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

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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 (κ_{electron}) was estimated by assuming the Wiedemann-Franz law ($\kappa_{\text{electron}} = L \cdot \sigma \cdot T$, where the L is $2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$).

	$\text{Ca}_{1/3}\text{CoO}_2$ ¹⁹	$\text{Na}_{0.75}\text{CoO}_2$	$\text{Sr}_{1/3}\text{CoO}_2$ ²¹	$\text{Ba}_{0.27}\text{CoO}_2$
$\sigma_{\text{in}} (\text{S cm}^{-1})$	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_{in}	0.048	0.067	0.078	0.11

Figure S1. Typical thermo-electromotive force (ΔV) vs. temperature difference (ΔT) 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_{0.75}CoO₂ after step 2, and (c) 0002 Ba_{1/3}CoO₂ 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) α -Al₂O₃ substrate. (a) After step 1 (CoO), (b) after step 2 (Na_{0.75}CoO₂), and (c) after step 3 (Ba_{1/3}CoO₂). The epitaxial relationship of (a) is (111)[110] CoO $\parallel$ (0001)[1-100] α -Al₂O₃, (b) is (0001)[1-120] Na_{0.75}CoO₂ $\parallel$ (0001)[1-100] α -Al₂O₃, and (c) is (0001)[1-120] Ba_{1/3}CoO₂ $\parallel$ (0001)[1-100] α -Al₂O₃, 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 CoO_2 layers are stacked parallel to the (0001) substrate surface whereas Ba and CoO_2 layers are inclined 55° to the $(1-100)$ substrate surface.

Figure S6. Thermal conductivity of the $\text{Ba}_{0.27}\text{CoO}_2$ epitaxial films at room temperature. (a) Decay curves of TDTR signal. The 55° inclined film shows faster decay. (b) Thermal conductivity of the $\text{Ba}_{0.27}\text{CoO}_2$ epitaxial films. The observed thermal conductivity of the *c*-axis oriented $\text{Ba}_{0.27}\text{CoO}_2$ epitaxial film ($\theta = 0^\circ$) was $1.3 \text{ W m}^{-1} \text{ K}^{-1}$ and that of the 55° inclined film was $2.8 \text{ W m}^{-1} \text{ K}^{-1}$. The thermal conductivity along the CoO_2 layer ($\theta = 90^\circ$) was obtained theoretically using these values.