



# Fabrication and high temperature thermoelectric properties of *c*-axis oriented Na<sub>0.68</sub>CoO<sub>2</sub>:Ag nanocomposite thin films



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## ABSTRACT

*c*-Axis oriented Na<sub>0.68</sub>CoO<sub>2</sub>:Ag composite thin films with metallic Ag nanoparticles embedded in the Na<sub>0.68</sub>CoO<sub>2</sub> matrix have been fabricated by post-annealing the PLD-grown CoO:Ag precursor film in Na vapor at high temperatures. The nanosized Ag inclusions can greatly improve the electrical conductivity while retaining the Seebeck coefficient of Na<sub>0.68</sub>CoO<sub>2</sub> films, resulting in an enhanced power factor. The power factor of the 5.0 wt.% Ag-added Na<sub>0.68</sub>CoO<sub>2</sub> films reaches 1.85 mW/m K<sup>2</sup> at 800 K, which is about 2 times higher than that of Ag-free films. Moreover, the thermal conductivity in these nanocomposite films is expected to be suppressed due to the enhanced phonon scatterings on nanoinclusions. The results demonstrated that adding Ag nanoinclusions is an effective way to improve the thermoelectric performance of Na<sub>x</sub>CoO<sub>2</sub> films.

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## 1. Introduction

Thermoelectric (TE) materials can convert thermal energy directly into electricity, making them attractive for waste heat conversion applications. The performance of a TE material is evaluated by the dimensionless figure-of-merit  $ZT = (S^2/\rho\kappa)T$ , where  $S$  is the Seebeck coefficient,  $r$  is the electric resistivity,  $\kappa$  is the thermal conductivity and  $T$  is the absolute temperature. Layered cobaltites have attracted great attention to the thermoelectric community in the past decade, particularly to those who are interested in high-temperature applications, because of their good thermoelectric performance, low cost and high resistance of oxidation at high temperature in air [1–5]. The crystal structure of layered cobaltites consists of the conducting CoO<sub>2</sub> layer and the insulating layer, which are alternately stacked along the *c*-axis [2]. This layered structure results in highly anisotropic electronic transport properties with *in-plane* resistivity being much smaller than that of *out-of-plane* [2]. Therefore, one effective method for optimizing TE performance of layered cobaltites is through texture control. *c*-Axis textured samples show a great enhancement in  $ZT$  relative to the randomly orientated ones [3,4]. Another promising method is to add metallic fine particles to the TE material matrix. Nong et al. reported in their recent work that the TE performance of

Ca<sub>3</sub>Co<sub>4</sub>O<sub>9</sub> ceramics can be greatly enhanced by incorporating a fine distribution of Ag particles about 200–400 nm in size due to the simultaneous decrease of phonon thermal conductivity and increase of power factor [5].

Na<sub>x</sub>CoO<sub>2</sub> is one of the prime examples of these layered cobaltites and has been intensely investigated [6–17]. Recently, several reports demonstrated that adding metallic Ag particles to Na<sub>x</sub>CoO<sub>2</sub> ceramics was effective in decreasing the resistivity, resulting in the improvement of power factor. However, due to the extremely large size of Ag particles in the composites, normally about 5–10 μm in size, Ag addition also led to a significant increase in thermal conductivity of Na<sub>x</sub>CoO<sub>2</sub> [15–17]. This eventually resulted in almost the same or even the decreased  $ZT$  values. Therefore, how to control the Ag particles to submicron or even nanometer level in Na<sub>x</sub>CoO<sub>2</sub> remains to be resolved. In addition, for miniaturizing the TE devices, thin film technology is advantageous because it is compatible with microelectromechanical system [10,11].

Based on these considerations, in this paper, we developed a novel method for fabrication of *c*-axis oriented Na<sub>x</sub>CoO<sub>2</sub>:Ag composite thin films with nanosized Ag particles well dispersed in the Na<sub>x</sub>CoO<sub>2</sub> matrix. The thermoelectric measurements showed that the Ag nanoparticles can lead to a significant improvement in power factor of Na<sub>x</sub>CoO<sub>2</sub>:Ag composite films, being about 2 times higher than that of pure films at the highest measured temperature of 800 K. Moreover, since the thermal conductivity can be reduced due to the increased phonon scattering on the nanoinclusions as well as at the Na<sub>x</sub>CoO<sub>2</sub> and Ag interfaces, the  $ZT$  of the Na<sub>x</sub>CoO<sub>2</sub>:Ag

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nanocomposite thin films is expected to be greatly improved in comparison with that of pure  $\text{Na}_x\text{CoO}_2$  thin films.

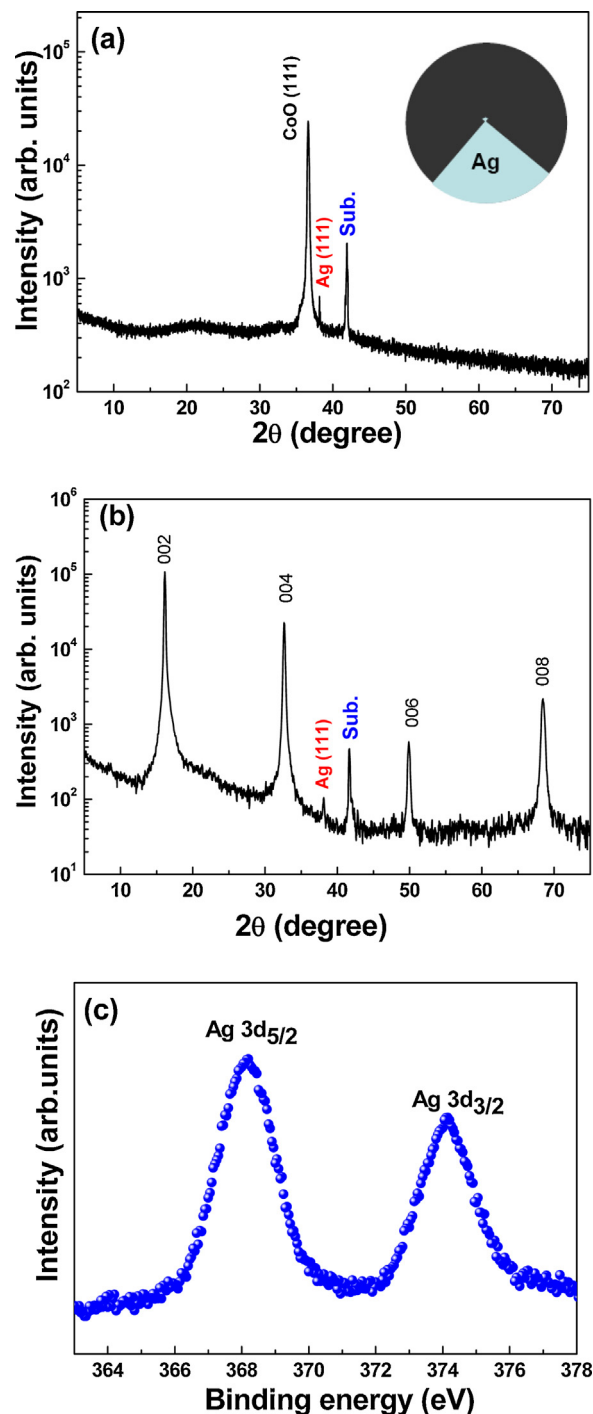
## 2. Experiments

The *c*-axis  $\text{Na}_x\text{CoO}_2$ :Ag nanocomposite thin films were fabricated using a two-step process. First, a (1 1 1)-oriented CoO film embedded with Ag nanoparticles was grown on the commercial *c*- $\text{Al}_2\text{O}_3$  substrate by pulsed laser ablation of a  $\text{Co}_3\text{O}_4$ :Ag composite target at the substrate temperature of 700 °C under the oxygen pressure about  $1 \times 10^{-4}$  Pa. Then, the CoO:Ag film, covered with  $\text{NaHCO}_3$  pellets, was sealed in an alumina crucible and annealed at 750 °C for 120 min in air to form the  $\text{Na}_x\text{CoO}_2$ :Ag composite thin film. In the post-annealing process, the (1 1 1)-oriented CoO film was first oxidized into the (1 1 1)-oriented  $\text{Co}_3\text{O}_4$  film at lower temperature of about 300–500 °C and then  $\text{Na}_x\text{CoO}_2$  film with *c*-axis orientation was formed at higher temperature via lateral diffusion of Na ion into  $\text{Co}_3\text{O}_4$  layer. An excimer laser with 308 nm radiation was used for the CoO/Ag precursor film deposition with a laser energy density of 1.5 J/cm<sup>2</sup> and a repetition rate of 3 Hz. The composite target was composed of a piece of  $\text{Co}_3\text{O}_4$  ceramic target and a piece of fan-shaped Ag foil (99.99%), as shown in the inset of Fig. 1a. The Ag concentration in the films can be easily controlled by changing the area of Ag foils attached on the  $\text{Co}_3\text{O}_4$  target surface. Three fan-shaped Ag foils (0°, 50° and 90°) were used in this work, and the weight ratio between Ag and  $\text{Na}_x\text{CoO}_2$  in the corresponding  $\text{Na}_x\text{CoO}_2$ :Ag composite films, determined by the energy-dispersive X-ray spectroscopy, was about 0, 2.7 and 5.0 wt.%, respectively. The film thickness was measured by a Dektak 150 Surface Profiler and it was about 200 nm for these three  $\text{Na}_x\text{CoO}_2$ :Ag composite films.

The crystal structure of the films was measured using a Philips X'Pert 4-circle diffractometer with Cu K $\alpha$  radiation. The film surface morphology and the Ag particles size were analyzed by atomic force microscopy (Nanoscope IV, Digital Instruments) with a tapping mode. The room temperature carrier concentration of the films was determined by Hall effect measurement. A VG ESCALAB5 X-ray photoelectron spectroscopy (XPS) with Mg K $\alpha$  ~1253.6 eV exciting radiation was used to detect the Ag chemical band in the composite films. The working pressure in the XPS chamber was approximately  $2 \times 10^{-7}$  Pa. Before the measurement, the sample was etched for about 10 min by low energy  $\text{Ar}^+$  in the XPS chamber in order to remove the impurities on the film surface. The electrical resistivity and Seebeck coefficient were simultaneously measured in air by the standard dc four-probe technique in a LSR-3 measurement system (Linseis, Germany) with the heating rate of 5 K/min.

## 3. Results and discussion

Fig. 1a shows the x-ray diffraction (XRD)  $\theta$ - $2\theta$  pattern of a CoO:Ag composite thin film on *c*- $\text{Al}_2\text{O}_3$  substrate. The film is composed of CoO as the main phase and metallic Ag as the second phase. Fig. 1b is the corresponding XRD  $\theta$ - $2\theta$  pattern of  $\text{Na}_x\text{CoO}_2$ :5 wt.% Ag composite thin film after this CoO:Ag precursor film being annealed in Na vapor for 2 h. All main peaks can be indexed as 0 0 *l* diffractions from  $\gamma$ - $\text{Na}_x\text{CoO}_2$  phase besides the substrate and metallic Ag peaks, indicating that the film is *c*-axis oriented. The Ag-free and 2.7 wt.% Ag added samples exhibit similar XRD  $\theta$ - $2\theta$  patterns, which were not shown here. There is no detectable shift of the  $\text{Na}_x\text{CoO}_2$  diffraction peak positions in the  $\theta$ - $2\theta$  patterns for all samples, indicating that Ag mainly precipitated as the second phase with metallic Ag form in the composite films rather than substituting for the Na or Co sites in  $\text{Na}_x\text{CoO}_2$ . The calculated *c*-axis lattice constant for all  $\text{Na}_x\text{CoO}_2$ :Ag composite films is about  $10.97 \pm 0.003$  Å, revealing that the Na concentration *x* in these three films is almost same, i.e. about 0.68 [8]. Fig. 1c is the Ag 3d photoelectron core levels obtained from the surface of 5.0 wt.% Ag-



**Fig. 1.** XRD  $\theta$ - $2\theta$  scans for (a) CoO:Ag and (b)  $\text{Na}_{0.68}\text{CoO}_2$ :Ag composite thin films with Ag addition of 5.0 wt.%. The inset of (a) is the schematic illustration of the composite target. (c) The XPS core-level-spectra of Ag 3d for the  $\text{Na}_{0.68}\text{CoO}_2$ :Ag composite thin film with Ag addition of 5.0 wt.%.

added sample. The peaks of Ag 3d<sub>5/2</sub> and Ag 3d<sub>3/2</sub> are located at 368.2 and 374.2 eV, respectively, which are corresponding to the normal XPS spectra of Ag metal. This result further demonstrates that Ag does not substitute for the Na or Co sites in  $\text{Na}_x\text{CoO}_2$  but dispersing the  $\text{Na}_x\text{CoO}_2$  matrix with a metallic form.

Fig. 2 presents the height and amplitude AFM images for the 0, 2.7 and 5.0 wt.% Ag-added samples. The Ag-free  $\text{Na}_x\text{CoO}_2$  film exhibits a very smooth surface with root mean square (rms) roughness of only 1.6 nm. With addition of Ag, the films surface is slightly deteriorated with rms increasing to 3.4 nm for the 5.0 wt.%

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