceramics are studied as promising materials for practical applications, such as MnO-, $SrTiO_3$-, or CoO-based ceramics [10–13]. The MnO- and $SrTiO_3$-based ceramics are well known as n-type thermoelectric elements while the CoO-based ones, as p-type. In this last type, the research is now focused on materials with high thermoelectric

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http://dx.doi.org/10.1016/j.ceramint.2015.05.031
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performances and high thermal stability, such as $Ca_3Co_4O_9$, with very interesting thermoelectric properties [14,15].

Crystallographic studies have demonstrated that Co-based materials possess a monoclinic structure which is, in turn, composed of two different layers. These layers are a common conductive CdI_2-type hexagonal CoO_2 layer with a two-dimensional triangular lattice and a block layer composed of insulating rock-salt-type (RS) layers. The two sublattices (RS block and CdI_2-type CoO_2 layer) are alternatively stacked to form the crystal structure. Moreover, they possess common *a*-axis and *c*-axis lattice parameters and β angles, but different b-axis length, causing a misfit along the *b*-direction [16,17].

Studies performed on these CoO-based ceramics have demonstrated that the Seebeck coefficient values are governed by the incommensurability ratio and/or the charge of the RS block layer [18]. This effect provides the basis for tuning up the thermoelectric properties by chemical substitutions in this family [19–24]. On the other hand, it is well established that electrical resistivity is drastically affected by the presence of secondary phases, porosity, and grains connectivity [25]. As a consequence, some metallic additions producing a small amount of liquid phase during sintering are usually employed to decrease electrical resistivity by improving the electrical connectivity between the grains [26].

Other important characteristic associated to the high crystallographic anisotropy of these materials is the formation of plate-like grains during the sintering process. This shape anisotropy opens the route to align preferentially the grains using physical, mechanical and/or chemical processes. Such processes should allow the alignment of the conducting planes leading to macroscopic properties comparable to the obtained on single crystals. Numerous methods have been reported to be efficient in producing well aligned bulk materials, such as hot uniaxial pressing [27,28], spark plasma sintering (SPS) [29,30], laser floating zone melting (LFZ) [31,32], electrically assisted laser floating zone (EALFZ) [33,34], templated grain growth (TGG) [35], *etc*. The main advantage of these techniques is the production of materials with very low electrical resistivity values due to the preferential alignment of conducting planes with the current flow direction. On the other hand, these methods possess some drawbacks, as the high price of the spark plasma device and the relatively long processing time of the hot uniaxial pressing or the TGG. In the case of the melt-growth processes, it has been reported that the final electrical properties are strongly dependent with the growth speed [36,37].

The aim of this work is to study the effect of doping on the microstructural and thermoelectric properties of $Ca_3Co_4O_9$ ceramics prepared by a simple and cheap procedure. With this goal, $Ca_{3-x}Na_xCo_4O_y$ (x=0, 0.01, 0.03, 0.05, 0.07, and 0.10) polycrystalline ceramics will be prepared using the classical solid state route. The structural and microstructural modifications produced by the Na addition will be related with the changes on the thermoelectric performances.

2. Experimental

$Ca_{3-x}Na_xCo_4O_9$ polycrystalline ceramic materials, with x=0.00, 0.01, 0.03, 0.05, 0.07, and 0.10, were prepared by the conventional solid state route using $CaCO_3$ (Panreac, 98+%), Na_2CO_3 (Panreac, 98+%), and Co_2O_3 (Aldrich, 98+%) commercial powders as starting materials. They were weighed in the appropriate proportions, well mixed and ball milled for 30 min at 300 rpm, in acetone media, in an agate ball mill. The obtained suspension has then been dried under infrared radiation until all the acetone has been evaporated. The resulting powder mixture was manually milled, to break the agglomerates, and subsequently thermally treated at 750 and 800 °C for 12 h under air, with an intermediate manual milling to decompose the carbonates [15]. After the thermal treatments, the powders were uniaxially pressed at 400 MPa for 1 min in order to obtain green ceramic parallelepipeds (3 mm × 2.5 mm × 14 mm), with an adequate size for their thermoelectric characterization. The green ceramics were then sintered in the optimal conditions found in previous works, consisting in one step heating at 900 °C during 24 h with a final furnace cooling [38].

Powder X-ray diffraction (XRD) patterns have been systematically recorded in order to identify the different phases in the sintered materials. Data have been collected at room temperature, with 2θ ranging between 5° and 60°, using a Rigaku D/max-B X-ray powder diffractometer working with Cu Kα radiation. Apparent density measurements have been performed on several samples for each composition after sintering, using 4.677 g/cm^3 as theoretical density [39].

Microstructural observations were performed on the samples surface, using a Field Emission Scanning Electron Microscope (FESEM, Carl Zeiss Merlin) fitted with an energy dispersive spectrometer (EDS). Several micrographs of the samples have been used to estimate grain sizes in all the samples by the line intercept method using Image-Pro Plus software. Electrical resistivity and Seebeck coefficient were simultaneously determined by the standard dc four-probe technique in a LSR-3 measurement system (Linseis GmbH), in the steady state mode between 50 and 800 °C under He atmosphere. From the resistivity values, the activation energy and the relative carrier concentration for each composition have been estimated. Moreover, with the electrical resistivity and Seebeck coefficient data, the power factor has been calculated in order to determine the samples performances. These properties have been compared with the results obtained in undoped samples and with those reported in the literature.

3. Results and discussion

Powder XRD patterns for the different $Ca_{3-x}Na_xCo_4O_9$ samples are displayed in Fig. 1 (from 5° to 40° for clarity). In these graphs, it is clear that all the samples have very similar diffraction patterns. In all cases major peaks are associated to the thermoelectric $Ca_3Co_4O_9$ phase, indicated by its reflection planes in Fig. 1f, in agreement with previously reported data [40]. Moreover, it is accompanied by small amounts of $Ca_3Co_2O_6$ (peaks shown by * in Fig. 1f) [40], while the peak marked by belongs to the (111) diffraction plane of Si, used as reference. On the other hand, careful observation of these diagrams shows that there is no Na-based secondary phase indicating that Na should have been incorporated into the