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Enhanced high temperature thermoelectric properties of Bi-doped c-axis oriented \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films by pulsed laser deposition

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\( \text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9 \) (\( x=0–0.4 \)) thin films were deposited on single-crystal sapphire (0001) substrates by pulsed laser deposition. Structural characterizations indicated that these thin films exhibited perfect c-axis orientation and were well crystallized. Surface chemical states analysis confirmed Bi-substitution for Ca in the thin films with \( x<0.4 \). For the thin film with \( x=0.4 \), excessive Bi were found isolated within the film. Due to their perfect orientation, in-plane electrical properties of these thin films measured from 300 to 740 K were found to be comparable to those of the single crystals. Furthermore, Bi-substitution was noted for the reduced electrical resistivity and enhanced Seebeck coefficient. The above superior properties resulted in a high power factor of 0.81 mW m\(^{-1}\) K\(^{-2}\) at 740 K for thin film \( \text{Ca}_{2.6}\text{Bi}_{0.4}\text{Co}_4\text{O}_9 \), which was about 29% improvement as compared to that of pure \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin film. The results suggested that Bi-doped \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films could be a promising candidate for thermoelectric applications at elevated temperatures. © 2010 American Institute of Physics. [doi:10.1063/1.3499324]

I. INTRODUCTION

Thermoelectric (TE) energy conversion is noted to be one of the promising technologies for energy recovery and power generation. It offers a direct way to reclaim the waste heat from systems such as automobiles, which is reckoned to be about 70% of the total primary energy. Among the various TE materials, misfit layered cobalt oxides are considered to be one of the most promising candidates to operate in air at high temperatures. This is due to their superior properties, such as low toxicity, thermal stability and high tolerance to oxidation etc., as compared to traditional intermetallic alloys. Among them, \( \text{Ca}_3\text{Co}_4\text{O}_9 \) is one of the best TE oxides that exhibits a high temperature TE figure of merit, \( ZT=T\frac{S^2}{\rho}\kappa \), of 0.83 at 1000 K, where \( S, T, \rho, \) and \( \kappa \) are the Seebeck coefficient, absolute temperature, electrical resistivity, and thermal conductivity, respectively, and \( S^2/\rho \) gives the power factor. The \( \text{Ca}_3\text{Co}_4\text{O}_9 \) crystal structure is composed of stacks of \( \text{CdI}_2 \)-type \( \text{CoO}_2 \) layer alternating with rock-salt-type \( \text{Ca}_2\text{Co}_4\text{O}_9 \) layer along the c-axis and can be denoted as \([\text{Ca}_3\text{Co}_4\text{O}_9]^{38}[\text{CoO}_2]_{1.62}\). Many attempts to improve TE efficiency by doping at Ca site have been reported for bulk \( \text{Ca}_3\text{Co}_4\text{O}_9 \). Particularly, it has been shown that Bi-substitution is effective to increase the Seebeck coefficient while maintaining the electrical resistivity of the system.⁵–⁹

It is noted that for many advanced applications, large size single crystals of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) are required. However, because of the strong anisotropy in crystal growth and electrical transport, large size single crystals are difficult to fabricate.⁸ On the other hand, randomly oriented \( \text{Ca}_3\text{Co}_4\text{O}_9 \) ceramics show poor TE performance. Thus, many efforts have been made to improve the texture of \( \text{Ca}_3\text{Co}_4\text{O}_9 \) ceramics by means of hot-forging,⁶ spark plasma sintering,⁷ and magnetic alignment⁸ processes. Recently, epitaxial or c-axis oriented \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films have been successfully prepared by radio-frequency sputtering,¹¹ pulsed laser deposition (PLD),¹²,¹³ and topotactic ion-exchange method.¹⁴ Due to the perfect crystal orientation, thin film in-plane TE properties were found to be better than the textured bulk ceramics and comparable to the single crystals. The thin film approach can also be applied to TE devices for localized cooling.¹⁵ Furthermore, thin film configuration facilitates further improvement of the TE performance by reducing the thermal conductivity via the lattice mismatches and/or scattering effects in the film, and at the same time, enhances the thermopower through structures such as superlattices or quantum wells.¹⁶ However, thus far, only pure \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films were fabricated and studied. In this work, we report for the first time a study on the effects of Bi-doping in high quality c-axis oriented \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films. High temperature electrical properties, which are essential but seldom reported for \( \text{Ca}_3\text{Co}_4\text{O}_9 \) thin films, will also be investigated. The property improvement by heavy doping into the highly-oriented thin films will open up tremendous opportunities for future TE applications.

II. EXPERIMENTAL SECTION

\( \text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9 \) (\( x=0, 0.1, 0.2, 0.3, \) and 0.4, named as CCO, Bi01, Bi02, Bi03, and Bi04 respectively) thin films with c-axis orientation were prepared on (0001) sapphire (c-plane) single crystal substrates by PLD method. The thin film growth was carried out at substrate temperature of 700 °C in 20 Pa (150 mTorr) oxygen pressure by using a KrF excimer laser (Lambda Physik Compex, \( \lambda=248 \text{nm} \)) with a laser energy density of \( \sim 1.2 \text{ J/cm}^2/\text{pulse} \) and the deposition rate was about \( \sim 2 \text{ nm/minute} \). The ceramic \( \text{Ca}_{3-x}\text{Bi}_x\text{Co}_4\text{O}_9 \) targets were synthesized as follows: oxides powders with nominal cation ratios (Table I) were first obtained by sol-gel method and then calcined at 700 °C. Due

"Electronic mail: asjma@ntu.edu.sg."
to its volatility, additional 10% of Bi was added. The resulting powders were pelletized into 1 in. diameter disks followed by sintering at 880 °C for 20 h. The chemical compositions of the final targets were confirmed by inductively coupled plasma (ICP) analysis using a Dual-view Optima 5300 DV ICP-optical emission spectrometry (OES) system (Perkin Elmer), and the results are shown in Table I. Table I also summarizes the thicknesses of the thin films, which were measured using an Alpha-Step IQ surface profiler. High resolution x-ray diffraction (HRXRD) data were collected using X’Pert MRD (PANalytical) with monochromatic Cu Ka radiation (λ=1.5406 Å) over 5°–55° range. Surface characterization was performed by an x-ray photoelectron spectroscopy (XPS) using Theta Probe XPS (Thermo Fisher Scientific) equipped with an aluminum anode (15 kV, 100 W, hv=1,486.6 eV) and a quartz monochromator. 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 XPS spectra. Transmission electron microscopy (TEM) images and selected-area electron diffraction (SAED) patterns were taken using a JEM-2100F (JEOL) at 200 kV. The in-plane electrical resistivity (ρab) and Seebeck coefficient (S) of the thin films were measured from room temperature to ~740 K by the standard four-probe method and the conventional steady state method, respectively. Room temperature carrier concentrations (n) of the thin films were determined by the Hall measurement (Bio Rad HL5500) with four-point-probe technique using van der Pauw geometry.

### III. RESULTS AND DISCUSSION

Figure 1(a) shows the HRXRD 2θ-ω scans of pure and Bi-doped Ca3Co4O9 thin films on (0001) sapphire substrate. Diffraction peaks of Ca3Co4O9 are indexed using four integers, h, k, l, and m, with the reciprocal-lattice vectors $\mathbf{q}$, from the formula, $q = ha^* + kb^* + lc^* + mb^*$ according to the reported misfit structure of Ca3Co4O9 with Cm̅ (0 1 0) superspace group. Besides the peak from sapphire (0006) substrate, only peaks from diffractions of (0000) Ca3Co4O9 planes are observed, indicating that the film is c-axis oriented. No extra peaks corresponding to any possible secondary phases, such as Bi2Ca2Co2O9, were observed for the Bi-doped Ca3Co4O9 thin films. The result reveals that the Bi large ions can be doped into the lattice of Ca3Co4O9 within the range x ≤ 0.4 without any detectable change in the crystal structure. It can be seen that diffraction peaks for the Bi-substituted samples tend to shift toward the lower 2θ angle as compared to that of pure CCO thin film, as shown in the fine scan of the (0040) peaks in Fig. 1(b). Based on the positions of the (0000) diffraction peaks, the c-axis lattice constants for each sample were calculated. Figure 1(c) shows that the c-axis lattice constants increase gradually with the amount of Bi composition (determined by XPS). This observation is consistent with the reported work on Bi-substituted Ca3Co4O9 bulk materials, indicating the enlargement of the crystallographic structure due to the larger Bi3+ (1.03 Å) substitution for Ca2+ (1.0 Å). Figure 2(a) shows the cross-sectional TEM image of the Bi03 thin film, where the atomic misfit layered structure on the sapphire substrate can be seen. Stacking faults and defects observed in the film layer are consistent with that reported for Ca3Co4O9 thin films fabricated by PLD. The SAED patterns of the film [Fig. 2(b)] and substrate [Fig. 2(c)], taken with the incident electron beam along the same direction, further confirmed the structure and the c-axis growth direction of the Ca3Co4O9 thin film. Both TEM image and SAED observation were found to be consistent with the well crystallized Ca3Co4O9 thin film with perfect c-axis orientation.

The cation composition in the pure and Bi-doped

<table>
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<tr>
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<th>Sol-gel solute Ca:Bi:Co</th>
<th>Target Ca:Bi:Co</th>
<th>Film Ca:Bi:Co</th>
<th>Film thickness (nm)</th>
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<tr>
<td>CCO</td>
<td>Ca3Co4O9</td>
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<td>3.04:0.00:4</td>
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<td>99.8</td>
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<tr>
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<td>Ca3.6Bi0.4Ca0.002O9</td>
<td>2.9:0.11:4</td>
<td>2.92:0.12:4</td>
<td>2.87:0.10:4</td>
<td>87.6</td>
</tr>
<tr>
<td>Bi02</td>
<td>Ca3.8Bi0.2Ca0.004O9</td>
<td>2.8:0.22:4</td>
<td>2.84:0.25:4</td>
<td>2.75:0.21:4</td>
<td>97.4</td>
</tr>
<tr>
<td>Bi03</td>
<td>Ca3.7Bi0.3Ca0.002O9</td>
<td>2.7:0.33:4</td>
<td>2.74:0.36:4</td>
<td>2.65:0.32:4</td>
<td>88.4</td>
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<tr>
<td>Bi04</td>
<td>Ca3.8Bi0.1Ca0.002O9</td>
<td>2.6:0.44:4</td>
<td>2.62:0.47:4</td>
<td>2.54:0.42:4</td>
<td>90.3</td>
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<td>90.3</td>
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![HRXRD scan](image_url) | ![SAED pattern](image_url) | ![TEM image](image_url)

**FIG. 1.** (a) HRXRD long scan of Ca1-xBi2xCo2O9 (x=0, 0.1, 0.2, 0.3, and 0.4) thin films, (b) fine scan of (0040) peaks, and (c) relationship between Bi content determined by XPS and c cell parameter calculated from the 2θ angle of (0000) peaks.
Ca₃Co₄O₉ thin films were investigated by XPS quantitative analysis using the area ratios of Ca 2p½, Co 2p½, and Bi 4f½/2 peaks and Taucgard-type background after calibration with their sensitivity factors. The calculated thin film compositions (by assigning Ca=4.0) are listed in Table I. Due to the volatile nature of Bi, Bi compositions of the thin films were found to be slightly less than their respective targets. However, the resulting amount of Bi in the thin films was still higher than the nominal composition due to the excess Bi initially used to fabricate the targets. In order to determine the Bi chemical states and confirm whether Bi was doped into the Ca₃Co₄O₉ structure, XPS fine scans of Bi 4f were performed and are shown in Fig. 3. It can be seen that the Bi 4f doublets for all the Bi–Ca₃Co₄O₉ thin films are located at about 158.3 and 163.6 eV, which are close to the reported Bi³⁺ values. For thin film of Bi₀₄, weak shoulders located at about 158.3 and 163.6 eV, which are close to the result, it is clear that, for thin films with x=0.4, Bi atoms are combined with oxygen and have doped into the Ca₃Co₄O₉ structure, whereas for the thin film with x=0.3 for our PLD fabricated Ca₃Co₄O₉ thin films, which is consistent with the limitation of reported Bi-doped Ca₃Co₄O₉ single crystals.

Figure 4 shows the in-plane (ab-plane) electrical resistivity (ρ_ab) versus temperature (T) for the as-prepared thin films on sapphire (0001). All samples show similar transport behavior with a gradually metal–insulator (MI) transition around 400–550 K. Upon further increase in the temperatures, Tbegins to exhibit semiconductorlike transport behavior. Such MI transition has been observed in many previous reports and is associated with a spin-state transition of Co ions and/or a first-order phase transition of Ca₃Co₄O₉ system. The electrical resistivity of the thin film is noted to be about 4–5.5 mΩ cm over the temperature range measured. These ρ values of the thin films are lower than that of most reported Ca₃Co₄O₉ ceramics. A remarkable reduction in ρ was observed for the Bi-doped films. Similar observation has also been reported for Bi-doped Ca₃Co₂O₅ bulk ceramics. The electrical resistivity can be expressed as ρ=1/(σnμe), where σ, n, and μ are the electrical conductivity, carrier concentration, and carrier mobility, respectively. From Hall effect, RH, measurements, in-plane (n=(1/εRH)), and μ=(1/ρTEE) of the thin films were calculated, as shown in the inset of Fig. 4. It is found that, n of Bi-doped Ca₃Co₂O₅ thin films shows a slight decrease with increasing Bi-doping content. According to the misfit layered structure of Ca₃Co₄O₉ system, the edge shared [CoO₂] layers are considered to be responsible for the electrical conduction, whereas the rock-salt-type [Ca₃Co₂O₇] layers are regarded as a charge reservoir to supply carriers into the CoO₂ layers. Trivalent Bi³⁺ substitution for divalent Ca²⁺ in the [Ca₂Co₃O₇] layers will inject electrons into the conductive [CoO₂] layer. In the condition of a constant oxygen composition, this results in a decreased n, as the carrier of Ca₃Co₂O₅ system is hole. Nevertheless, it has been reported that, Bi-substitution can also effectively reduce the oxygen deficiency in Ca₃Co₂O₅ phase. The increase oxygen content can enlarge the number of hole carriers and compensate the decrease amount of n by Bi nonequal-valence substitution.
for Ca. Therefore, the influence of Bi-substitution on $n$ is reckoned to be not significant, and the reduction in $\rho$ arises from the improvement in $\mu$.

In order to understand the high temperature conduction mechanism, both thermally activated conduction model and adiabatic small polaron hopping conduction (SPHC) model were used to examine the data in the high temperature region, where $T > 550$ K. The plots of $\ln(\rho/T)$ versus 1000/$T$ for all the samples lie on straight lines above 550 K, as shown in Fig. 5, indicating the SPHC behavior of these thin films. According to the SPHC mechanism of Ca$_3$Co$_4$O$_9$, the temperature dependence of electrical resistivity can be generally expressed as

$$\frac{1}{\rho} = \sigma = n e a^2 \left(\frac{A}{T}\right) \exp\left(-\frac{E_a}{k_B T}\right),$$

where $a$ is the intersite distance of hopping, $E_a$ is the activation energy, $k_B$ is the Boltzmann constant, and $A$ is the pre-exponential terms related to the scattering mechanism. Apart from $n$, only $a$ and $E_a$ could be influenced by ion substitution. From the slopes of the plots in Fig. 5, $E_a$ is found in the range of 68–72 meV, which is slightly lower than the reported values (77–85 meV) for Ca$_3$Co$_4$O$_9$ ceramics. It is reported that grain boundaries and interfaces can act as an energy filter and eliminate the lower energy carriers. As a result, random orientation, small crystal size and/or more structural defects will result in larger activation energy. As confirmed in the earlier analysis, our pure and Bi-doped Ca$_3$Co$_4$O$_9$ thin films show good crystallization and perfect $c$-axis orientation. Hence, smaller amount of grain boundaries and interfaces can be expected. This, in turn, will contribute to the reduction in $E_a$. PLD method has thus shown its advantage to facilitate the forming of Ca$_3$Co$_4$O$_9$ thin films with lower electrical resistivity than ceramics obtained by conventional solid state processing method. Furthermore, it is found that, for all the thin film samples, $E_a$ is almost independent of the Bi-substitution. This is consistent with the above mentioned mechanism that, Bi-substitution at the [Ca$_3$CoO$_2$] layers does not change the hopping process, which happened at the [CoO$_2$] layers. Therefore, the reduction in $\rho$ in Bi-substituted Ca$_3$Co$_4$O$_9$ thin films should be attributed to the change in $a$. As shown in the earlier XRD result, Bi-substitution with larger ion diameter enlarges the lattice constant of Ca$_3$Co$_4$O$_9$. This provides a direct influence on the intersite distance of hopping. Moreover, Bi-substitution is helpful to moderate the misfit relation of the [Ca$_2$CoO$_3$] and the [CoO$_2$] subsystems and eliminate structural defects and stacking faults, thereby reduces the scattering of hole carriers and increases $a$. In conclusion, although Bi$^{3+}$ substitution for Ca$^{3+}$ is noted to decrease the $p$-type carrier concentration, the electrical resistivity of the thin films can still be reduced by the increase in carrier mobility from the increased intersite distance of hopping.

The temperature dependence of Seebeck coefficient ($S$) for the pure and Bi-doped Ca$_{3-x}$Bi$_x$Co$_4$O$_9$ thin films are presented in Fig. 6. All the samples show a positive $S$ over the entire temperature range (300–740 K) indicating that major carriers in these thin film samples are holes, which is in agreement with the Hall effect measurements. Compared with pure CCO thin film, $S$ of the Ca$_{3-x}$Bi$_x$Co$_4$O$_9$ ($x < 0.4$) thin films increases with Bi content and shows a similar temperature dependence. For the Bi03 thin film, $S$ reaches ~177 $\mu$V/K at ~740 K, which is similar to that of the Bi-doped Ca$_3$Co$_4$O$_9$ single crystals. In the Ca$_{3-x}$Co$_3$O$_9$ system, $S$ can be expressed by the Mott formula,

$$S(T) = \frac{1}{eT} \int_{-\infty}^{\infty} \frac{f(e)}{\sigma(e)} \frac{\partial \sigma(e)}{\partial e} de,$$

where $\sigma(e)$ and $f(e)$ represent electrical conductivity and Fermi–Dirac distribution function at energy $e$. The product of the TE coefficient and temperature can be, therefore, understood as a mean energy flow carried by a conduction electron. By using the condition of $\partial f(e)/\partial e = \delta(e-E_F)$, and $\sigma = en\mu(e)$, Eq. (2) can be written as:

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

where $\mu(e)$, $e$, and $k_B$ are energy correlated carrier mobility, electronic specific heat, and Boltzmann constant, respectively. In the Ca$_3$Co$_4$O$_9$ system, the first term of Eq. (3) is considered to be dominant, similar with the Drude picture $S \sim c_e/n$. As discussed above, the carrier concentration $n$ decreases with the increase in Bi-doping content. So the change in $S$ can generally be explained by the variation in $n$. For the Bi04 thin film, $S$ is lower than that of Bi03 sample, and
shows even lower $S$ than pure CCO thin film at high temperature above 700 K. This may be due to the excessive Bi isolated in the thin film, which are contributing as $n$-type minority carriers. The power factors, $P$, of the present thin films are calculated from the measured $\rho$ and $S$, as shown in Fig. 7. The thin film sample of Bi03 is noted to show the highest $P$ value over the temperature range investigated. The thin film power factor has improved by $\sim 29\%$ and reached $\sim 0.81$ mW m$^{-1}$ K$^{-2}$ at 740 K compared to pure Ca$_3$Co$_4$O$_9$. Moreover, due to their perfect orientation, Bi-doped Ca$_{3-x}$Bi$_x$Co$_4$O$_9$ thin films shows higher power factor than Bi-doped poly crystalline ceramics ($\sim 0.5$ mW m$^{-1}$ K$^{-2}$). This huge enhancement on the power factor indicates the great potential of doped Ca$_3$Co$_4$O$_9$ materials for TE thin film devices.

IV. CONCLUSION

In summary, Bi-doped Ca$_3$Co$_4$O$_9$ thin films were prepared by PLD method using Bi-mixed Ca$_3$Co$_4$O$_9$ ceramic targets. The thin films were well crystallized with perfect $c$-axis orientation. Bi could be successfully doped into the Ca$_3$Co$_4$O$_9$ crystal lattice structure for the thin films Ca$_3-x$Bi$_x$Co$_4$O$_9$ ($x < 0.4$). For the thin film $x = 0.4$, the Bi content was found to exceed the doping limit and resulted in isolated Bi within the film. By using the PLD method, the in-plane electrical properties of the pure and Bi-doped Ca$_3$Co$_4$O$_9$ thin films, measured from room temperature to $\sim 740$ K, were found to be comparable to that reported for single crystals. Moreover, Bi-substitution at Ca site can effectively increase carrier mobility, hence reduce the electrical resistivity, and Seebeck coefficient of the thin films can be improved simultaneously. As a result, the highest power factor of Bi03 sample reached 0.81 mW m$^{-1}$ K$^{-2}$ at 740 K, suggesting that Bi-doped Ca$_3$Co$_4$O$_9$ thin films could be a promising candidate for TE applications at elevated temperatures.


