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The effects of sintering temperature on preparation, resistivity, and thermopower of *c*-axis oriented $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$ films fabricated using sol–gel spin coating method

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Abstract

We report fabrication of the *c*-axis oriented $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$ films by a simple sol–gel spin coating method. The films prepared in the temperature range of 650–700 °C show nonmetallic temperature dependence of resistivity in the whole investigated temperature range, whereas the films prepared in the temperature range of 750–775 °C show metallic temperature dependence in the high temperature regime. Sintering the films at higher temperature leads to larger grains, lower resistivity and smaller thermoelectric power. This can be explained in the framework of the barrier theory and confirmed by the higher hole carrier concentration from the Hall measurements according to Seto's derivation between the carrier concentration and the barrier height. The temperature dependence of resistivity resembles that of the in-plane single crystal of $Ca_3Co_4O_{9+\delta}$ in terms of the Fermi-liquid behavior. The effects of lower sintering temperature on the transport coefficient A and Fermi-liquid scale $T*$ of Fe-substituted cobaltite films seems to be similar to applying hydrostatic pressure on a single crystal of $Ca_3Co_4O_{9+\delta}$. The temperature dependence of resistivity in the nonmetallic region follows the variable-range hopping conduction in the form of $T^{-1/3}$, due to the 2-dimensional character of the films.

Keywords: Thermoelectrics; Cobaltites; Sintering temperature; Barrier theory; X-ray diffraction; Atomic force microscopy; Electrical measurements and properties

1. Introduction

Layered cobalt oxides of $Ca_3Co_4O_{9+\delta}$ have been extensively studied in the recent years due to their potential applications in thermoelectric devices [1–4]. For practical applications, thermoelectric materials require large thermoelectric power (TEP), low electrical resistivity and low thermal conductivity to obtain a high figure of merit $Z=S^2/\rho k$, where S, ρ, k are respectively TEP, electrical resistivity and thermal conductivity. The structure of $Ca_3Co_4O_{9+\delta}$ crystal is composed of an alternative stack of CdI_2-type CoO_2 layer and rock-salt-type Ca_2CoO_3 layer along the *c*-axis. Enhancement of the thermoelectric figure of merit might rely on reducing dimensionality of the materials through enhancing thermopower by increasing $\partial g(E)/\partial E$ near the Fermi energy, where $g(E)$ is the density of states, and lowering the lattice thermal conductivity by increasing the boundary phonon scattering. Epitaxial growth of thin films is one of the preparation methods to serve this purpose [5].

Thin films of $Ca_3Co_4O_{9+\delta}$ have recently been prepared by using pulsed laser deposition [6–8], rf-planar magnetron sputtering [9] and topotactic ion-exchange method [5]. The sol–gel spin coating method is one of the promising fabrication methods of oxide films, which has good advantages of low fabrication cost, easy stoichiometry control and high deposition rate. We have recently reported the transport behavior of $Ca_3Co_{4-x}Fe_xO_{9+\delta}$ polycrystalline samples prepared by solid-state reaction method [10]. It is found that the sample with $x=0.05$ shows the lowest room temperature resistivity and the highest thermoelectric power. Herein, we report the effects of sintering temperature on fabrication and transport properties of $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$ films obtained by the sol–gel spin coating method. Films showing

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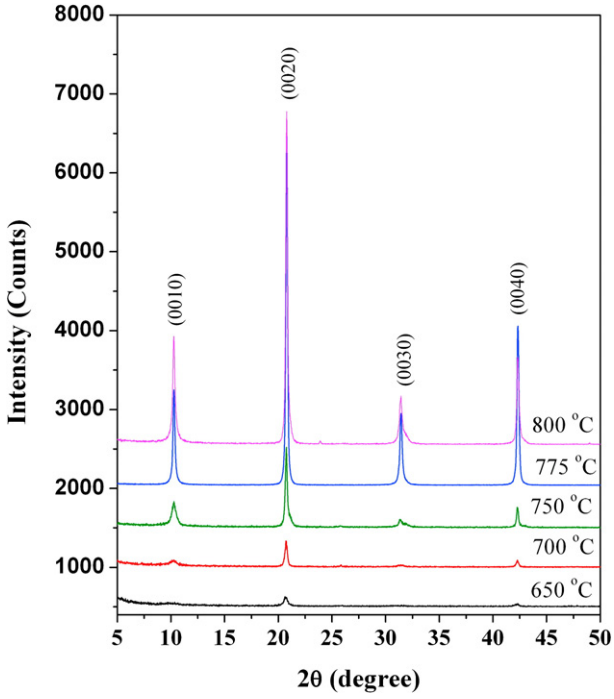

Fig. 1. XRD patterns of $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$ films prepared at different sintering temperatures. The reflection peaks are indexed according to the 4D superspace of X2/m(0b0)s0 and indicate films with highly *c*-axis alignment are fabricated.

metallic temperature dependence can be achieved at the sintering temperature of 750–775 °C. We also find higher sintering temperature results in a larger grain size of the films and leads to a lower resistivity and smaller thermopower, which can be explained by the barrier theory.

2. Experimental details

The precursors of the cobaltite films were prepared by dissolving the calcium nitrate (6.376 g), cobalt nitrate (10.3463 g), and iron nitrate (0.1818 g) in appropriate proportion in de-ionized water (45 ml), followed by addition of citric acid (1.8913 g) and ethylene glycol (0.5586 g). The above amount of citric acid and ethylene glycol is the optimized quantity of obtaining good quality films. The above solution was then heated at ~80 °C with constant stirring until a viscous fluid was formed after sufficient evaporation of water. This gel was used for spin coating and it could be stored for up to 3–4 days without solidification. Solidification of the gel was observed after keeping the above gel for more than 3–4 days. The sapphire (0001) substrates were thoroughly cleaned by acetone, isopropyl alcohol and finally by de-ionized water with the help of an ultrasonic bath for 5 min in each. The substrates were immersed in a mixture solution of H_2O_2 and H_2SO_4 (1:1, v/v) for 15 min to make the surface hydrophilic. The precursor films of $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$

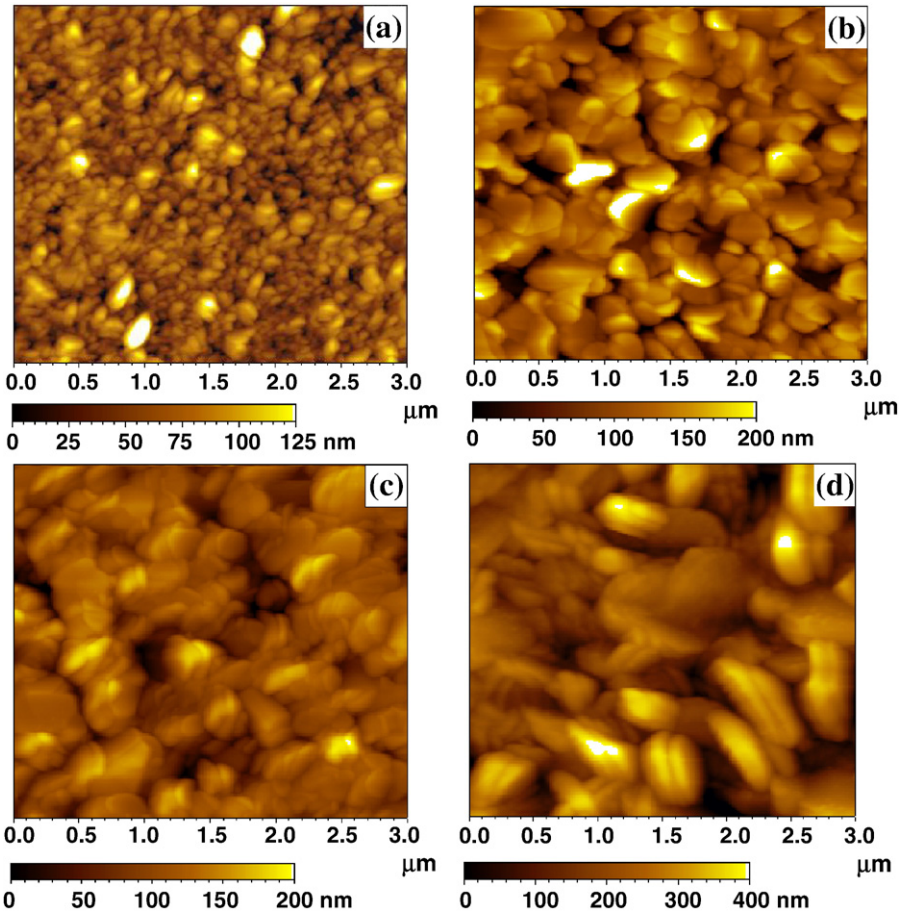

Fig. 2. AFM images of the $Ca_3Co_{3.95}Fe_{0.05}O_{9+\delta}$ films prepared at sintering temperature of (a) 650 °C, (b) 700 °C, (c) 750 °C and (d) 775 °C.