Observations of Co\(^{4+}\) in a Higher Spin State and the Increase in the Seebeck Coefficient of Thermoelectric Ca\(_3\)Co\(_4\)O\(_9\)

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(Received 25 August 2011; published 8 May 2012)

Ca\(_3\)Co\(_4\)O\(_9\) has a unique structure that leads to exceptionally high thermoelectric transport. Here we report the achievement of a 27% increase in the room-temperature in-plane Seebeck coefficient of Ca\(_3\)Co\(_4\)O\(_9\) thin films. We combine aberration-corrected Z-contrast imaging, atomic-column resolved electron energy-loss spectroscopy, and density-functional calculations to show that the increase is caused by stacking faults with Co\(^{4+}\)-ions in a higher spin state compared to that of bulk Ca\(_3\)Co\(_4\)O\(_9\). The higher Seebeck coefficient makes the Ca\(_3\)Co\(_4\)O\(_9\) system suitable for many high temperature waste-heat-recovery applications.


Thermoelectric (TE) materials have attracted increasing attention over the last two decades, when theoretical predictions suggested that the TE efficiency could be enhanced through nanostructural engineering, which led to experimental studies demonstrating proof-of-principle high-efficiency materials [1]. Initially, complex bulk materials were found to exhibit high TE efficiencies [2–4], followed by nanostructured Bi\(_2\)Te\(_3\)-Bi\(_2\)Se\(_3\) superlattices which showed a TE figure of merit (\(zT\)) in excess of 2 at room temperature [5].

The focus of research on TE devices has since shifted primarily to nanostructures, such as quantum dots, superlattices, or nanowires. However, many of these systems are unstable at high temperatures and toxic. They are also difficult and expensive to synthesize for large-scale applications. Layered complex oxides such as Ca\(_3\)Co\(_4\)O\(_9\) exhibit large in-plane TE transport behavior, are stable at high temperatures, and contain mostly cheap and nontoxic elements.

Ca\(_3\)Co\(_4\)O\(_9\) is an incommensurately layered oxide, consisting of two separate subsystems, Co\(_2\) and Ca\(_2\)Co\(_2\)O\(_3\), each fulfilling a different role in achieving remarkably high TE properties at room and elevated temperature. Along the \(c\)-axis of Ca\(_3\)Co\(_4\)O\(_9\), Cd\(_2\)-type Co\(_2\) layers are separated by a triple-layer of insulating rocksalt-type Ca\(_2\)Co\(_2\)O\(_3\). The Co\(_2\) acts as the highly conductive hole-doped electron crystal. The insulating Ca\(_2\)Co\(_3\) acts as the phonon-glass and charge reservoir layers.

The high Seebeck coefficient in Ca\(_3\)Co\(_4\)O\(_9\) has been attributed to a number of different mechanisms, including the occurrence of a mixed-valence state in the Co\(_2\) layer [6], or the increased entropy of the localized electrons in the degenerated cobalt 3\(d\) states [7]. Several studies have suggested that varying the compressive strain on the Co\(_2\) subsystem could provide a viable path to further increase the Seebeck coefficient, \(S\), in Ca\(_3\)Co\(_4\)O\(_9\) [8–10]. There appear to be two ways of exerting further compressive strain on the Co\(_2\) subsystem, by doping the rocksalt layers or by epitaxial thin-film growth on lattice mismatched substrates. While there is a large number of doping studies showing moderate increases in either the Seebeck coefficient or the electrical conductivity of bulk Ca\(_3\)Co\(_4\)O\(_9\) (see, for example, Refs. [11,12]), detailed thin film studies [13] have shown that pristine Ca\(_3\)Co\(_4\)O\(_9\) films grow largely unstrained on a variety of oxide substrates and do not exhibit any significant increase in the in-plane Seebeck coefficient. Furthermore, an in-depth survey of the published literature reveals that the Seebeck coefficient of pristine bulk Ca\(_3\)Co\(_4\)O\(_9\) is limited to \(S_{\text{max}} \approx 135\) \(\mu\)V/K at room temperature (see, for example, [14]), suggesting the presence of a fundamental limit to further increasing the thermoelectric properties of layered cobalt oxides.
In this Letter, we demonstrate that controlling the defect structure in Ca$_3$Co$_4$O$_9$ thin films can hold the key to further increasing the Seebeck coefficient. By synthesizing highly textured Ca$_3$Co$_4$O$_9$ films with a large concentration of CoO$_2$ stacking faults, we are able to increase the in-plane Seebeck coefficient from $S_{\text{bulk}} = 135 \, \mu V/K$, in bulk, to $S_{\text{film}} = 180 \, \mu V/K$ in thin Ca$_3$Co$_4$O$_9$ films at room temperature, while maintaining an electrical resistivity of $10.5 \pm 0.5 \, m\Omega \, cm$ [see insert in Fig. 1(a)]. We attribute the large concentration of stacking faults to the rapid growth dynamics and the reduced thickness of the films. Using a combination of atomically-resolved Z-contrast imaging and electron energy-loss spectroscopy (EELS) in aberration-corrected scanning transmission electron microscopy (STEM), and first-principles calculations, we show that the high Seebeck coefficient in Ca$_3$Co$_4$O$_9$ thin films on SrTiO$_3$ [001] is due to the presence of CoO$_2$ stacking faults, which stabilize the transition of Co$^{4+}$-ions from a low spin-state in bulk Ca$_3$Co$_4$O$_9$ to an intermediate spin in the thin films at room temperature and above.

Figure 1(a) shows the in-plane Seebeck coefficient in the temperature range between 10 K and 400 K of the nominally 40 nm thick Ca$_3$Co$_4$O$_9$ films on SrTiO$_3$ and of highly textured Ca$_3$Co$_4$O$_9$ bulk. For temperatures 25 K, we find a significant increase in the Seebeck coefficient with decreasing temperature as previously reported by Tang et al. [15] In the low temperature regime above 25 K, both samples show the typical linear dependence of the Seebeck coefficient with temperature, suggesting a Fermi-liquid behavior [16]. When plotting the Seebeck coefficient as a function of the normalized Fermi temperature, as suggested by Limette et al. [16], we find that the bulk and thin film Ca$_3$Co$_4$O$_9$ exhibit the same linear temperature dependence of the Seebeck coefficient (see Supplemental Materials Fig. S2 [17]).

At temperatures higher than 200 K, the in-plane Seebeck coefficient reaches a plateau. However, the value of the Seebeck coefficient in this regime is significantly higher in the Ca$_3$Co$_4$O$_9$ thin films compared to any reported bulk Ca$_3$Co$_4$O$_9$ values. The high-temperature behavior of the Seebeck coefficient in Ca$_3$Co$_4$O$_9$ is governed by the Heikes formula,

$$S = \frac{k_B}{e} \ln \left( \frac{g_3+}{g_4+} \frac{1-x}{x} \right), \quad (1)$$

where $x$ is the Co$^{4+}$ concentration, $g_3+$ and $g_4+$ are the orbital degeneracy of Co$^{3+}$ and Co$^{4+}$ in the CoO$_2$-layers. We have previously shown that the CoO$_2$-layers in bulk Ca$_3$Co$_4$O$_9$ are highly hole-doped, resulting in a mixed Co valence state with $x = 0.5$ [18].

Figure 1(b) shows the calculated Seebeck coefficient using Eq. (1) for different Co$^{3+}$ and Co$^{4+}$ spin states, including the Co$^{3+}$ low spin state (LS, $t^6_{2g}e^0_{g}$), the Co$^{3+}$ intermediate-spin state (IS, $t^5_{2g}e^1_{g}$), the Co$^{3+}$ high-spin state (HS, $t^5_{2g}e^2_{g}$), as well as the Co$^{4+}$ low-spin state (LS, $t^6_{2g}e^0_{g}$) and Co$^{4+}$ intermediate-spin state (IS, $t^5_{2g}e^1_{g}$). It is generally accepted that both the Co$^{3+}$ and Co$^{4+}$-ions in the CoO$_2$-layers are in the low spin state for undoped bulk, thereby imposing an upper limit on the Seebeck coefficient for $x = 0.5$ of $S = 154 \, \mu V/K$, as widely observed experimentally at room temperature. Our measured value of the in-plane Seebeck coefficient of $S_{\text{bulk}} = 135 \, \mu V/K$ is therefore very close to this limit, yet the measured Seebeck coefficient in the thin film, $S_{\text{film}} = 180 \, \mu V/K$, cannot be explained using this model, or any modified version, such as the one proposed by Pollet et al. [19]. We believe that the increase in the Seebeck coefficient will also be observed at temperatures higher than 400 K.

The increase in the Co$^{4+}$-ion spin state results in a larger contribution to the Seebeck coefficient as shown in Fig. 1, with a new upper limit of $S_{\text{max}} = 275 \, \mu V/K$. The result suggests that stacking faults within the incommensurably layered Ca$_3$Co$_4$O$_9$ provide a significant fraction.

FIG. 1 (color online). (a) Seebeck coefficients for thin film and bulk Ca$_3$Co$_4$O$_9$. Insert: In-plane electrical resistivity as a function of temperature $T$. (b) Calculated Seebeck coefficients using Eq. (1) for different spin states as a function of cobalt valence in the CoO$_2$ layers. The dashed line shows the Co$^{4+}$ concentration found in the CoO$_2$ layers.
of Co$^{4+}$-ions in the intermediate-spin state to the CoO$_2$-layers.

Figures 2(a) and 2(b) show atomic-resolution Z-contrast images of the Ca$_3$Co$_4$O$_9$ thin-film on SrTiO$_3$. Our imaging study shows that the average film thickness is 30 nm. Some regions of the image show Ca$_3$Co$_4$O$_9$ along the [110] direction, with the Ca$_2$CoO$_3$ layer exhibiting the usual trilayer structure [see Fig. 2(d)], while in other areas the structure appears to be rotated out of the zone-axis orientation. Such interlayer rotation along the c-direction has not been observed in any of the previously analyzed Ca$_3$Co$_4$O$_9$ thin films deposited on either SrTiO$_3$ LaAlO$_3$, or (La$_{0.8}$Sr$_{0.2}$)(Al$_{0.65}$Ta$_{0.35}$)O$_3$ [13]. In addition to this in-plane rotation, the images also show stacking faults in the form of double CoO$_2$ layers. The influence of stacking faults, which are found on average every 10 unit-cell in the thin film, and the effects of the interlayer rotation on the thermoelectric transport properties will be discussed next.

Two-dimensional atomically-resolved EEL spectrum images (SI) were acquired from the thin films, and the Co $L_{2,3}$-ratio was used to determine the doping concentration in the CoO$_2$-layers in bulk Ca$_3$Co$_4$O$_9$ [18,20]. Similar to bulk, we find that the Co valence in the Ca$_2$CoO$_3$-layers of the thin films is 3.5 ± 0.1 [see insert in Fig. 2(c) and Supplemental Materials Fig. S3 [17]]. No change in the Co valence in the CoO$_2$ stacking faults or the CoO$_2$ layers between two rotated Ca$_2$CoO$_3$ layers can be detected. This suggests that neither one of these structural defects has any influence on the doping (or mobile hole concentration) in the CoO$_2$ layers.

Figures 2(e) and 2(f) show the O $K$-edge taken from the CoO$_2$ and the Ca$_2$CoO$_3$ layers, as well as the CoO$_2$ stacking faults. The O $K$-edge for all positions shows a strong prepeak centered at 533 eV and split into two distinct peaks, which stem from transitions into the hybridized Co 3$d$ $t_{2g}$ and $e_g$ orbitals. This feature is followed by a shoulder located about 10 eV above the edge onset, which is due to transitions from the O 2$p$ to the Ca 4$s$ orbitals. As can be seen in Figs. 2(e) and 2(f) the O $K$-edge prepeak has the lowest intensity in the CoO columns in middle of the Ca$_2$CoO$_3$-layer, but shows the strongest intensity in the shoulder 10 eV above the edge onset. This can be explained by the lower Co valence and the stronger bonding between CaO and CoO in the Ca$_2$CoO$_3$-layer. The O $K$-edge prepeak in the CoO$_2$ layer shows a distinct increase due to the higher Co valence.
and the presence of mobile holes in the CoO$_{2x}$ layers \cite{18,20}. The intensity of the two prepeaks is still very similar, but the second peak appears to have shifted approximately 0.4 eV towards lower energy compared to the Ca$_3$CoO$_2$-layer. The O K-edge spectra obtained from the CoO$_2$ stacking faults show a further increase in the prepeak intensity.

The spectra taken from the Co and O atomic columns within the stacking fault show an increase in the peak located at 533.9 eV, while the intensity ratio between the two prepeaks is significantly different for each position. The intensity ratio between the first and second prepeak in the CoO$_2$ layers is 0.95, this ratio drops to 0.72 and 0.85 for the Co and O atomic columns in the stacking fault, respectively. We notice that the Co L-edge and O K-edge taken from CoO$_2$-layers at the boundary between two rotated Ca$_3$CoO$_4$O$_8$ layers does not show any significant difference compared to Ca$_3$CoO$_2$O$_9$ bulk (Supplemental Materials Fig. S3 \cite{17}).

To further understand the reason for the higher prepeak intensity in the CoO$_2$ stacking faults and its influence on the thermoelectric transport properties, we study the possible mechanisms that give rise to the observed changes in the O K-edge prepeak intensity. It was previously reported that the O K-edge prepeak intensity is a sensitive measure of the Co$^{3+}$ spin state in cubic perovskite system \cite{21}, and the splitting of the O K-edge prepeak stems from the Ligand-field splitting of hybridized Co 3d orbitals into $t_{2g}$ and $e_g$. Since the spectra for Co$^{3+}$ do not exhibit any splitting of the O K-edge prepeak \cite{22}, the changes in the O K-edge prepeak intensity could either indicate either an increased Co valence state or a higher spin state of the Co$^{4+}$ ions in the CoO$_2$ stacking faults.

As we have shown earlier, the Co valence state remains unchanged in the CoO$_2$ stacking faults, and an increased concentration of Co$^{4+}$ ions would also result in an overall decrease in the Seebeck coefficient [see Fig. 1(b)]. We therefore propose that the increase in the O K-edge prepeak intensity stems from a different occupancy of the Co$^{4+}$ $t_{2g}$ and $e_g$ orbitals, as the result of an increased spin state of the Co$^{4+}$ ions. Such a spin-state transition can explain the observed increase in the in-plane Seebeck coefficient, since the combination of Co$^{3+}$-ions in the low spin state and Co$^{4+}$-ions in the intermediate spin state will result in a significantly higher Seebeck coefficient. It was previously suggested that such a spin-state transition occurs at 420 K in bulk Ca$_3$CoO$_2$O$_9$ and is responsible for the observed changes in electrical resistivity and the increasing Seebeck coefficient above 420 K \cite{20,23}. Earlier calculations by Landron et al. \cite{24} have shown that the orbital degeneracy of the Co$^{3+}$ ions in CoO$_2$ strongly depends on the Co-O bondangle, which is directly correlated to the energy of the $a_{1g}$ and $e'_g$ orbitals. Therefore, an alternative explanation for the measured increase in the Seebeck coefficient could be that the introduction of extra layers in the stacking fault will distort the CoO$_2$ octahedra and thereby impact the filling and the relative positions of these orbitals. Consequently, the spin degeneracy of the Co$^{4+}$ ions is increased, resulting in an increasing Seebeck coefficient. Such a model does not, however, explain the observed increase in the O K-edge prepeak intensity, since changing the occupancy of the $a_{1g}$ and $e'_g$ orbitals should only change the shape, but not the overall intensity of the O K-edge prepeak.

To further explore the observed changes in the near-edge fine-structure of the O K-edge, first-principles density functional theory (DFT) calculations were performed on an approximated unit-cell for Ca$_3$Co$_4$O$_9$. The incommensurate structure was modeled with a 66 atom cell \cite{25}. The electronic structure was then calculated using the projector-augmented wave method and the generalized gradient approximation.

The calculated fine-structure of the CoO layers [Fig. 3(a)] reproduces the experimentally observed prepeak splitting. Furthermore, by comparing the experimental prepeak intensity ratio with the calculated spectra, we find that the O K-edge prepeak in the CoO layer mostly represents the in-plane Co-O bonding (i.e., $p_x$ and $p_y$), with a measured energy difference between the peaks, $\Delta d = 1.3$ eV, close to the calculated value of 0.9 eV. For the CoO$_2$ layer, the splitting is again reproduced by the calculations, but the modeled $\Delta d$ is smaller than in the CoO layer. The predicted shift of the prepeak intensity in the CoO$_2$ layers was not, however, observed experimentally, which is attributed to the limitations of using a small, approximate unit cell in our calculations.

As expected, the out-of-plane (i.e., $p_z$) Co-O bonding is significantly enhanced in the CoO$_2$ layers, represented by the high intensity peak located at 532.6 eV in the
experimental spectra, while the peak at 533.9 eV is attributed to the in-plane \((p_t, p_g)\) Co-O bonding. The observed changes in the prepeak intensity ratio within the \(\text{CoO}_2\) stacking faults, in particular, the increased intensity of the second prepeak, appear to stem from additional contributions of the \(p_t\) and \(p_g\) states. The higher intensity of the first prepeak in the O columns compared to the Co columns in the stacking fault is attributed to a higher concentration of \(p_g\) states. This increase in the density of \(p_g\) states could be attributed to an increased strain in the stacking fault or a difference in the interlayer bonding due to the presence of two \(\text{CoO}_2\) layers. We have previously shown that the first O \(K\)-edge prepeak in the experimental data [Fig. 2(f)] stems from transitions into the Co \(t_{2g}\) orbitals which correspond to the lowest energy empty states above \(E_f\) shown in our DFT calculations, i.e., the \(p_t\) states [Fig. 3(b)]. We can, therefore, directly relate the measured changes in the O \(K\)-edge prepeak intensities to the increased density of empty \(\text{Co}^{4+}\) \(t_{2g}\) states as the result of a \(\text{Co}^{4+}\) spin-state transition.

In summary, we have shown that thin \(\text{Ca}_3\text{Co}_4\text{O}_9\) films grown on \(\text{SrTiO}_3\) exhibit a significant increase in the Seebeck coefficient, while the electrical resistivity remains at bulk levels. We attribute the higher Seebeck coefficient to \(\text{CoO}_2\) stacking faults present throughout the film, which stabilize the \(\text{Co}^{4+}\)-ions in an intermediate spin state, as opposed to the low spin state found in bulk \(\text{Ca}_3\text{Co}_4\text{O}_9\). This work was supported by the NSF [DMR-0846748 (R.F.K.), DMR-0938330 (J.C.I.)], by ORNL’s Shared Research Equipment (SHaRE) User Program, sponsored by the DOE Office of Basic Energy Sciences (J.C.I.), DOE [DE-FG02-09ER46554 (M.P.P., S.T.P.)], by DOE [DE-AC02-06CH11357 (S.K., B.D.)], by the McMinn Endowment (S.T.P) at Vanderbilt University, and the U.S. Army Research Office (W911NF-10-1-0147). S.Ö. acknowledges support by the National Science Foundation under the Independent Research/Development program while working at the Foundation.