

Strain engineering is an appealing route to controlling electronic [1], ferroic [2–4], and structural properties in complex oxide heterostructures [5, 6]. The sensitivity to strain arises from the strong electron-, spin-, and orbital-lattice coupling inherent to transition metal oxides [7–9]. In ABO_3 perovskites (Fig. 1a), the flexible corner-shared BO_6 octahedral network allows epitaxial strain to be accommodated by either bond-length distortions (Fig. 1b,c), and/or by changes in the magnitude and phase of the octahedral rotations (Fig. 1d,e). Previous work has demonstrated how strain-based manipulation of bond-length distortions can be used to dramatically enhance ferroelectricity [10, 11]. A less explored, yet perhaps equally productive [12, 13] strategy is the control of *bond angles* to manipulate magnetism, metal-insulator transitions, and superconductivity through tuning of superexchange pathways and electronic bandwidths. However, the current understanding of strain–bond angle relationships is limited, in part due to the experimental challenge of measuring oxygen positions in thin films [14–16]. This limited understanding of how strain alters both bond lengths and angles is a clear obstacle to engineering tailored functionalities into oxide films and heterostructures.

In perovskite oxides, octahedral rotations offset the oxygen atoms from the face-centered positions effectively doubling the pseudocubic unit cell, producing a distinctive set of half-order Bragg peaks depending on the tilt pattern [17]. The octahedra can rotate about the pseudocubic $[1\ 0\ 0]$ (a), $[0\ 1\ 0]$ (b), and/or $[0\ 0\ 1]$ (c) directions [18–20]; these rotation angles are referred to as α , β , and γ , respectively, and are depicted in Fig. 1a. To describe the phase of the octahedral rotations along each axis, we employ the Glazer notation, in which a superscript is appended to each axis to indicate whether neighboring octahedra rotate in-phase (+), out-of-phase (−) or if rotations are absent (0) [18]. In the absence of cation-site displacements, the allowed and forbidden half-order diffraction peaks are a direct fingerprint of the octahedral rotations in perovskite oxides.

While half-order peaks have been employed previously to identify crystallographic space groups of perovskite films [21], in this work we demonstrate how these Bragg peaks can be used to *quantify the octahedral rotations and bond angles* of strained perovskite oxide films. The oxygen positions, and thus the bond angles and lengths, are obtained by comparing the intensities of a systematic series of half-order Bragg peaks with the calculated structure factor of the oxygen octahedra. Combining the diffraction results with density functional calculations, we examine the evolution of the rotation angles with strain for a model functional oxide. The relative simplicity of the experimental approach, requiring only high flux x-ray