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Effect of Ag-doping on crystal structure and high temperature thermoelectric properties of c-axis oriented Ca₃Co₄O₉ thin films by pulsed laser deposition

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Abstract

Ag-doped Ca₃Co₄O₉ thin films with nominal composition of Ca₃₋ₓAgₓCo₄O₉ (x = 0–0.4) have been prepared on sapphire (0001) substrates by pulsed laser deposition (PLD). Structural characterizations and surface chemical states analysis have shown that Ag substitution for Ca in the thin films can be achieved with doping amount of x ≤ 0.15; while when x > 0.15, excessive Ag was found as isolated and metallic species, resulting in composite structure. Based on the perfect c-axis orientation of the thin films, Ag-doping has been found to facilitate a remarkable decrease in the in-plane electrical resistivity. However, if doped beyond the substitution limit, excessive Ag was observed to severely reduce the Seebeck coefficient. Through carrier concentration adjustment by Ag-substitution, power factor of the Ag-Ca₃Co₄O₉ thin films could reach 0.73 mWm⁻¹K⁻² at around 700 K, which was about 16% higher than that of the pure Ca₃Co₄O₉ thin film.

Key words:

Thermoelectric; Ca₃Co₄O₉; Thin film; Doping

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1. Introduction

Thermoelectric (TE) materials and devices have great potential to provide alternative solutions to worldwide energy crisis and global warming, as they are able to harvest clean energy from waste heat and provide refrigeration without using harmful gas. Among the various TE materials, misfit layered cobalt oxide Ca$_3$Co$_4$O$_9$ has been considered to be the most promising candidates for high temperature TE application due to its remarkable TE performance and superior properties, such as low toxicity, high thermal stability and low cost [1]. The performance of a TE material is evaluated by the dimensionless figure-of-merit $ZT = S^2T/(\rho\kappa)$, where $S$, $T$, $\rho$ and $\kappa$ are the Seebeck coefficient (also called thermopower), absolute temperature, electrical resistivity and thermal conductivity, respectively [2]. For a Ca$_3$Co$_4$O$_9$ single crystal, the $ZT$ value can reach 0.83 at 1000 K [3].

The crystal structure of Ca$_3$Co$_4$O$_9$ is composed of the CdI$_2$-type CoO$_2$ layer and the rocksalt-type Ca$_2$CoO$_3$ layer alternately stacking along the $c$-axis [4]. Although this misfit layered structure is considered to be beneficial for TE properties, the large anisotropy leads to poor TE performance for randomly oriented polycrystalline materials, and difficulty in fabricating large Ca$_3$Co$_4$O$_9$ single crystals for volume production [5]. Nevertheless, it is found that thin film configuration with well controlled crystal orientation can cater for the electrical transport of carriers along favorable direction and overcome this issue. In addition, thin films can promote the reduction of thermal conductivity by phonon scattering effect [6], and facilitates Micro-Electro-Mechanical System (MEMS) processing towards on-chip devices [7]. Epitaxial or $c$-axis oriented Ca$_3$Co$_4$O$_9$ thin films have been prepared by various techniques, such as radiofrequency (RF) sputtering [8], pulsed laser deposition (PLD) [9, 10], atomic layer deposition (ALD) [11] and topotactic ion-exchange method [12]. The in-plane power factor of a pure Ca$_3$Co$_4$O$_9$ thin film has been reported to reach 0.51 mWm$^{-1}$K$^{-2}$ at around 920 K, which is higher than the value of textured bulk ceramics, and comparable to that of single crystals [13]. Such improvement in TE performance could be ascribed to the enhanced energy filtering effect as a result of the nanostructures and grain boundaries inside the thin films [9, 13].

Meanwhile, research work towards TE performance enhancement in Ca$_3$Co$_4$O$_9$ bulk
materials have also been carried out through foreign cation-doping using alkali metals [14], alkaline earth metals [15], rare earths [16, 17] and transition metals [18]. Among them, Ag-substitution at the Ca site has been found to effectively reduce the electrical resistivity of Ca$_3$Co$_4$O$_9$, and thus improve the TE performance [19]. It has also been found that if Ag is not doped into the Ca$_3$Co$_4$O$_9$ lattice, but instead is added as a metallic phase to form bulk composite ceramics, a decrease in electrical resistivity can still be achieved [20, 21]. Through the doping and the addition of Ag, a high ZT value above 0.5 at 1000 K has been reported in Ca$_{2.7}$Ag$_{0.3}$Co$_4$O$_9$/Ag-10%, which is so far the highest ZT value reported for polycrystalline Ca$_3$Co$_4$O$_9$ system [22]. It should be noted that although both approaches can reduce electrical resistivity, different mechanisms are involved: Ag-substitution increases p-type major carrier concentration; while metallic Ag addition contributes to electrical conduction by composite effect. It is therefore necessary to identify the exact amount of Ag substituted and to fully characterize the Ag dopant species in heavily Ag-doped Ca$_3$Co$_4$O$_9$ system. As indicated in previous works, having a thin film configuration of such material can facilitate the above mentioned characterization using XPS and Hall effect analysis [23]. In this work, we report the Ag-doping effect and TE enhancement in c-axis oriented Ca$_3$Co$_4$O$_9$ thin films. The Ag-doping level and dopant species are fully characterized. The influences of light and heavy Ag-doping on carrier concentration as well as high temperature electrical properties of these thin films are also investigated.

2. Experimental details

Ca$_{3-x}$Ag$_x$Co$_4$O$_9$ (x = 0, 0.1, 0.2, 0.3 and 0.4, named as CCO, Ag01, Ag02, Ag03 and Ag04 respectively in the subsequent text) thin films with c-axis orientation were prepared on (0001) sapphire (c-plane) single crystal substrates by PLD method at 700°C in 20 Pa (150 mTorr) oxygen pressure. A KrF excimer laser (Lambda Physik Compex, $\lambda$ = 248 nm) was used with a laser energy density of ~1.2 J/cm$^2$ per pulse corresponding to a deposition rate around 2 nm/min. To prepare the PLD targets, the Ca$_{3-x}$Ag$_x$Co$_4$O$_9$ precursor powders were first synthesized by sol-gel method [17], then shaped into 1-inch diameter pellets and sintered at 880°C for 20 hours. Due to the strong volatile nature of Ag during PLD process [24], double
amounts of the designed composition of Ag were added in the targets. Chemical compositions of the targets, obtained by inductively coupled plasma (ICP) analysis (Dual-view Optima 5300 DV ICP-OES, Perkin Elmer), are listed in Table 1 with the corresponding sample names and the elemental ratio in the precursor solutions.

The thicknesses of the thin films were measured using an Alpha-Step IQ surface profiler. High resolution X-ray diffraction (HR-XRD) data were collected using X’Pert MRD (PANalytical) with monochromatic Cu Kα radiation (λ = 1.5406Å) over 5–55° range. Chemical states and elemental composition were analyzed by using an X-ray photoelectron spectroscopy (XPS) (Al anode, hv = 1,486.6 eV, Theta Probe XPS, Thermo Fisher Scientific) on the thin film surfaces. The C 1s peak located at 284.5 eV was assigned to carbon from adventitious contaminations, and was used as the criterion to rectify binding energies of the XPS spectra. The in-plane electrical resistivity (ρab) and Seebeck coefficient (S) of the thin films were measured from room temperature to ~700 K by the standard four-probe method and the conventional steady state method, respectively. Room temperature carrier concentrations (p) of the thin films were determined by the Hall measurement (Bio Rad HL5500) with four-point-probe technique using van der Pauw geometry.

3. Results and discussion

Fig. 1 shows the HR-XRD 2θ–ω scans of pure and Ag-doped Ca₃Co₄O₉ thin films on (0001) sapphire substrate over 5–55° range. Thin films Ag01 and Ag02 show similar XRD patterns to that of the pure thin film, CCO. Besides the peak from sapphire (0006) substrate, only peaks from diffractions of (00l) Ca₃Co₄O₉ planes can be observed, indicating that the ab-planes in the Ca₃Co₄O₉ thin films are parallel to the (0001) sapphire substrate surface and both films are c-axis oriented. However, for thin films Ag03 and Ag04, an extra peak at ~38.12° can be observed. This peak corresponds to Ag (111), which indicates the presence of Ag existing as a metallic phase other than those doped into the Ca₃Co₄O₉ crystal structure. The influence of Ag-doping on the crystal lattice of Ca₃Co₄O₉ thin films was investigated by calculating the c-axis parameters of the pure and Ag-doped Ca₃Co₄O₉ thin films from the
XRD data. For each thin film, the average c-axis parameter was calculated by using Bragg equation according to every position of the (00l) peaks in the HR-XRD pattern. It can be seen from Fig. 2 that the c-axis lattice constant increases gradually with the Ag amount (as determined by XPS). The ionic radii of Ag$^{1+}$ and Ca$^{2+}$ in six-coordination are 1.15 and 1.00 Å, respectively [19]. Thus, for light Ag-doping, the substitution of the larger Ag$^+$ ions for Ca$^{2+}$ can result in the enlargement of the Ca$_3$Co$_4$O$_9$ unit cell. This observation is consistent with the reported work on Ag-substituted Ca$_3$Co$_4$O$_9$ poly-crystals [19]. However, it is found that the c-lattice parameter of Ca$_3$Co$_4$O$_9$ thin films continues to increase for the heavily Ag-doped samples beyond the Ag-substitution limit (as indicated in the subsequent XPS analysis). Such c-direction expansion is likely to be associated with the thin film strain relaxation [25, 26].

Due to the lattice misfit from substrate, the c-axis lattice parameter of the highly oriented Ca$_3$Co$_4$O$_9$ thin films (10.73–10.79 Å in this work, and 10.73–10.78 Å in others [10-12]) is slightly lower than that of the bulk value (10.81–10.99 Å [4, 15, 19]). In the case of heavy Ag-doping, Ag segregation or crystallization can introduce large amount of structural defects and can release the thin film strain from the substrate. Thus, as the Ag-dopant further increases, the c-lattice of thin film starts to be relaxed and increases towards the value of the bulk.

In order to study the doping effect on TE properties, the exact amounts of Ag dopant in these thin films were determined by using the area ratios of Ca (2p$_{3/2}$), Co (2p$_{3/2}$), and Ag (3d$_{5/2}$) peaks. The results are summarized in Table 1. It is found that, even after doubling the amount of Ag in the targets, the final Ag compositions in the resultant as-prepared thin films were still lower than the designed values, indicating that a substantial amount of Ag atoms were “lost” during the PLD process. The yield of Ag by the laser ablation is only about 36% in this thin film fabrication process (with reference to the yield of Co taken as 100%). Further, the chemical states of Ag dopant within the Ag-Ca$_3$Co$_4$O$_9$ thin films were investigated by XPS fine scan of the Ag 3d peaks, as shown in Fig. 3. For thin films Ag01 and Ag02, the peaks of Ag 3d$_{3/2}$ and 3d$_{5/2}$ are located at 373.7 and 367.7 eV, respectively, and the spin energy separation is 6.0 eV. This is the characteristic of Ag–O bond [27], indicating that the silver
species existing in these two thin films is Ag$^+$ ion rather than metallic Ag (Ag$^0$). It should be noted that Ag oxide will decompose into metallic Ag at temperatures above 400°C, while the deposition of the Ag-doped Ca$_3$Co$_4$O$_9$ thin films was carried out on a substrate at 700°C. Thus, neither Ag$_2$O nor AgO phases would be generated in the PLD process and all the Ag$^+$ ions in samples Ag01 and Ag02 should come from the Ag$^+$ substituted at Ca site in the Ca$_3$Co$_4$O$_9$ crystal structure. In other words, it can be concluded that most Ag atoms in thin films Ag01 and Ag02 have successfully substituted into the Ca site in the crystal structure. On the other hand, for samples Ag03 and Ag04, the 3d peaks of Ag in the XPS spectra are found to shift to higher binding energy, indicating that chemical states of Ag atoms are not uniform in these two Ca$_3$Co$_4$O$_9$ thin films. The Ag 3d peaks were further decomposed into two components, Ag$^+$ with binding energy of 373.7 and 367.7 eV, and Ag$^0$ with binding energy of 374.2 and 368.2 eV [27], as shown in Fig. 3. The Ag$^+$ : Ag$^0$ atomic ratio were calculated based on the 3d$_{5/2}$ peaks deconvolution using Gaussian–Lorentzian sum functions and Tougaard-type background subtraction, and the results are listed in Table 1. It can be found that with heavy doping of Ag, some metallic Ag$^0$ atoms are present in the Ag03 and Ag04 films. Moreover, as the Ag content in the thin films increases, the amount of Ag$^0$ is found to increase significantly, while there is only a slight increase for the substitution amount, Ag$^+$. These XPS results clearly indicated that the Ag contents for thin films Ag03 and Ag04 have gone beyond the substitution limit of Ag in the Ca$_3$Co$_4$O$_9$ crystal structure. The excess amount of Ag atoms exists as metallic Ag$^0$ phase within the thin films, which is consistent with the XRD results.

A recent work done on Ag-doped Ca$_3$Co$_4$O$_9$ poly-crystalline bulk samples prepared by conventional solid state reaction route reported heavy Ag-doping of nominally 10 at% at the Ca site (corresponding to $x = 0.3$ in Ca$_{3-x}$Ag$_x$Co$_4$O$_9$) [19]. However, the exact amount of Ag in Ca$_3$Co$_4$O$_9$ was not provided and the characterization on the species of the Ag-dopant was limited. According to our study, a lower Ag-substitution limit in the Ca$_3$Co$_4$O$_9$ structure was suggested to be about 5 at%. First of all, it should be noted that the radius of Ag$^+$ ion (1.15 Å) is much larger than that of Ca$^{2+}$ (1.00 Å) ion. The substitution of Ag for Ca, or any possible interstitial Ag atom, can lead to large lattice distortion accompanied with a large increase in
the system energy. Thus, heavy-doping of Ag is not favorable in the Ca$_3$Co$_4$O$_9$ structure. Furthermore, due to the weak Ag–O bond at high temperature, Ag cannot combine with oxygen. So, it will be difficult for Ag atoms to get into the Ca$_3$Co$_4$O$_9$ structure through high-temperature processing routes. It is hence unlikely to achieve heavy Ag$^+$ substitution through either solid state reaction or PLD methods. In addition, in the case of PLD fabrication, the dissociative Ag atoms are unstable at high temperature under vacuum and tend to evaporate from the substrate surface. As a result, the deposition yield of Ag is fairly low and the as-prepared thin films possess less Ag content than in the corresponding targets.

The temperature dependence of the in-plane electrical resistivity, $\rho$, of the pure and Ag-doped Ca$_3$Co$_4$O$_9$ thin films on sapphire (0001) was measured for the temperature range of 300 to 720 K. As shown in Fig. 4, all the thin film samples show a low electrical resistivity around 3.5–5.5 m$\Omega$cm over the temperature range measured. The $\rho$ values of the thin films obtained in the present work are lower than that of the reported poly-crystalline Ca$_3$Co$_4$O$_9$ bulk (6–12 m$\Omega$cm) [22], and are comparable to that reported for single crystal [3]. The superior electrical conduction property is attributed to the highly oriented thin film structure achieved by PLD processing as previously reported [9, 23]. For thin films Ag01 and Ag02, electrical resistivity shows similar transport behavior to that of un-doped Ca$_3$Co$_4$O$_9$ thin film CCO, namely, metallic-like behavior at room temperature, and semiconducting-like behavior at elevated temperatures. Moreover, when compared with the pure Ca$_3$Co$_4$O$_9$ thin film, the resistivity of samples Ag01 and Ag02 decreases significantly with increasing Ag content within the entire temperature range measured, indicating that Ag substitution for Ca have efficiently reduced the $\rho$ of the c-axis oriented Ca$_3$Co$_4$O$_9$ thin films. It is worth noting that the electrical resistivity of the Ag-doped Ca$_3$Co$_4$O$_9$ thin films obtained in this work is 3.86 m$\Omega$cm at ~675 K for Ag02, which is one of the lowest values reported thus far for Ca$_3$Co$_4$O$_9$ based materials. The electrical resistivity can be expressed as $\rho = 1/\sigma = 1/(\mu p e)$, where $\sigma$, $p$, $\mu$ and $e$ are the electrical conductivity, p-type carrier concentration, carrier mobility and electron charge of carrier, respectively. As shown in the inset of Fig. 4, the increases in both $p$ and $\mu$ by Ag-
substitution for Ca contribute to the superior electrical conduction property, which is consistent with that reported for Ag-doped Ca₃Co₄O₉ poly-crystalline bulk materials [22].

On the other hand, for thin films Ag03 and Ag04, the $\rho$-$T$ curves exhibit metallic-like behavior in the entire measured temperature range. Although the electrical resistivity decreases with increasing Ag content at the low temperature range (300-550 K), the $\rho$ values of samples Ag03 and Ag04 are higher than that of Ag02 at the high temperature range above 600 K. This is similar to that reported for Ca₃Co₄O₉ poly crystalline materials with Ag added as metallic phase [21, 22]. Further investigation through Hall effect measurement has indicated that the effective carrier concentration, $p$, for thin films Ag03 and Ag04 decreases with increasing Ag content. Thus, it can be concluded that further increase in Ag doping content results in composite effect since metallic Ag offers electron conduction in a p-type Ca₃Co₄O₉ semiconductor matrix.

Further study on the electrical conduction mechanism in these Ag-Ca₃Co₄O₉ thin films was carried out by data analysis using both thermally activated conduction (TAC) model and adiabatic small polaron hopping conduction (SPHC) model in the high temperature region for $T > 550$ K. As shown in Fig. 5, the plots of $\ln(\rho/T)$ versus $1000/T$ for all the samples lie on straight lines for temperatures above 550 K, indicating the SPHC behavior in these thin films. According to the SPHC mechanism of Ca₃Co₄O₉, the temperature dependence of electrical resistivity can be generally expressed as [18, 23]

$$\frac{1}{\rho} = \sigma = p e a^2 \left(\frac{A}{T}\right) \exp\left(\frac{-E_a}{k_B T}\right)$$  \hspace{1cm} (Eq. 1)

where $a$, $E_a$, $k_B$ and $A$ are the intersite distance of hopping, activation energy, Boltzmann constant and a pre-exponential term related to the scattering mechanism, respectively. From the slopes of the plots in Fig. 5, $E_a$ of the pure and Ag-doped Ca₃Co₄O₉ thin films can be calculated, and the results are shown in the inset of Fig. 5. It can be seen that, for CCO, Ag01 and Ag02 films, $E_a$ remains almost constant within the range of 71-73 meV, while $E_a$ values of Ag03 and Ag04 samples are much lower, indicating the different conduction mechanism in
these two films. For the lightly Ag-doped thin films Ag01 and Ag02, the decrease of electrical resistivity can be attributed to the substitution of univalent Ag\(^+\) for divalent Ca\(^{2+}\) in Ca\(_3\)Co\(_4\)O\(_9\). It has been reported that the edge shared CoO\(_2\) layers are responsible for the electrical conduction, whereas the rock-salt-type [Ca\(_2\)CoO\(_3\)] layers are regarded as a charge reservoir to supply hole-type charge carriers into the CoO\(_2\) layers [28]. Considering a constant oxygen composition and based on the valence equilibrium, the substitution of Ag\(^+\) for Ca\(^{2+}\) will create more electrical holes, and thus decrease \(\rho\). Since the substitution happens at the [Ca\(_2\)CoO\(_3\)] layers, which do not disturb the CoO\(_2\) sub-lattice, the polaron hopping energy remains constant and the transport mechanism is therefore unchanged by the Ag-doping. On the other hand, for the heavily Ag-doped samples Ag03 and Ag04, the metallic-like electrical transport behavior arises from the existence of the secondary metallic Ag phase as confirmed by XRD and XPS analysis. In the dense and highly oriented Ca\(_3\)Co\(_4\)O\(_9\) thin films, Ag clusters are likely to locate at grain boundaries, stacking faults and interfaces, and form connections between cobaltite grains. At low temperature, carrier scattering effect at the structural defects is not pronounced, and hence the electrical resistivity of Ag03 and Ag04 can be reduced effectively by metallic Ag. However, at high temperature above 600 K, the polaron hopping process of Ca\(_3\)Co\(_4\)O\(_9\) will be greatly influenced by the presence of metallic Ag. In addition, much more structure defects and grain boundaries can act as scattering centers and eliminate the low energy carriers. It can be imagined that such scattering effect is more severe at high temperature. As a result, the Ag03 and Ag04 samples exhibit higher \(\rho\) at the high temperature range. For the individual composition, \(\rho_{\text{Ag}} < \rho_{\text{Ca}_3\text{Co}_4\text{O}_9}\). So carriers would transport through Ag clusters rather than Ca\(_3\)Co\(_4\)O\(_9\) grains in the composite structure, and electrical transportation of Ag03 and Ag04 changes into metallic-like behavior. [21].

Temperature dependence of the in-plane Seebeck coefficient, \(S\), for pure and Ag-doped Ca\(_3\)Co\(_4\)O\(_9\) thin films is plotted in Fig. 6. The positive sign of \(S\) for all the thin film samples indicates that hole carrier is still dominant in these samples, which is consistent with the Hall effect results. In addition, \(S\) values of the Ag-doped Ca\(_3\)Co\(_4\)O\(_9\) thin films show similar trends
as the pure \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin film, namely, \( S \) increases with increasing temperature over the entire temperature range measured. It is also clearly shown that \( S \) decreases slightly with increasing Ag content for thin films Ag01 and Ag02, while decreases significantly for thin films Ag03 and Ag04. Ag04 exhibits the lowest \( S \) in the temperature range studied. This dependence of \( S \) on the Ag-doping amounts is also found to be consistent with that reported for Ag-doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) poly-crystalline bulk materials [29]. In the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) system, \( S \) can be expressed by the Mott formula as [14]:

\[
S(T) = \frac{c_e}{p} + \frac{\pi^2 k_B^2 T}{3e} \left[ \frac{\partial \ln \mu(\varepsilon)}{\partial \varepsilon} \right]_{\varepsilon = E_F}
\]  

(Eq. 2)

where \( c_e \) is the electronic specific heat. It has been reported that for \( \text{Ca}_3\text{Co}_4\text{O}_9 \)-based materials, \( S \) follows with the Drude picture: \( S \sim c_e/p \), where the first term in Eq. 2 is dominant [14]. Therefore, for thin films Ag01 and Ag02, the increase in carrier concentration, \( p \), can directly result in the decrease in Seebeck coefficient. However, for samples Ag03 and Ag04 multiphase system, the modification of effective carrier concentration becomes insignificant. Instead, the decrease in \( S \) in these two samples should be attributed to the existence of the metallic Ag phase within the \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films. For materials with more than one type of charge carriers, the Seebeck coefficient could be expressed as [22]

\[
S = \sum \left( \frac{\sigma_i}{\sigma} \right) S_i, 
\]  

(Eq. 3)

and for samples Ag03 and Ag04 it can be rewritten as

\[
S = \frac{\sigma_{\text{Ca}_3\text{Co}_4\text{O}_9}}{\sigma_{\text{Ca}_3\text{Co}_4\text{O}_9} + \sigma_{\text{Ag}}} S_{\text{Ca}_3\text{Co}_4\text{O}_9} + \frac{\sigma_{\text{Ag}}}{\sigma_{\text{Ca}_3\text{Co}_4\text{O}_9} + \sigma_{\text{Ag}}} S_{\text{Ag}}, 
\]  

(Eq. 4)

which can be transformed into

\[
S = S_{\text{Ca}_3\text{Co}_4\text{O}_9} + \frac{\sigma_{\text{Ag}}}{\sigma_{\text{Ca}_3\text{Co}_4\text{O}_9} + \sigma_{\text{Ag}}} \left( S_{\text{Ag}} - S_{\text{Ca}_3\text{Co}_4\text{O}_9} \right),
\]  

(Eq. 5)

since \( S_{\text{Ag}} \) is much smaller than \( S_{\text{Ca}_3\text{Co}_4\text{O}_9} \), and the second term in Eq. 5 is negative. As a result, \( S \) of \( \text{Ca}_3\text{Co}_4\text{O}_9/\text{Ag} \) multi-phase material can be expected to be lower than that of the single phase \( \text{Ca}_3\text{Co}_4\text{O}_9 \) system. And the decrease in \( S \) for thin films Ag03 and Ag04 can be observed.
Finally, the temperature dependence of power factor, $P$, of the pure and Ag-doped Ca$_3$Co$_4$O$_9$ thin films, was calculated from the measured $\rho$ and $S$ and plotted as shown in Fig. 7. For all samples, $P$ values increase with increasing temperature. In addition, thin films Ag01 and Ag02 show higher power factor due to the positive enhancement on carrier concentration and mobility through the successful Ag-substitution at Ca site. Despite the increase in Ag amount, samples Ag03 and Ag04 exhibit decreasing $P$ values because $S$ is much suppressed by the presence of the metallic Ag phase. Among these thin film samples, the highest $P$ value reaches ~0.73 mW/(mK$^2$) for thin film Ag02 at 705 K, which is about 16% higher than that of the pure Ca$_3$Co$_4$O$_9$ thin film and is among the best values reported for Ca$_3$Co$_4$O$_9$ materials [3, 22]. The present results have demonstrated the great potential of Ag-doped Ca$_3$Co$_4$O$_9$ thin films for thermoelectric applications. Meanwhile, the understanding of the influences of both Ag-substitution and Ag-addition has also shed light on the future effort of carrier tuning by cation-doping towards the improvement of TE performance.

4. Conclusions

In summary, Ag-doped Ca$_3$Co$_4$O$_9$ thin films with $c$-axis orientation have been prepared by PLD method. Careful characterization of the Ag-Ca$_3$Co$_4$O$_9$ thin films revealed that substitution limit of Ag at Ca site is only about 5 at% in Ca$_3$Co$_4$O$_9$ thin films. For the thin films doped with higher amount of Ag, excess Ag is found to exist as isolated metallic phase in the films. In addition, Ag$^+$ and Ag$^0$ doping in Ca$_3$Co$_4$O$_9$ thin films give different influences on the in-plane electrical properties. Ag$^+$-substitution at the Ca site can increase both the carrier concentration and mobility. As a result, despite a slight reduction in Seebeck coefficient, the in-plane electrical resistivity can be drastically decreased, contributing to the great enhancement in the power factor. However, for the heavily doped samples with Ag$^0$ phase, although the resistivity can be further decreased, Seebeck coefficient is severely reduced simultaneously. Among these Ag-doped Ca$_3$Co$_4$O$_9$ thin films, the highest power factor of ~0.73 mWm$^{-1}$K$^{-2}$ was achieved for thin film Ag02 (Ca$_{2.88}$Ag$_{0.15}$Co$_4$O$_9$) at 705 K, which is about 16% higher than that of the pure Ca$_3$Co$_4$O$_9$ thin film. This indicates the great potential of Ag-doped Ca$_3$Co$_4$O$_9$ thin films for thermoelectric applications.
References


Table and Figure captions

**Table 1.** Chemical compositions of sol-gel solutions, PLD targets and the as-prepared thin films as well as their thicknesses.

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<tr>
<th>Sample Name</th>
<th>Sol-gel solution Ca:Ag:Co</th>
<th>Target Ca:Ag:Co</th>
<th>Thin Film Composition Ca:Ag:Co</th>
<th>Ag*: Ag0 (%)</th>
<th>Nominal Formula</th>
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<td>CCO</td>
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<td>3.02:0.00:4</td>
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<td>2.7:0.6:4</td>
<td>2.73:0.59:4</td>
<td>2.₈₈:0.₂₂:4</td>
<td>70.7:29.3</td>
<td>Ca₂.₈₈Ag₀.₁₅₅Co₄O₉/Ag₀.₆₄</td>
<td>108.6</td>
</tr>
<tr>
<td>Ag04</td>
<td>2.6:0.8:4</td>
<td>2.₆₂:0.₇₇:4</td>
<td>2.₈₆:0.₂₉:4</td>
<td>5₃.₉:4₆.₁</td>
<td>Ca₂.₈₈Ag₀.₁₅₅Co₄O₉/Ag₀.₁₃₄</td>
<td>98.8</td>
</tr>
</tbody>
</table>

**Fig. 1.** HR-XRD long-scan patterns of pure and Ag-doped Ca₃Co₄O₉ thin films.

**Fig. 2.** Relationship between c-axis parameter (calculated from the 2θ angle of (00l) peaks) and Ag content (determined by XPS by assessing Co = 4).

**Fig. 3.** (Color online) XPS fine scan spectra of Ag 3d (5/2) and (3/2) for Ag-doped Ca₃Co₄O₉ thin films.

**Fig. 4.** (Color online) Temperature dependence of in-plane electrical resistivity, ρ, for pure and Ag-doped Ca₃Co₄O₉ thin films. The inset gives Ag content dependence of carrier concentration, p, and carrier mobility, μ.

**Fig. 5.** (Color online) Plot of ln(ρ/Τ) versus 1000/Τ for pure and Ag-doped Ca₃Co₄O₉ thin films. The lines denote the linear fitting. And the inset gives the evaluated activation energy, Eₐ.

**Fig. 6.** (Color online) Temperature dependence of in-plane Seebeck coefficient, S, for pure and Ag-doped Ca₃Co₄O₉ thin films.
**Fig. 7.** (Color online) Temperature dependence of in-plane power factor, $P$, for pure and Ag-doped Ca$_3$Co$_4$O$_9$ thin films.
Highlights

 présence d’Ag dans $c$-axe orienté Ca$_3$Co$_4$O$_9$ films obtenus par dépôt d’ondes pulsées.

- La limite d’Ag substitution à la Ca site est trouvée à ~5 at% et de l’Ag-doping entraîne une structure composite.

- L’Ag-substitution augmente la concentration et la mobilité des chargeurs; tandis que l’Ag-compositing grand potentiel ne réduisent la coefficient Seebeck.

- Puissance facteur atteint ~0.73 mWm$^{-1}$K$^{-2}$, qui est une amélioration de 16%.
Figure 2

The graph shows the relationship between the c parameter (Å) and Ag content (x in Ca\(_{3-x}\)Ag\(_x\)Co\(_4\)O\(_9\)) for various samples labeled as CCO, Ag01, Ag02, Ag03, and Ag04.
Figure 3

The figure shows the binding energy distribution for four samples, labeled Ag01 to Ag04. Each plot compares raw data (circles) with fitted data (solid lines) and includes peaks at various binding energies. The peaks at 373.7 eV and 367.7 eV are labeled for Ag01, while Ag02 has peaks at 373.7 eV and 367.7 eV. Ag03 has peaks at 373.9 eV and 367.8 eV, and Ag04 has peaks at 374.0 eV and 368.0 eV. The plots illustrate the binding energy distribution for silver (Ag) in these samples.
Figure 4

The graph illustrates the temperature dependence of resistivity, $\rho$ (m$\Omega$ cm), and mobility, $\mu$ (cm$^2$/Vs), for various samples labeled CCO, Ag01, Ag02, Ag03, and Ag04. The resistivity data is plotted against temperature (K) on the x-axis, while the y-axis represents $\rho$ ($10^{20}$ cm$^{-3}$). The inset shows a closer view of the resistivity and mobility for Ag03, Ag02, and Ag01 samples. The mobility data is also shown for the same temperature range.