Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Full Length Article

Sintering behavior, microstructure and thermoelectric properties of calcium cobaltite thick films for transversal thermoelectric multilayer generators

Thomas Schulz[a], Timmy Reimann[a], Arne Bochmann[a], Andre Vogel[b], Beate Capraro[b], Björn Mieller[c], Steffen Teichert[a], Jörg Töpfer[a,*]

[a] Univ. Applied Sciences Jena, Dept. SciTec, C.-Zeiss-Promenade 2, 07745, Jena, Germany,
[b] Fraunhofer IKTS, M. Faraday-Str. 1, 07629, Hermsdorf, Germany
[c] Federal Institute for Materials Research and Testing BAM, Unter den Eichen 87, 12205, Berlin, Germany

ARTICLE INFO

Keywords:
Thermoelectric oxides
Thermoelectric generator
Multilayer,

ABSTRACT

The sintering behavior and the thermoelectric performance of $Ca_3Co_4O_9$ multilayer laminates were studied, and a multilayer thermoelectric generator was fabricated. Compacts and multilayer samples with anisotropic microstructure and residual porosity were obtained after conventional sintering at 920 °C, whereas dense and isotropic multilayer samples were prepared by firing at 1200 °C and reoxidation at 900 °C. A hot-pressed sample has a dense and anisotropic microstructure. Samples sintered at 920 °C exhibit low electrical conductivity due to the low density, whereas the Seebeck coefficient is not sensitive to preparation conditions. However, thermal conductivity of multilayers is very low, and, hence acceptable ZT values are obtained. A transversal multilayer thermoelectric generator (TMLTEG) was fabricated by stacking layers of $Ca_3Co_4O_9$ green tapes, AgPd conductor printing, and co-firing at 920 °C. The TMLTEG has a power output of 3 mW at $\Delta T = 200$ K in the temperature interval of 25 °C to 300 °C.

1. Introduction

Thermoelectric energy conversion based on the transfer of waste heat into electricity is regarded as one of the promising energy harvesting technologies. Thermoelectric generators (TEG) are systems that produce electric power through harvesting the energy of a temperature gradient. Typically, a standard TEG is composed of a series of many two-leg elements, each of them consisting of individual legs of p- and n-type semiconducting thermoelectric materials. In most TEGs, classic TE semiconductors, e.g. Bi_2Te_3, PbTe, etc., are used as thermoelectric materials [1]. However, oxide thermoelectric materials have also attracted a lot of attention because of their stability at high temperatures, nontoxicity, and availability [2,3].

$Ca_3Co_4O_9$ (CCO) has been reported as one of the promising p-type thermoelectric oxide materials with ZT increasing with temperature and reaching ZT = 0.3 at 800 °C [2,3]. CCO is a misfit layer compound with a crystal structure that comprises a stacking in the c-direction of CoO_2 layers (built from edge-sharing CoO_6 octahedra) and triple Ca_2CoO_3 rock salt layers which can be characterized as $[Ca_2CoO_3]_xCoO_2$ [4]. CCO shows a large Seebeck coefficient of $S \geq 100$ μV/K at room temperature that increases with temperature [2]. Because of its layered structure, CCO samples typically exhibit an anisotropic microstructure with platelets oriented along the c-axis, which causes anisotropy of the thermoelectric properties [5]. The conventional synthesis of CCO samples is limited by its low thermal stability: CCO decomposes at 926 °C into $Ca_3Co_2O_6$ and $Ca_{1-x}Co_xO$ [6,7]. The thermoelectric performance depends on the sintering temperature: a maximum power factor was found after sintering at 920 °C, at higher sintering temperature the resistivity increases because of partial CCO decomposition [8]. Therefore, conventional sintering of CCO to prepare dense ceramic samples with high electrical conductivity and power factor is challenging. Pressure-assisted techniques, e.g. spark plasma sintering (SPS) and hot pressing were used to fabricate dense samples with improved texture and thermoelectric properties [9,10] [e.g. 9,10]. Alternatively, a two-step synthesis of dense CCO samples via a high-temperature sintering and subsequent annealing was reported recently [11–13]. Upon the initial high-temperature densification step, CCO completely decomposed into a $Ca_{1-x}Co_xO/Ca_yCo_{1-y}O$ mixture. Subsequent long anneals at 900 °C lead to the re-formation of a polycrystalline, dense CCO ceramics with small and randomly oriented grains and an excellent power factor of 420 μW/K^{2}m at 800 °C [11].

Dual-leg thermoelectric generators, using sintered CCO pellets as p-type legs, have already been fabricated. As an example, a TEG with eight dual-leg pairs of CCO in combination with n-type $CaMnO_3$ was

* Corresponding author at: Univ. Appl. Sciences Jena, Carl-Zeiss-Promenade 2, 07745 Jena, Germany.
E-mail address: joerg.toepfer@eah-jena.de (J. Töpfer).

https://doi.org/10.1016/j.jeurceramsoc.2017.11.017
Received 22 September 2017; Accepted 7 November 2017

reported, that is capable of generating a power output of about 0.3 W at a temperature gradient of about 1000 K [14]. As an alternative concept of thermoelectric power generation, transversal thermoelectric generators (TTEGs) were proposed [15–17]. In TTEGs, the transverse thermoelectric effect generates a thermovoltage perpendicular to the direction of the heat flow. This is in contrast to conventional TEGs, which rely on the longitudinal thermoelectric effect; in which case the voltage is provided along the thermal gradient. For application of the transversal thermoelectric effect in generators, two-phase stacked synthetic materials with anisotropic thermoelectric properties were designed, which consist of slabs of a thermoelectric semiconductor with a large Seebeck coefficient (either p- or n-type), and a metal with large electrical and thermal conductivity [15–17].

In the field of low-power thermoelectric generators, multilayer generator architectures are gaining interest. Instead of combining many two-leg elements consisting of p- and n-type blocks to compose a standard TEG, Hayashi et al. recently fabricated oxide-based multilayer thermoelectric generators (MLTEG), using a standard ceramic multilayer technology [18]. Tapes of n- and p-type thermoelectric oxides are stacked alternatively, separated by an insulating layer and connected by metal contacts. The laminated multilayer stack is co-fired to give a multilayer generator consisting of many dual-leg thermoelectric pairs in series. However, due to the complex multilayer architecture and the number of different materials (two TE oxides, insulator, metal) in the multilayer stack, the practical realization of co-firing remains challenging. Later, another type of multilayer generator was prepared, consisting of n-type $SrTiO_3$ layers and NiMo metal layers [19]. This MLTEG has a maximum power of about 10 mW at $\Delta T = 100$ K [19]. Very recently, Funahashi et al. have demonstrated, that a MLTEG of $Ca_3Co_4O_9$ and ZnO may also be prepared using the cold sintering technology [20].

Recently, the multilayer technology has been adapted to prepare oxide multilayer thermoelectric generators that use the transverse thermoelectric effect. As proof of principle, $La_{1.97}Sr_{0.03}CuO_4$ (LSCO) p-type thermoelectric oxide pellets were stacked interweaved with diagonal layers of printed silver paste contacts [21]. This simple transversal TEG has a maximum output power of about 1 mW at a small temperature difference of $\Delta T = 30$ K [21]. Next, a monolithic transversal multilayer thermoelectric generator (TMLTEG) was fabricated by stacking green tapes of p-type LSCO, printing AgPd stripes onto the green tapes at a certain angle relative to the direction of the heat flow, and co-firing at 1000 °C [22]. This transversal multilayer TEG device exhibits a maximum power output of 4.0 mW at $\Delta T = 225$ K, which agrees well with results of three-dimensional numerical simulations utilizing the transport parameters of the two materials and the geometry data of the device [22]. Moreover, five of these TMLTEGs were combined to a meander-type TMLTEG device with a maximum electrical power output of 30.2 mW at a $\Delta T = 208$ K [23]. This device is able to provide sufficient energy to power a simple electronic sensor application with transmission functions at temperature gradients as low as $\Delta T = 35$ K [23].

In this contribution, we report for the first time on the fabrication of a transversal multilayer thermoelectric generator (TMLTEG) using p-type CCO layers in combination with Ag contacts, and co-firing at 920 °C. We will compare the sintering behavior, anisotropic microstructure formation and thermoelectric properties of CCO multilayers prepared by different sintering routines. The design, fabrication and performance of a CCO-based transversal multilayer TEG with a maximum output power of about 3.0 mW at $\Delta T = 200$ K will be presented.

2. Experimental

$Ca_3Co_4O_9$ (CCO) powder was prepared by the mixed-oxide route using $CaCO_3$ (Merck, pure) and Co_3O_4 (Alfa Aesar, 99.7%) as starting materials. $CaCO_3$ was calcined at 1000 °C for 5 h to transform it into CaO. Co_3O_4 was heated to 800 °C for 3 h for drying. Both oxides were weighed after cooling and mixed for 6 h in a roller mill with isopropanol using zirconia grinding media. The dried mixture was calcined twice at 900 °C for 15 h with intermediate homogenization and sieving. The powder was milled in isopropanol in a planetary ball mill (Fritsch Pulverisette 5) using a POM polymer grinding vessel with zirconia grinding beads (1 mm diameter) for one hour between the calcinations, and for 3 h after calcination, respectively. The fine-milled CCO powder has an aggregate particle size of $d_{50} = 2.1$ µm as measured by laser diffraction. The BET specific surface of the powder is $S = 3.3\ m^2/g$.

Samples were consolidated by uniaxial pressing (diameter 10 mm and 40 mm) with addition of a solution of polyvinyl alcohol as pressing aid and a pressure of 300 MPa. The pellets were conventionally sintered (CS) at 920 °C (heating rate 10 K/min) for 24 h in air. CCO green tapes with a thickness of 120 µm were prepared by tape casting. The calcined and ground CCO powder was mixed with solvent (methyl ethyl ketone and ethanol), binder, and dispersant to give slurry, which was cast on a Mylar carrier tape using a doctor-blade casting unit. For sintering experiments and measurements of the thermoelectric properties, twenty-one layers of CCO tape were stacked, laminated at 80 °C and 20 MPa, and sintered for 24 h at 920 °C (ML CS). The samples were heated with 0.5 K/min to 500 °C for debindering, and then with 2.5 K/min to 920 °C. For comparison, CCO tape laminates composed of six layers were hot pressed using an ATV PHP-603 sintering press. To avoid reactions of the CCO laminate with the porous SiC setter plates of the press, the multilayer laminate was placed between sacrificial zirconia tapes. The heating rate was 0.5 K/min to 500 °C and 2.5 K/min to 920 °C. An axial pressure of 10 MPa was applied during dwell time at 920 °C for 24 h and removed before cooling with 2.5 K/min (ML HP). Another batch of laminates was fired using the two-step synthesis process as already reported as an alternative sintering (AS) process to prepare dense CCO pellet samples [13]. In that case, laminates were fired at 1200 °C in air for 6 h (heating rate 0.5 K/min to 500 °C, and 2.5 K/min to 1200 °C), and then cooled to 900 °C with 10 K/min and annealed at 900 °C for 72 h (ML AS).

For multilayer generator preparation, metal contact stripes (width: 450 µm; distance 350 µm, angle: 30°) were screen printed onto the CCO tapes using AgPd paste (DP 6134). Ten thermoelectric layers with printed stripe electrodes were stacked and covered with an additional oxide thermoelectric layer, and laminated. Multilayer laminates were heated at a rate of 0.5 K/min to 500 °C for slow debindering. Sintering was performed for 6 h at 920 °C in air (ML CS). The fabricated transversal thermoelectric multilayer generators (TMLTEG) have dimensions of 38 mm × 3.3 mm × 5.8 mm.

The particle size of the CCO powder was measured using laser diffraction (Malvern Mastersizer 2000). The specific surface S of the powder was measured by nitrogen adsorption (BET, Nova 2000, Quantachrome Instruments). The bulk density of the sintered samples was measured using Archimedes' method; the measured density values are given relative to the theoretical density of 4.68 g/cm^3 calculated using the lattice parameters from ref. [4]. Scanning electron microscopy (SEM) was performed with a ZEISS Ultra 55 microscope. The phase composition of all samples was studied by X-ray diffraction (XRD, Co K_α radiation) with a Bruker D8 Discovery diffractometer. The microstructural anisotropy was characterized by measuring pole figures of the (002) and (111) lattice planes with a tilt angle Psi $\chi = 0 - 80°$ (increment $\Delta\chi = 5°$) in a full circle Phi $\phi = 0 - 360°$ (increment $\Delta\phi$ = various). In order to measure the pole figure with a nearly constant local resolution the increment $\Delta\phi$ was selected depending on the χ values and the increment $\Delta\chi$ following $\cos(\Delta\phi(\chi)) \approx (\cos(\Delta\chi) - \cos^2\chi)/\sin^2\chi$. The pole figures were calculated using Bruker Multex 3.0; further data evaluation and plotting was performed using the MTEX toolbox 4.3 for MATLAB (The MathWorks Inc., Natick, USA). Resistivity and Seebeck coefficients were measured between room temperature and 700 °C using a Linseis LSR3 system. The thermal conductivity was obtained from measurements of the thermal diffusivity λ with a Linseis Laser flash system LFA1200, and a Linseis