Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting information for:

Cation placement control in double-perovskite $GdBaCo_2O_6$ and its impact on magnetism via spin-state modification

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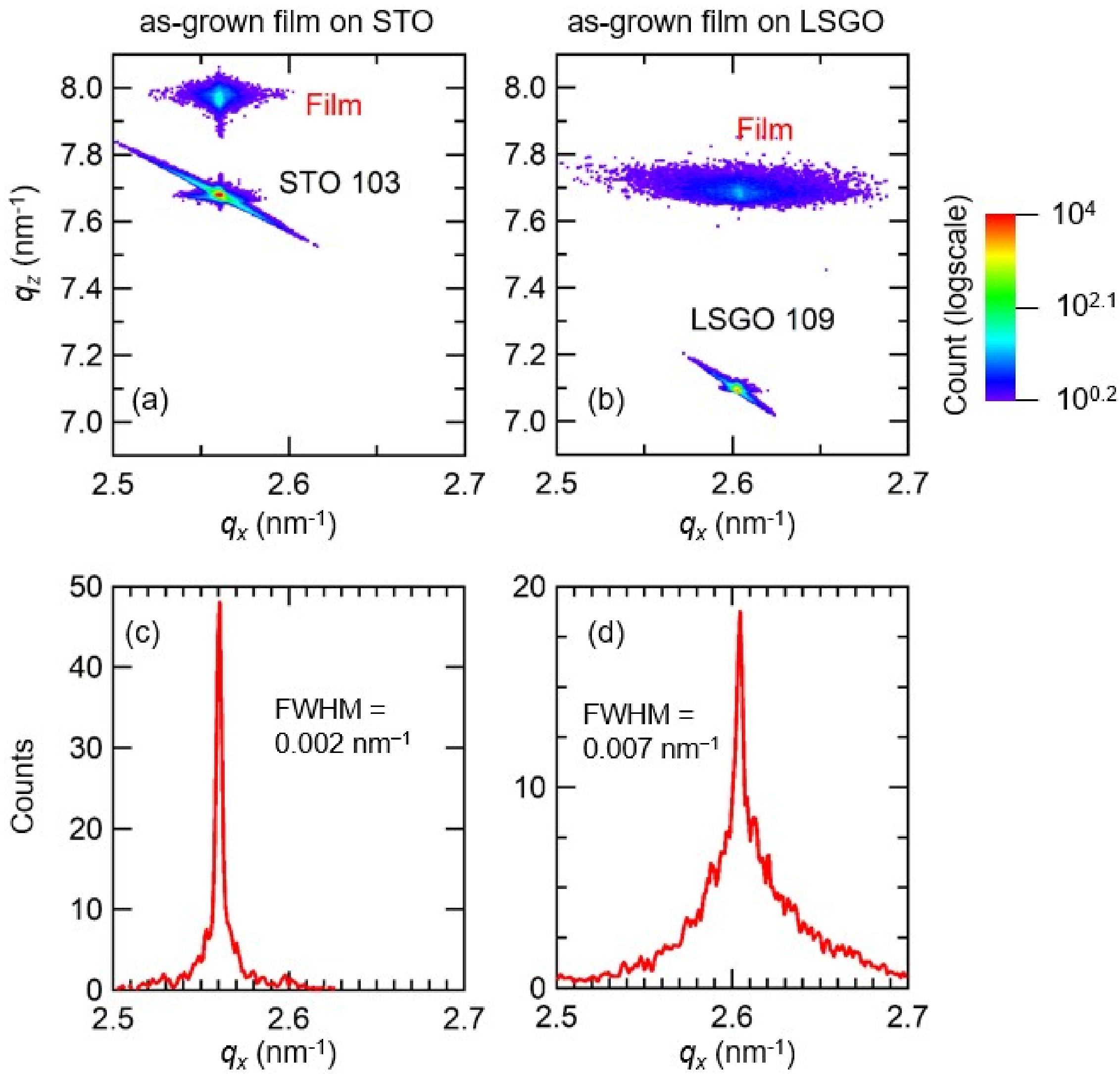

Figure S1. Reciprocal space mapping (RSM) and the q_x-direction dependence of the peak intensity of the films obtained from the RSM for the as-grown films on (a,c) STO and (b,d) LSGO substrates.

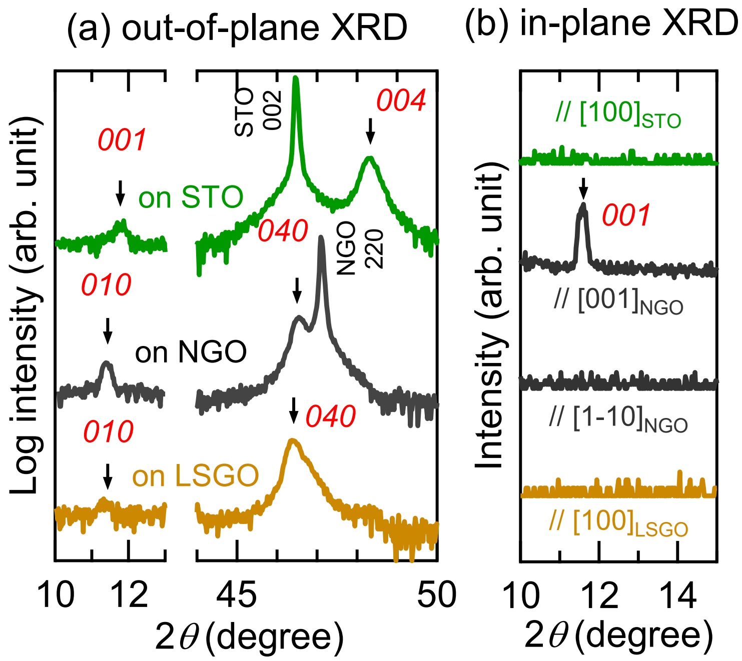

Figure S2. (a) Out-of-plane and (b) in-plane XRD $2\theta-\theta$ patterns for the $GdBaCo_2O_{5.5}$ films on the $SrTiO_3(001)$, $NdGaO_3(110)$, and $LaSrGaO_4(001)$ substrates. We also prepared $GdBaCo_2O_{5.5}$ thin films on NdGaO3(110) substrates (NGO) and conducted out-of-plane and in-plane XRD measurements using the same XRD equipment as for the other films grown on STO and LSGO. NGO has a rectangular in-plane lattice with lattice parameters of [1−10] = 7.729 Å and [001] = 7.710 Å. Because of this, the $GdBaCo_2O_{5.5}$ film exhibited an orthorhombic structure; the in-plane lattice was fixed in the $[001]_{NGO}$ direction but relaxed in the $[1-10]_{NGO}$ direction, resulting in out-of-plane (7.811 Å) and in-plane (7.729 and 7.635 Å) lattice constants. Due to these anisotropic lattice constants, the film on NGO showed both the 010 and 001 superlattice peaks in the out-of-plane and in-plane $[001]_{NGO}$ $2\theta-\theta$ patterns, respectively. On the other hand, no superlattice peak was detected in the in-plane $[1-10]_{NGO}$ pattern. Thus, when high ionic ordering exists in the films, superlattice peaks can be observed using our XRD system. However, we utilized our laboratory's XRD equipment without employing techniques such as synchrotron radiation. Therefore, while the degree of ordering is low, there is a possibility that the films still have some short-range ionic ordering.

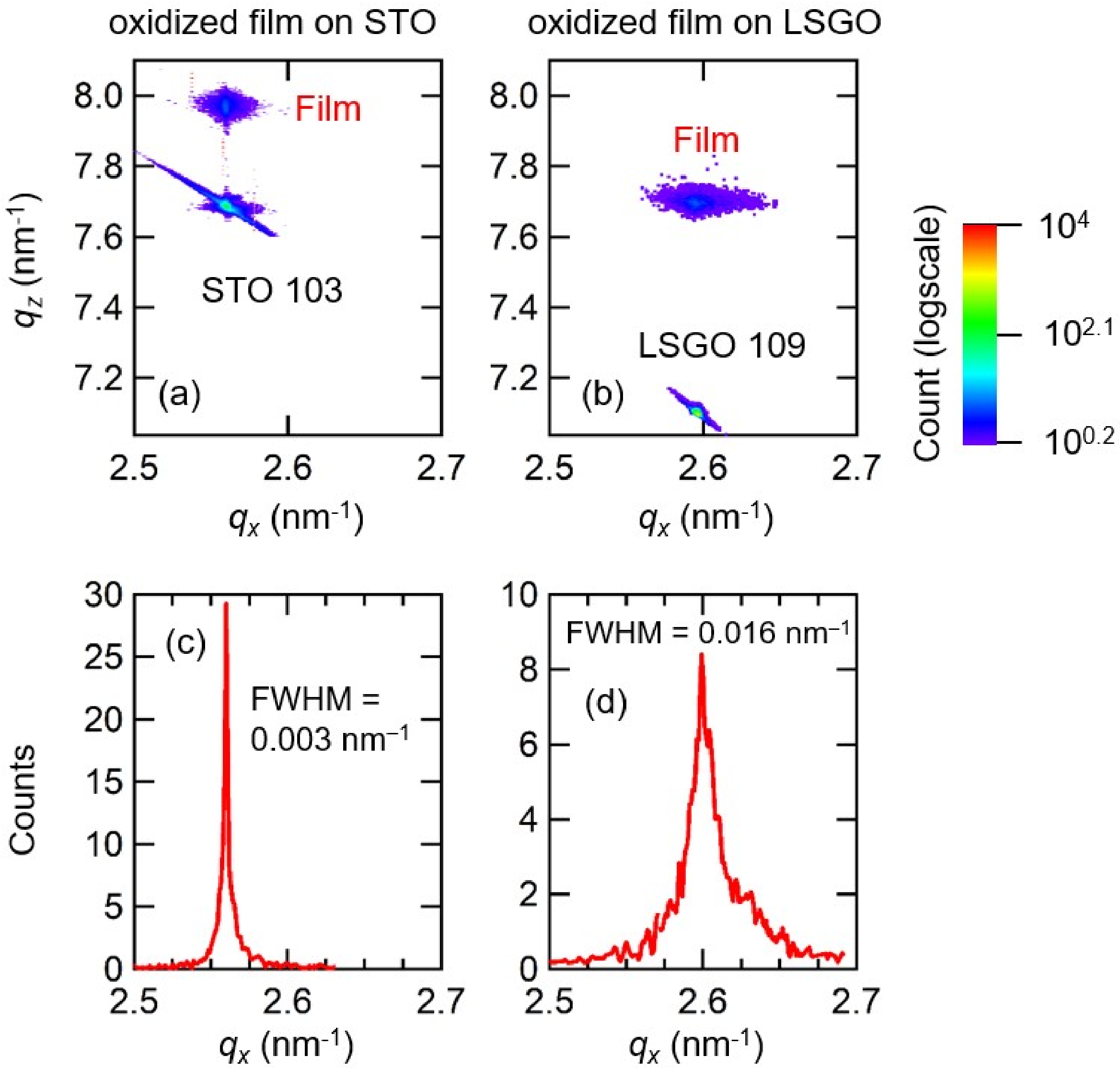

Figure S3. Reciprocal space mapping (RSM) and the q_x-direction dependence of the peak intensity of the films obtained from the RSM for the oxidized films on (a,c) STO and (b,d) LSGO substrates.

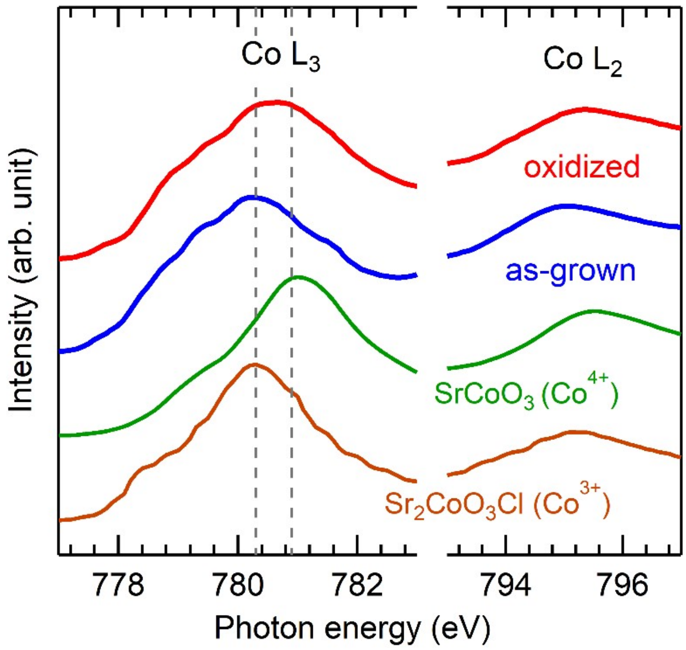

Figure S4. XAS Co *L*-edge spectra for the as-grown and oxidized $GdBaCo_2O_x$ films grown on STO substrates. The figure also includes the reference spectra of Sr_2CoO_3Cl with Co^{3+} and $SrCoO_3$ with Co^{4+} [Guillou, F. *et al.*, *Phys. Rev. B* 2013, *87*, 115114. Potze, R. H. *et al.*, *Phys. Rev. B* 1995, *51*, 11501−11506. Katayama, T. *et al.*, *Chem. Mater.* 2023, *35*, 1295.]. The photon energy of the Co L_3-edge peak for the as-grown film closely matches that of Sr_2CoO_3Cl, indicating that Co is trivalent in the as-grown film, thus confirming the chemical composition as $GdBaCo_2O_{5.5}$. Conversely, the photon energy of the Co *L*3-edge peak for the oxidized film is centered between those of Sr_2CoO_3Cl and $SrCoO_3$, suggesting a mixture of Co^{3+} and Co^{4+} in the oxidized film, and hence indicating the composition as $GdBaCo_2O_6$ with $Co^{3.5+}$. It is noted that determining Co spin states from XAS involves several challenges: (1) The XAS spectral shape depends not only on the spin state but also on the coordination environment. Since $GdBaCo_2O_6$ has distorted CoO_6 octahedra, it is difficult to compare with undistorted compounds like $LaCoO_3$. (2) Among the six possible states (Co^{3+} high-spin (HS), Co^{3+} intermediate-spin (IS), Co^{3+} low-spin (LS), Co^{4+} HS, Co^{4+} IS, and Co^{4+} LS), some reference data are still not available. Due to these reasons, it is extremely difficult to determine the spin state from XAS alone.

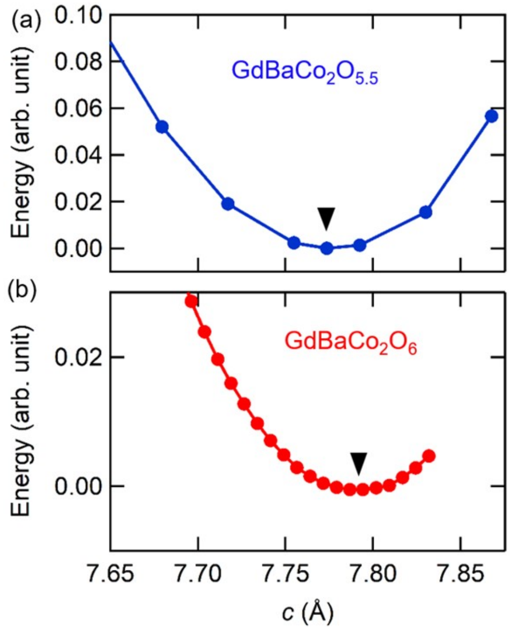

Figure S5. The relationship between the *c*-axis length and energy of $GdBaCo_2O_{5.5}$ and $GdBaCo_2O_6$. Here, the *a*- and *b*-axis lengths were fixed at 3.905 Å.

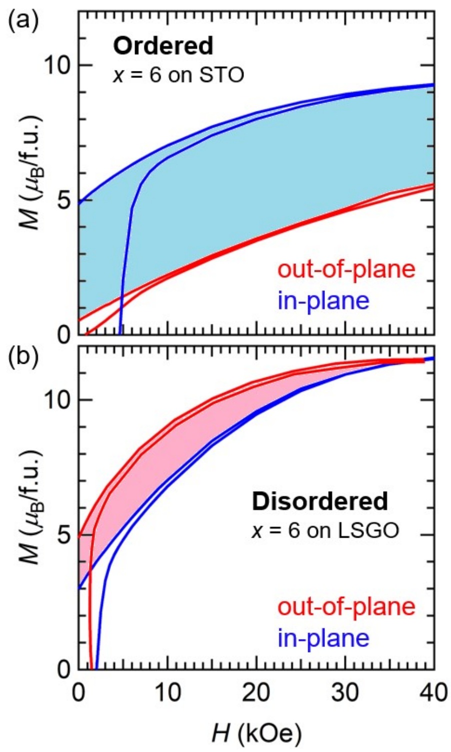

Figure S6. In-plane and out-of-plane *M*–*H* curves for the (a) A-site-ordered $x = 6$ film at 2 K and (b) A-site-disordered $x = 6$ film at 5 K.

Table S1. The intensity ratio of the 001 to 006 peak (I_{001}/I_{006}) for the as-grown and oxidized films on STO substrates, together with the simulation results.

	Experimental		Simulation from the DFT calculation results	
	As-grown film on STO	oxidized film on STO	$GdBaCo_2O_{5.5}$ film on STO	$GdBaCo_2O_6$ film on STO
I_{001}/I_{006}	74.0 %	103 %	87.6 %	176 %