



<b>Title</b>	Layered cobalt oxide epitaxial films exhibiting thermoelectric $ZT = 0.11$ at room temperature
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<b>Citation</b>	Journal of Materials Chemistry A, 9(1), 274-280 <a href="https://doi.org/10.1039/d0ta07565e">https://doi.org/10.1039/d0ta07565e</a>
<b>Issue Date</b>	2021-01-07
<b>Doc URL</b>	<a href="http://hdl.handle.net/2115/83799">http://hdl.handle.net/2115/83799</a>
<b>Type</b>	article (author version)
<b>Additional Information</b>	There are other files related to this item in HUSCAP. Check the above URL.
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## Electronic Supplementary Information

### Layered cobalt oxide epitaxial films exhibiting thermoelectric $ZT = 0.11$ at room temperature

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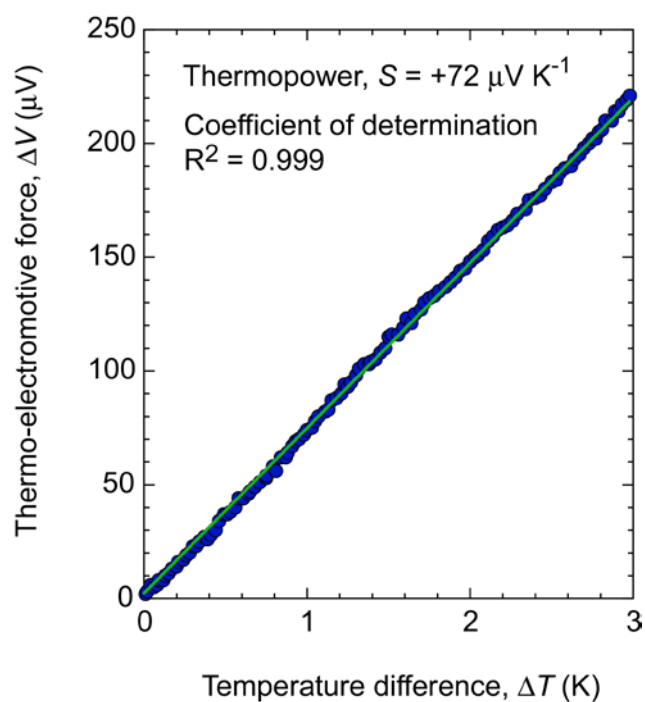
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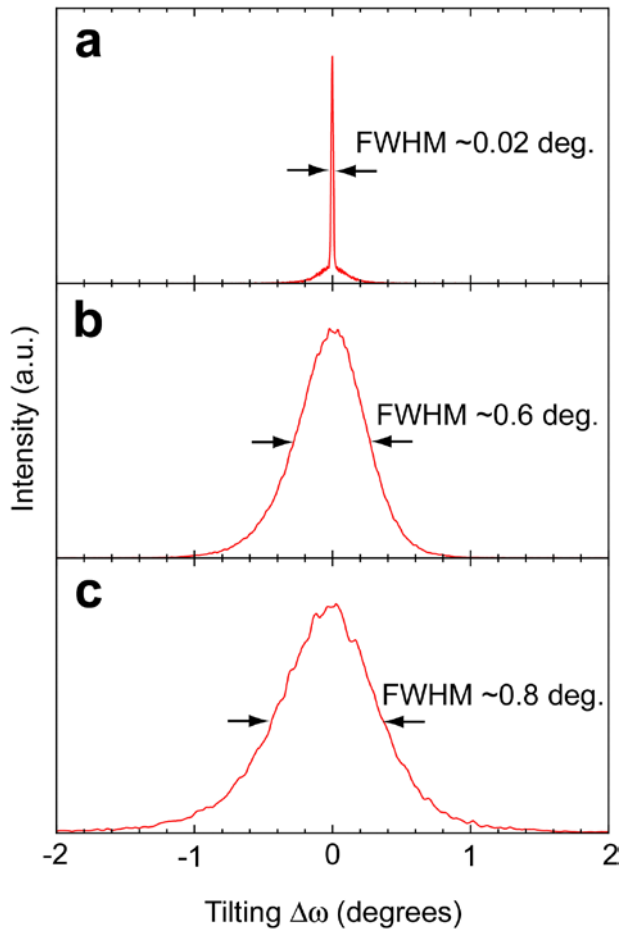
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**Table S1.** Thermoelectric properties of the layered cobaltite epitaxial films in the in-plane direction at room temperature. In addition to the observed properties, we calculated the lattice thermal conductivity ( $\kappa_{\text{lattice}} = \kappa_{\text{obsd}} - \kappa_{\text{electron}}$ ). The electron thermal conductivity ( $\kappa_{\text{electron}}$ ) was estimated by assuming the Wiedemann-Franz law ( $\kappa_{\text{electron}} = L \cdot \sigma \cdot T$ , where the  $L$  is  $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$ ).

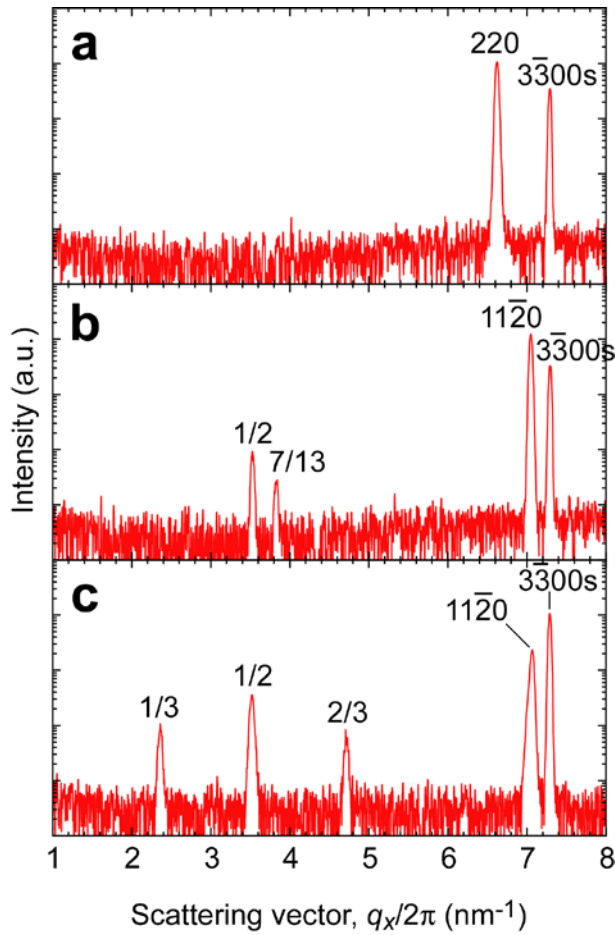
	$\text{Ca}_{1/3}\text{CoO}_2$ <sup>19</sup>	$\text{Na}_{0.75}\text{CoO}_2$	$\text{Sr}_{1/3}\text{CoO}_2$ <sup>21</sup>	$\text{Ba}_{0.27}\text{CoO}_2$
$\sigma_{\text{in}}$ ( $\text{S cm}^{-1}$ )	1330	1330	890	2310
$S_{\text{in}}$ ( $\mu\text{V K}^{-1}$ )	+90	+96	+115	+72
$\text{PF}_{\text{in}}$ ( $\text{mW m}^{-1} \text{K}^{-2}$ )	1.08	1.23	1.18	1.20
$\kappa_{\text{in obsd}}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	6.79	5.46	4.51	3.29
$\kappa_{\text{in electron}}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	0.98	0.97	0.65	1.69
$\kappa_{\text{in lattice}}$ ( $\text{W m}^{-1} \text{K}^{-1}$ )	5.81	4.49	3.86	1.60
$ZT_{\text{in}}$	0.048	0.067	0.078	0.11



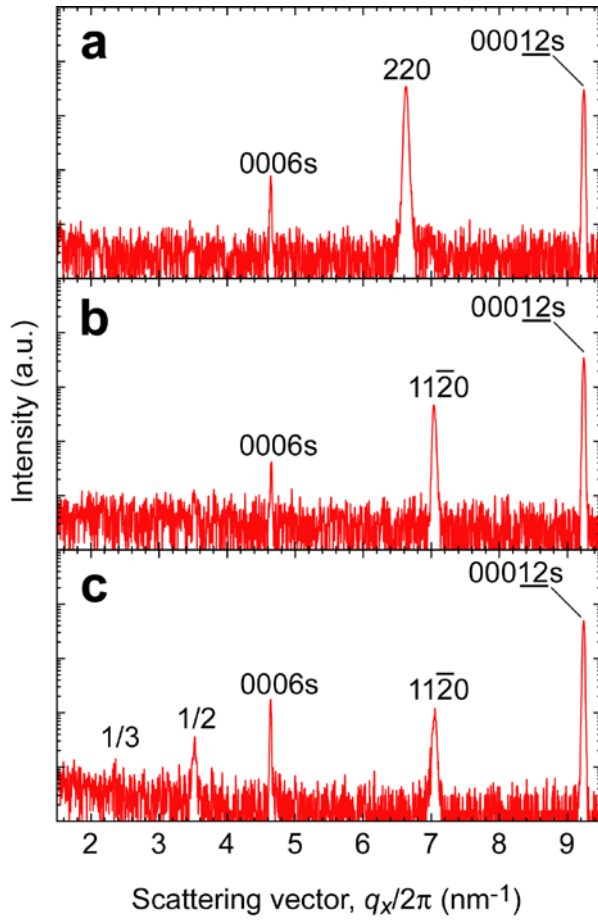
**Figure S1.** Typical thermo-electromotive force ( $\Delta V$ ) vs. temperature difference ( $\Delta T$ ) plot of the resultant  $\text{Ba}_{0.27}\text{CoO}_2$  epitaxial film at room temperature. The thermopower ( $S$ ) was calculated to be  $+72 \mu\text{V K}^{-1}$  as the linear slope of the  $\Delta T - \Delta V$  plot. The coefficient of determination ( $R^2$ ) was 0.999.



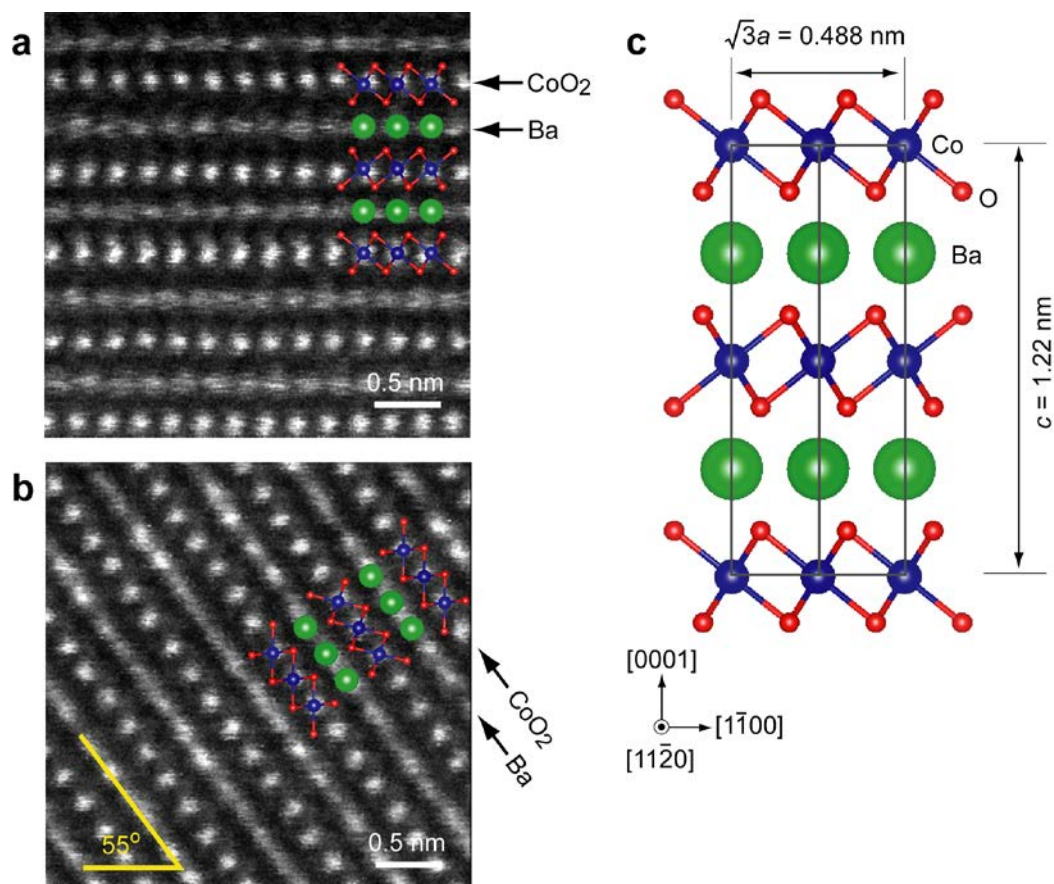
**Figure S2.** Average crystal tilting of the resultant films in the out-of-plane direction. Out-of-plane X-ray rocking curves of (a) 111 CoO after step 1, (b) 0002 Na<sub>0.75</sub>CoO<sub>2</sub> after step 2, and (c) 0002 Ba<sub>1/3</sub>CoO<sub>2</sub> after step 3. The full-width at half maximum (FWHM) values are (a)  $\sim 0.02^\circ$ , (b)  $\sim 0.6^\circ$  and (c)  $\sim 0.8^\circ$ , respectively. Since the topographic AFM images of these films [Figs. 3(d)–(f)] show grain growth tendency, the increasing tendency of the FWHM values reflects the warp of the films, not mosaicity.



**Figure S3.** Change in the in-plane XRD pattern of the resultant films on (0001)  $\alpha\text{-Al}_2\text{O}_3$  substrate. (a) After step 1 (CoO), (b) after step 2 ( $\text{Na}_{0.75}\text{CoO}_2$ ), and (c) after step 3 ( $\text{Ba}_{1/3}\text{CoO}_2$ ). The epitaxial relationship of (a) is  $(111)[110]$  CoO  $\parallel$   $(0001)[1-100]$   $\alpha\text{-Al}_2\text{O}_3$ , (b) is  $(0001)[1-120]$   $\text{Na}_{0.75}\text{CoO}_2$   $\parallel$   $(0001)[1-100]$   $\alpha\text{-Al}_2\text{O}_3$ , and (c) is  $(0001)[1-120]$   $\text{Ba}_{1/3}\text{CoO}_2$   $\parallel$   $(0001)[1-100]$   $\alpha\text{-Al}_2\text{O}_3$ , respectively. Several diffraction peaks due to sublattices of Na ( $1/2$  and  $7/13$ ) and Ba ( $1/3$ ,  $1/2$ , and  $2/3$ ) are clearly seen in (b) and (c).

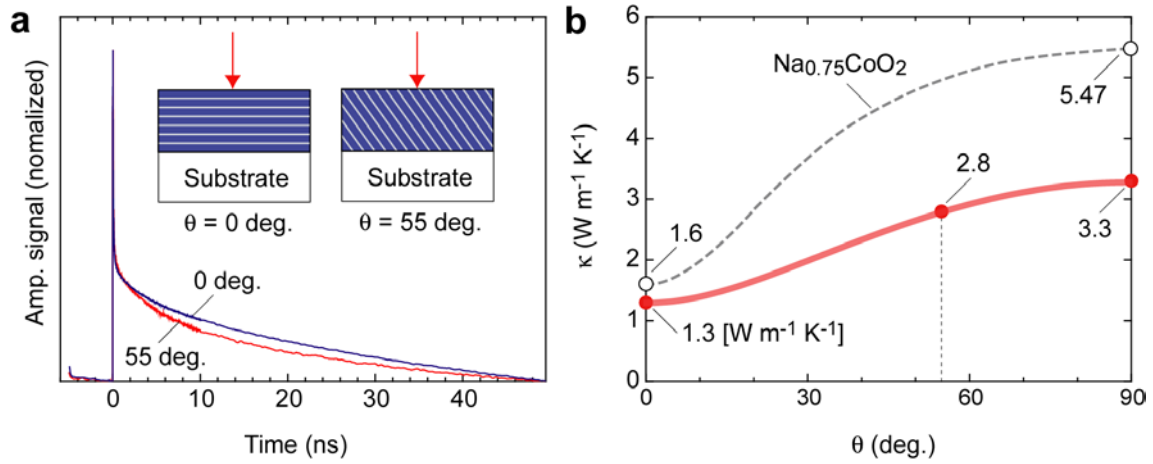


**Figure S4.** Change in the in-plane XRD pattern of the resultant films on (1-100)  $\alpha$ - $\text{Al}_2\text{O}_3$  substrate. (a) After step 1 (CoO), (b) after step 2 ( $\text{Na}_{0.75}\text{CoO}_2$ ), and (c) after step 3 ( $\text{Ba}_{1/3}\text{CoO}_2$ ). The epitaxial relationship of (a) is  $[110] \text{CoO} \parallel [0001] \alpha\text{-Al}_2\text{O}_3$ , (b) is  $[1-120] \text{Na}_{0.75}\text{CoO}_2 \parallel [0001] \alpha\text{-Al}_2\text{O}_3$ , and (c) is  $[1-120] \text{Ba}_{1/3}\text{CoO}_2 \parallel [0001] \alpha\text{-Al}_2\text{O}_3$ , respectively. Several diffraction peaks due to sublattices of Ba (1/3 and 1/2) are clearly seen in (c).



**Figure S5.** The atomic arrangement of the  $\text{Ba}_{0.27}\text{CoO}_2$  films. The magnified HAADF-STEM image of the film grown on (a) (0001)  $\alpha$ - $\text{Al}_2\text{O}_3$  substrate and (b) (1-100)  $\alpha$ - $\text{Al}_2\text{O}_3$  substrate. The schematic crystal structure of  $\text{Ba}_{1/3}\text{CoO}_2$  (c) is superimposed in the STEM images. The Ba and  $\text{CoO}_2$  layers are stacked parallel to the (0001) substrate surface whereas Ba and  $\text{CoO}_2$  layers are inclined  $55^\circ$  to the (1-100) substrate surface.





**Figure S6.** Thermal conductivity of the Ba<sub>0.27</sub>CoO<sub>2</sub> epitaxial films at room temperature. (a) Decay curves of TDTR signal. The 55° inclined film shows faster decay. (b) Thermal conductivity of the Ba<sub>0.27</sub>CoO<sub>2</sub> epitaxial films. The observed thermal conductivity of the *c*-axis oriented Ba<sub>0.27</sub>CoO<sub>2</sub> epitaxial film ( $\theta = 0^\circ$ ) was 1.3 W m<sup>-1</sup> K<sup>-1</sup> and that of the 55° inclined film was 2.8 W m<sup>-1</sup> K<sup>-1</sup>. The thermal conductivity along the CoO<sub>2</sub> layer ( $\theta = 90^\circ$ ) was obtained theoretically using these values.