ENHANCED THERMOELECTRIC PROPERTIES OF $Ca_3Co_4O_9$ BY POST SINTERING METHOD

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Received 23 June 2016; Revised 24 August 2016; Accepted 30 August 2016

ABSTRACT

Polycrystalline $Ca_3Co_4O_9$ (Ca–349) thermoelectric material was synthesized by solid state reaction (SSR), sintering and post sintering methods. The crystal structure of Ca–349 material was confirmed by X–ray diffraction (XRD), and transmission electron microscopy (TEM) techniques. The Seebeck coefficient, electrical resistivity, and thermal conductivity were measured by steady state method at a temperature range of 300–473 K. It was found that the Ca–349 post sintered material showed Seebeck coefficient and electrical resistivity values similarly to those in literature review. The thermal conductivity was decreased, and the dimensionless figure of merit increased to more than 100% compared with literature review.

KEYWORDS: *ceramic materials, electrical properties, thermal properties, crystal structure*

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INTRODUCTION

Thermoelectric (TE) materials are one of the promising materials for alternative energy and clean energy in the future. They convert temperature difference into an electricity and can also change an electricity to temperature difference between end sides of *p*– and *n*–type materials. The TE material performance is defined by dimensionless figure of merit ($ZT = S^2T\,\rho^{-1}\,\kappa^{-1}$) where S is Seebeck coefficient, ρ is electrical resistivity, κ is thermal conductivity, and T is absolute temperature. The Ca–349 material can be prepared by many processes such as sol–gel, hot press, hydrothermal, spark plasma sintering, and SSR. However, the SSR method is the most easily processed and ZT value can be enhanced by post sintering method.

In this paper, synthesis of Ca–349 powder by SSR and bulk by post sintering method in air to adjust the crystal structure and enhance thermoelectric properties. The S, ρ, κ and ZT values of Ca–349 bulk were investigated.

MATERIALS AND METHODS

Polycrystalline Ca–349 material was synthesized by SSR and post sintering methods using $CaCO_3$ (Lot 7, QREC New Zealand), and Co_2O_3 (Lot 71020, Sigma–Aldrich Laborchemikalien) precursor powders. The precursor powders were mixed by zirconia balls milling method for 2 h in air. The mixed precursor powders were calcined at 1073 K for 10 h a heating rate of 293 K min^{-1} in air with grinded and pressed into initial discs at 500 MPa into discs size of $2\times2\times0.3$ cm^3. The discs sintered at 1123 K for 12 h

in air in to first bulk sample then slowly cooled dawn to room temperature according to the thermal inertia of heat in furnaces to prevent cracks in the samples. The first bulk sample was grinded and pressed to sinter again at an identical condition into final bulk sample. The phase transformation of final sample (post sintering) powder was analyzed using XRD.

The crystal structure of post sintered Ca–349 powder was analyzed by XRD using Cu Kα (λ = 1.54056), voltage 40 kV, current 30 mA, scan speed 2.0° min^{-1} and a scan range of 10–70°. The microstructure of post sintered Ca–349 powder was observed by SEM and TEM. The Seebeck coefficient, electrical resistivity and thermal conductivity of the post sintered Ca–349 bulk sample were measured using steady state method at a temperature range of 300–473 K. In addition, the dimensionless figure of merit of post sintered Ca–349 sample is calculated.

RESULTS AND DISCUSSION

The XRD patterns of the calcined and post sintered Ca–349 powder are shown in Fig. 1. All peaks have been matched with the PDF card # 00–058–0661 of Ca–349 material indicating monoclinic symmetry. Therefore, the Ca–349 material was successfully prepared using the SSR and post sintering methods. The calculated lattice parameters are a = 4.8656 Å, b = 4.58799 Å and c = 10.6417 Å with β = 82.36°. The morphologies from SEM images of post sintered Ca–349 powder are shown in Fig. 2. The figure shows randomly oriented grains with different geometry and average sizes of about 5 µm. The defect–free periodic crystal structure with visible distinct layers of a Ca–349 unit cell is shown in Fig. 3 (a). The brighter vertically running lines were spaced by 10.6399 Å along the c–axis agree with c lattice parameter calculated (10.6417 Å) for post sintered Ca–349 material. The spacing of the crystal planes was calculated by $d = L\lambda R^{-1}$, where d is the spacing of the crystal planes, L is the camera length in pixels, λ is the electron wavelength, and R is distances from the central spot in pixels. The diffraction patterns were indexed by measuring the distances from the central bright spot (0,0,0) to each of the individual spots, as shown in Fig. 3 (b).

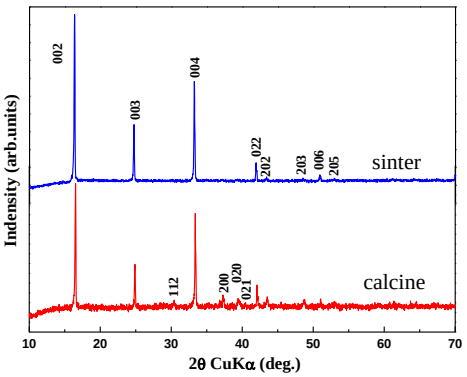


Fig. 1. XRD patterns of calcined Ca–349 powder at 1073 K for 10 h (red line) and sintered at 1123 K for 12 h (blue line)

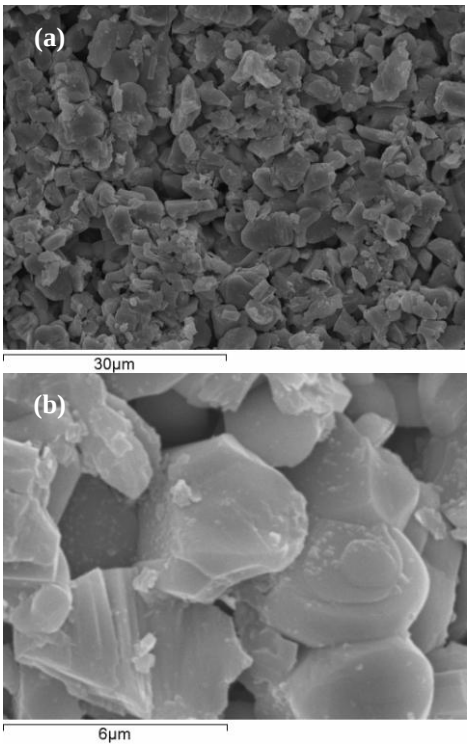
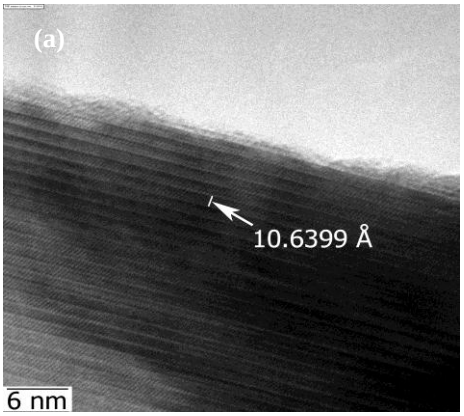


Fig. 2. SEM images of post sintered Ca–349 (a) powder (b) bulk sample



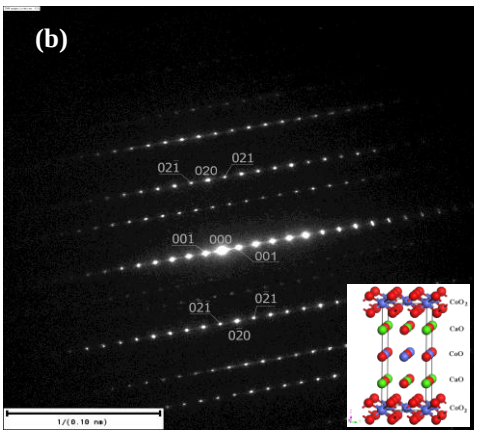


Fig. 3. TEM image of post sintered Ca–349 powder (a) high resolution image (b) diffraction patterns

In Fig. 4 (a), Seebeck coefficient of post sintered Ca–349 material shows as a function of temperature at 300−423 K along with the literature data [1-6]. The absolute value of the Seebeck coefficient was slightly increased with increasing temperature correspond with literature data. Seebeck coefficient value was slightly varied between 123−128 μV K^{-1} with positive value at all temperatures indicating *p*−type thermoelectric materials. The electrical resistivity of post sintered Ca–349 bulk sample at temperature range of 300−423 K is seen in Fig. 4(b). The post sintered Ca–349 bulk sample exhibited similar behavior to literature data [1-6]. The electrical resistivity of the post sintered Ca–349 bulk sample shows the lowest value of about 3.85 mΩ cm at 423 K and decreases with increasing temperature indicating semiconductor−like behavior [1, 2, 4]. The thermal conductivity of post sintered Ca–349 bulk sample was compared with literature data, as shown in Fig. 4(c). The thermal conductivity values are obtained about 0.8 W $m^{-1}K^{-1}$ at 423 K and slightly decreases with increasing temperature. These are lower than literature data. The ZT values of post sintered Ca–349 sample were evaluated from the S, ρ and κ values, as shown in Fig. 4(d). The ZT values increased with increasing temperature and are higher than reported literature data [1-7] about 0.07 at 423 K.

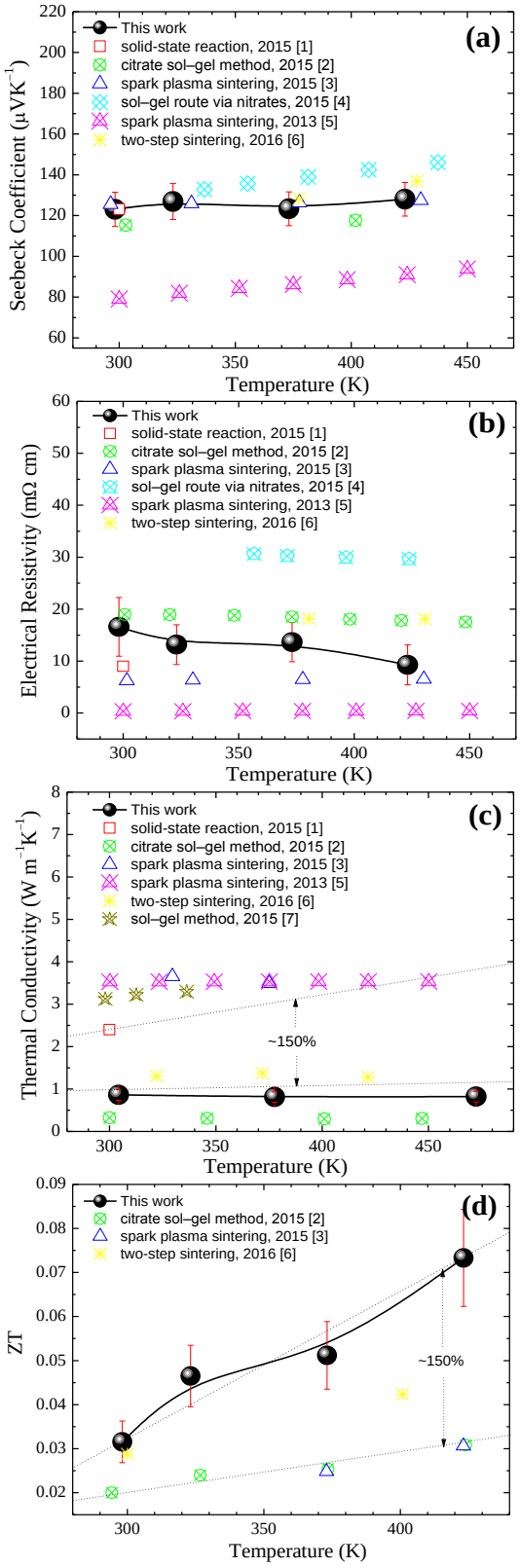


Fig. 4. Temperature dependent on (a) Seebeck coefficient, (b) electrical resistivity, (c) thermal conductivity and (d) ZT of post sintered Ca–349 material together with literature data

CONCLUSION

Polycrystalline Ca–349 with good thermoelectric properties was synthesized by SSR and post sintering methods. The crystal structure and TE properties of the post sintered Ca–349 material were studied. Crystallites characteristics from XRD and TEM results show phase of the Ca–349 material. The TE properties of post sintered Ca–349 bulk sample showed low thermal conductivity of about 0.82 W $m^{-1} K^{-1}$ at 423 K and the highest ZT of about 0.07 at 423 K which was more than the first sintering of 150%.

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