Supplementary information

Engineering thermoelectric and mechanical properties by nanoporosity in calcium cobaltate films from reactions of Ca(OH)₂/Co₃O₄ multilayers

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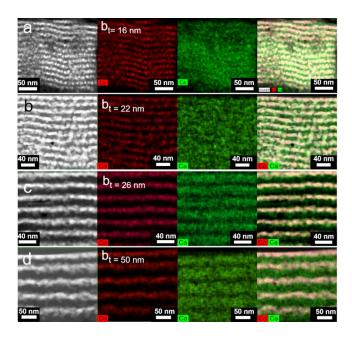


Figure S1. STEM image and EDX spectral maps of Co and Ca from as-deposited CaO/Co₃O₄ multilayer films with different Ca(OH)₂/Co₃O₄ bilayer thickness b_t formed after air-exposure for one month: (a) b_t = 15 nm, (b) b_t = 22 nm, (c) b_t = 26 nm, and (d) b_t = 50 nm.

STEM images indicate increasing interface roughness with increasing of b_t . The EDX spectral maps for $b_t = 16$ nm and 22 nm indicate distinct alternating Co-containing layers corresponding to Co₃O₄. In contrast, the Ca is distributed uniformly across the multilayers (Fig. S1a and 1b), indicating Ca diffusion. EDX spectral maps for higher b_t show distinct layers of Co and Ca (Fig. S1c and 1d), but with a greater interface waviness.

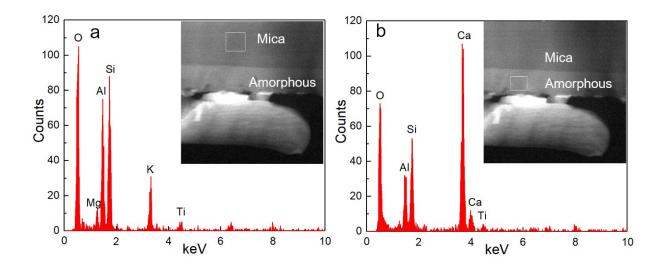
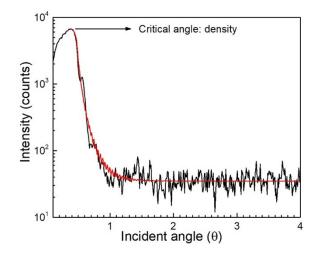


Figure S2. EDX spectra from (a) the mica substrate and (b) the interfacial amorphous layer formed during $Ca_3Co_4O_9$ thin film synthesis by annealing multilayers of $Ca(OH)_2/Co_3O_4$ specified by characteristic $Ca(OH)_2/Co_3O_4$ bilayer thickness $b_t=26$ nm. Insets show the STEM images.

EDX spectra from mica shows O, Mg, Al, Si, and K (Fig. S2a). EDX spectra from the amorphous glass layer shows O, Al, Si, and Ca (Fig. S2b), suggesting that the interfacial amorphous layer is formed by the diffusion of Ca into, and reaction with, the mica substrate.



Figre S3. X-ray reflectivity (XRR) of $Ca_3Co_4O_9$ films on sapphire as a function of incidence angle. Simulations (red) overlaid on the measured data revealed the film density (relate to the total external reflection angle) to be ~3 g cm⁻³.