Supplementary information

to

Strain enhancement due to oxygen vacancies in perovskite oxide films

M. Tyunina[1,2*], J. Levoska[1], O. Pacherova[2], T. Kocourek[2], A. Dejneka[2]

[1]*Microelectronics Research Unit, Faculty of Information Technology and Electrical Engineering, University of Oulu, P. O. Box 4500, FI-90014 Oulu, Finland*

[2]*Institute of Physics of the Czech Academy of Sciences, Na Slovance 2, 18221 Prague, Czech Republic*

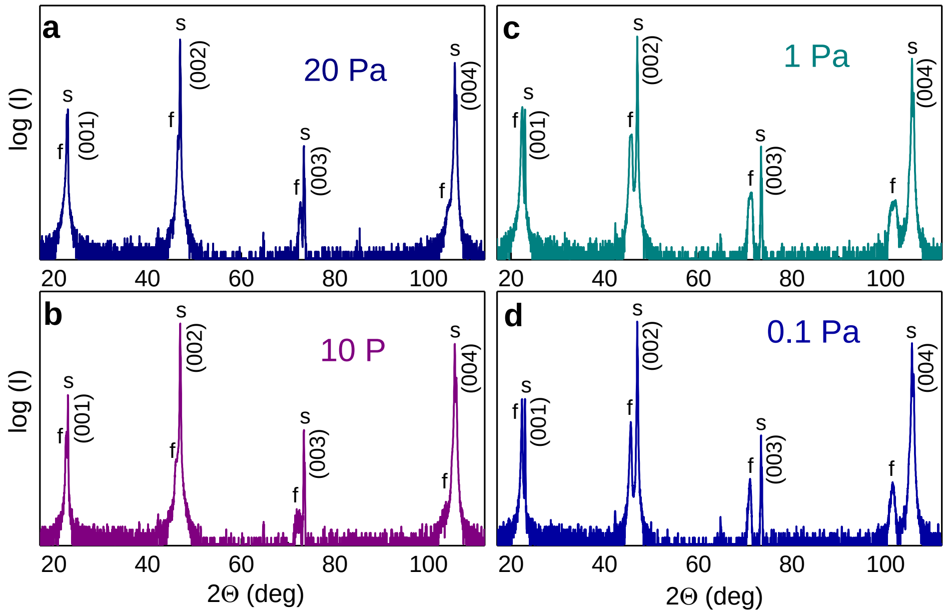

Fig. S1. XRD Θ-2Θ scans in the NNO/LSAT films. Deposition pressure is marked on the plots. The peaks from the films and substrates are marked by "f" and "s", correspondingly.

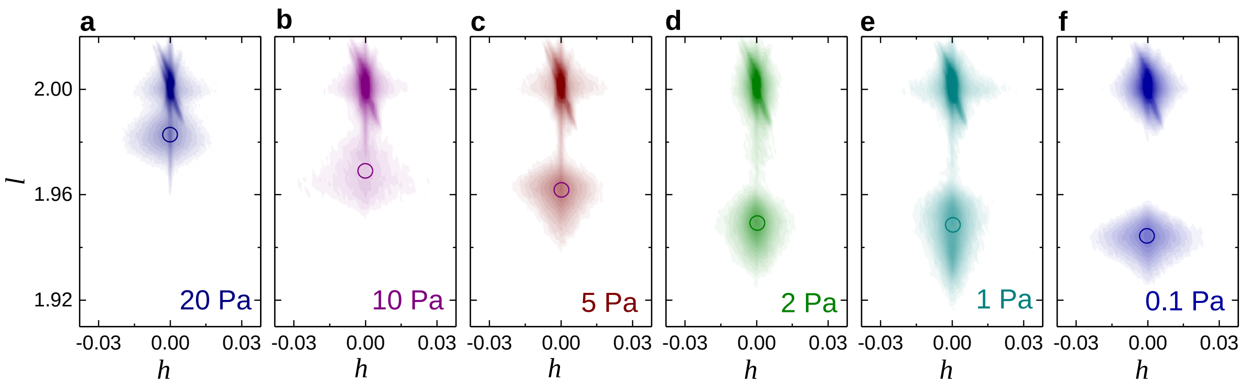

Fig. S2. Reciprocal space maps around (002) lattice points in the NNO/LSAT films deposited at different pressures of oxygen. Coordinates are expressed in reciprocal lattice units of LSAT. The peaks from the films are marked by open circles.

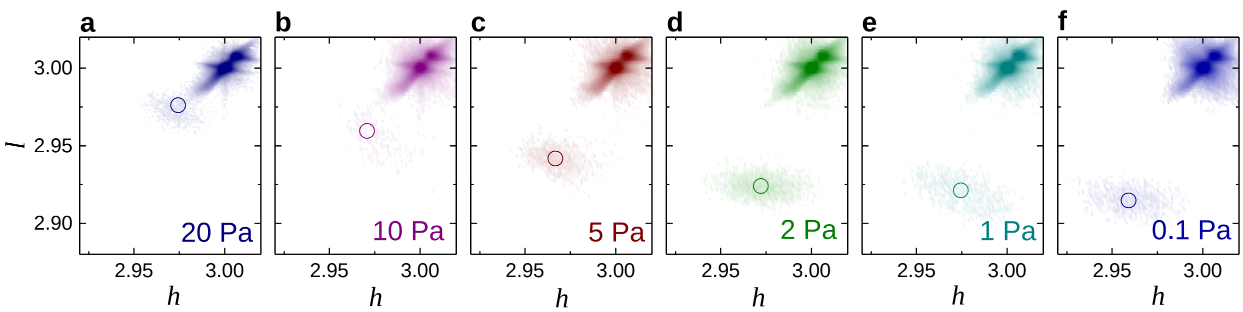

Fig. S3. Reciprocal space maps around (303) lattice points in the NNO/LSAT films deposited at different pressures of oxygen. Coordinates are expressed in reciprocal lattice units of LSAT. The peaks from the films are marked by open circles.

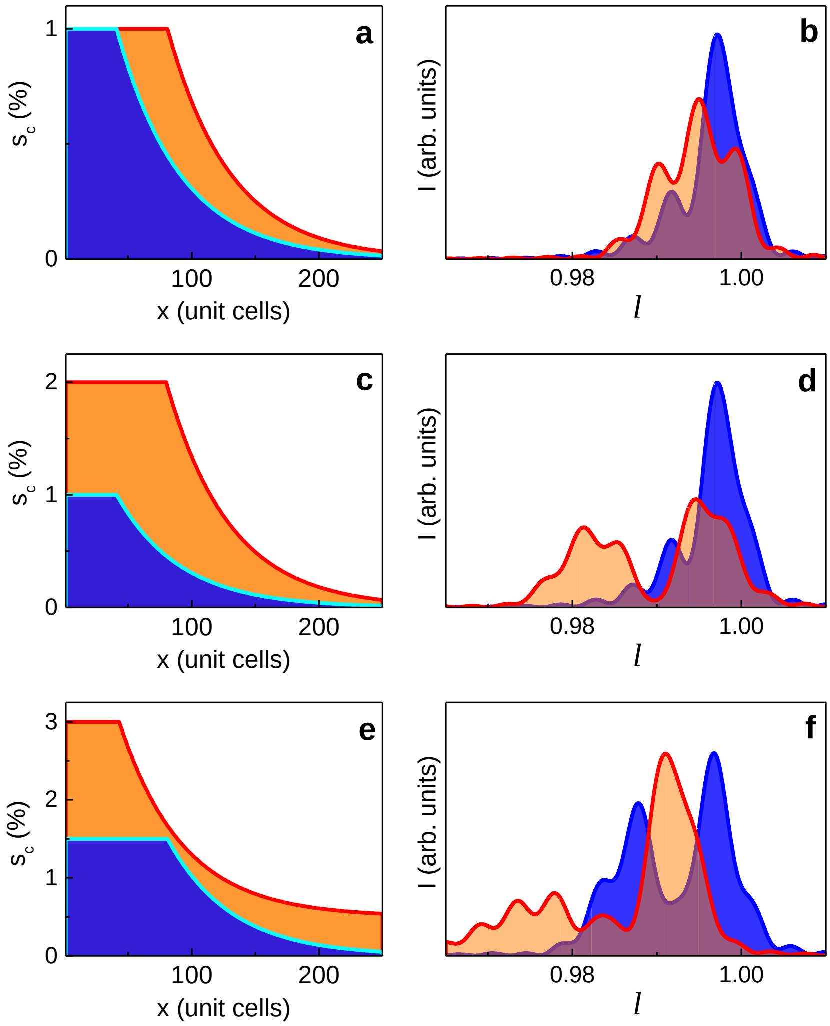

Fig. S4. (a,c,d) Assumed out-of-plane strain sc as a function of distance x from the film-substrate interface and (b,d,f) corresponding calculated XRD intensity around (001) lattice points. The intensity shown by blue (orange) color in (b) corresponds to the profiles shown by similar colors in (a). Likewise, in (d) – (c) and in (e) – (f).

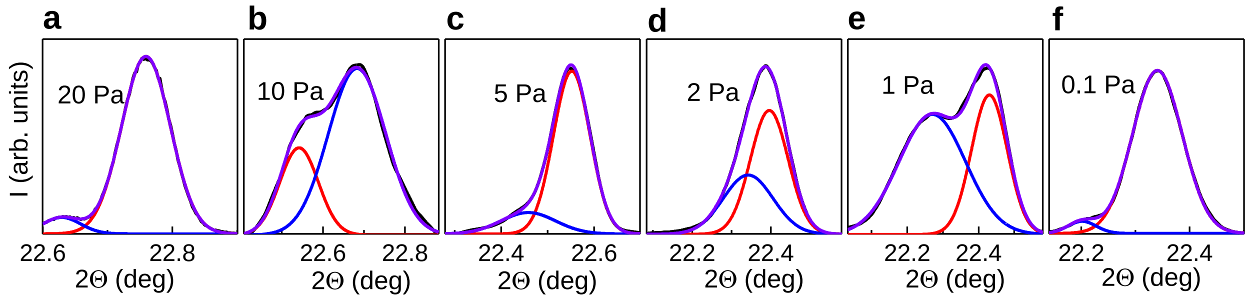

Fig. S5. XRD Θ-2Θ scans around (001) perovskite peaks in the NNO/LSAT films. Deposition pressure is marked on the plots. Measured and fitted intensity are shown by black and violet colors, respectively. Red and blue curves show fitting peaks.

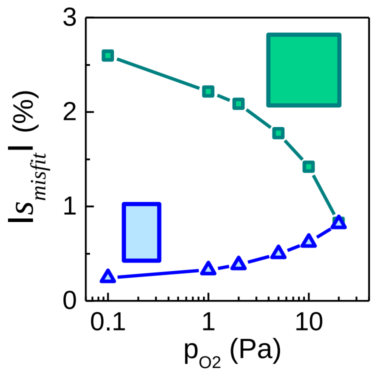

Fig. S6. Effective in-plane misfit strain as a function of oxygen pressure in the NNO/LSAT films. The upper (lower) curve corresponds to isotropic (anisotropic) chemical expansion.

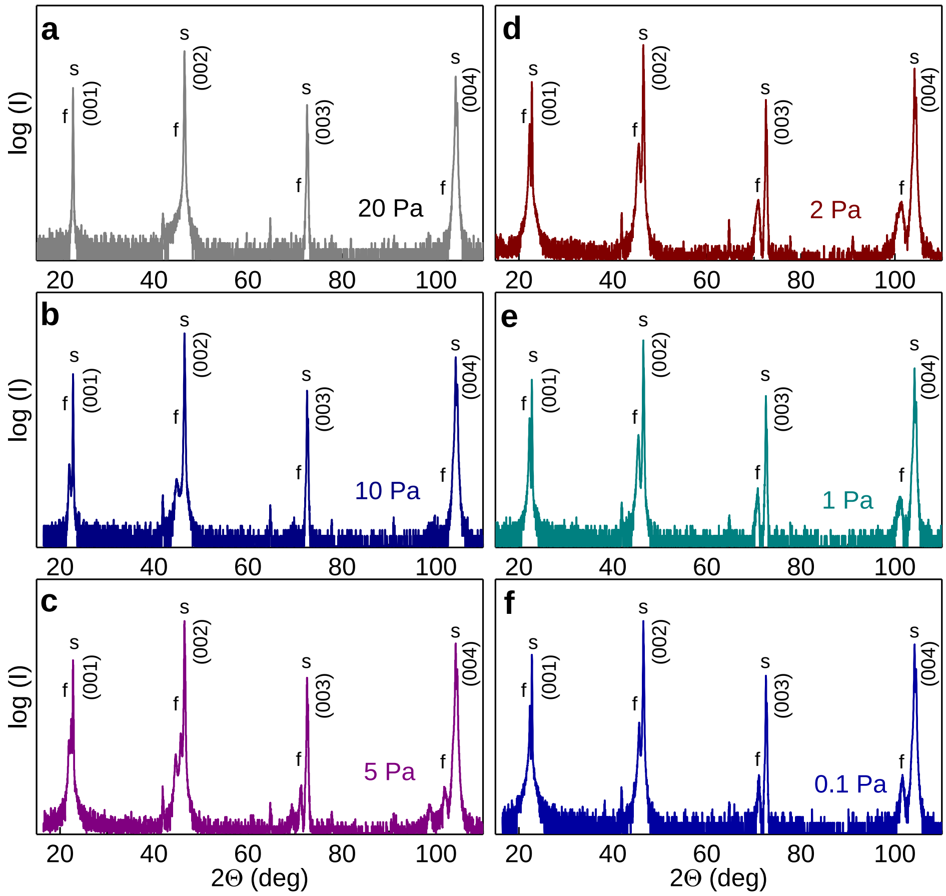

Fig. S7. XRD Θ-2Θ scans in the KNNO/STO films. Deposition pressure is marked on the plots. The peaks from the films and substrates are marked by “f” and “s”, correspondingly.

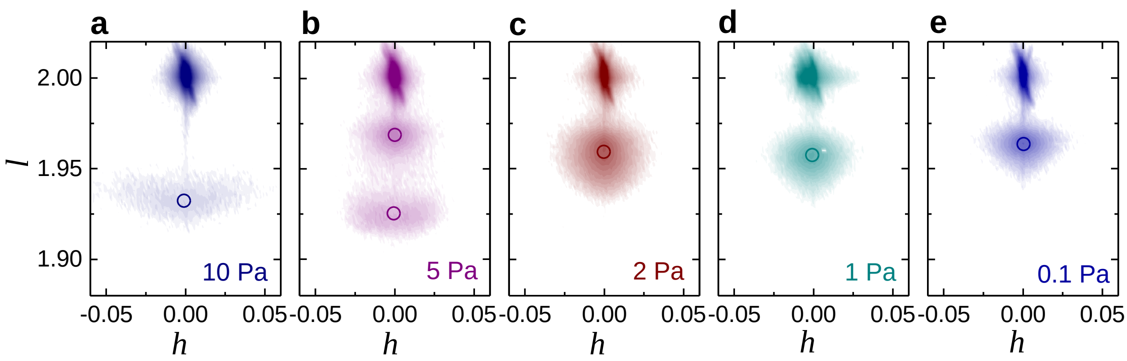

Fig. S8. Reciprocal space maps around (002) lattice points in the KNNO/STO films deposited at different pressures of oxygen. Coordinates are expressed in reciprocal lattice units of STO. The peaks from the films are marked by open circles.

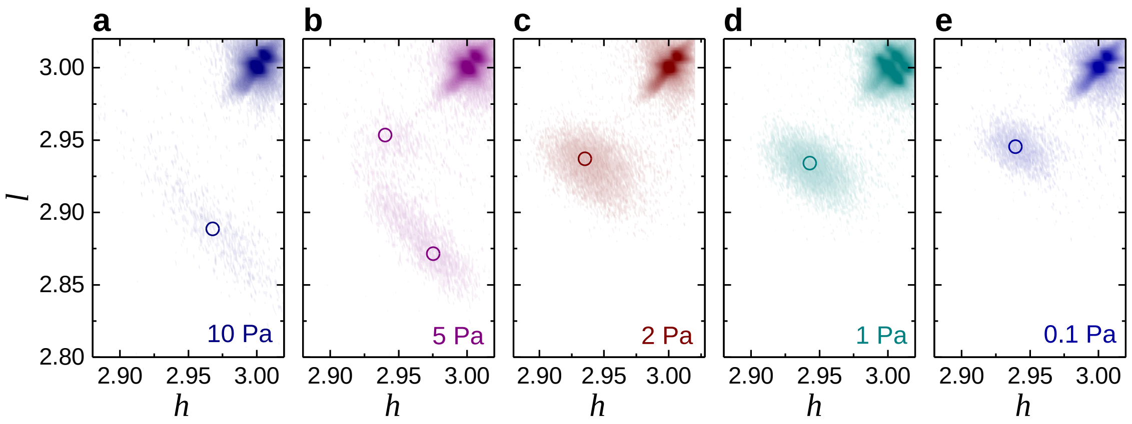

Fig. S9. Reciprocal space maps around (303) lattice points in the KNNO/STO films deposited at different pressures of oxygen. Coordinates are expressed in reciprocal lattice units of STO. The peaks from the films are marked by open circles.

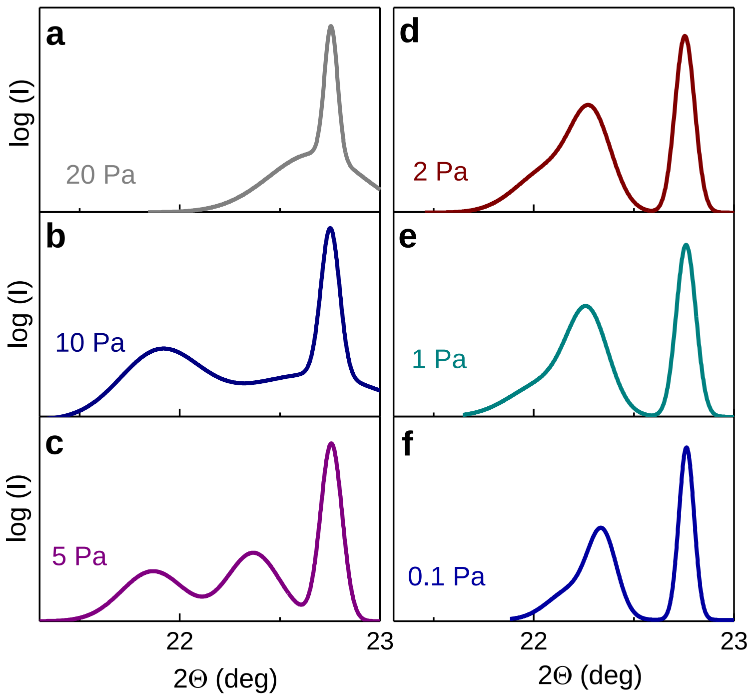

Fig. S10. XRD Θ-2Θ scans around the (001) perovskite diffractions in the KNNO/STO films deposited at different oxygen pressures. Sharp peaks are from the STO substrates.

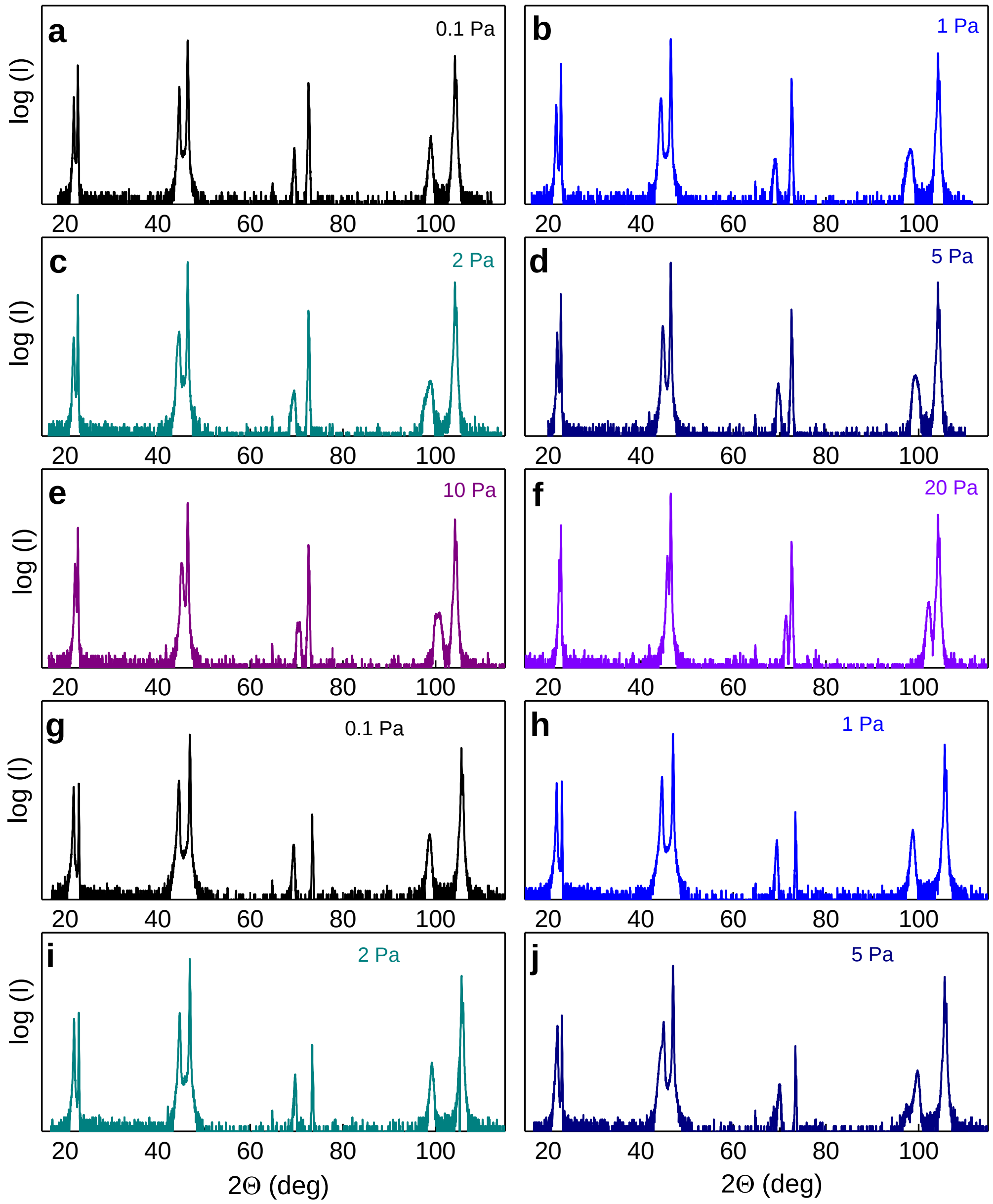

Fig. S11. XRD Θ-2Θ scans in the BSTO films on (a-f) STO and (g-j) LSAT. Deposition pressure is marked on the plots.

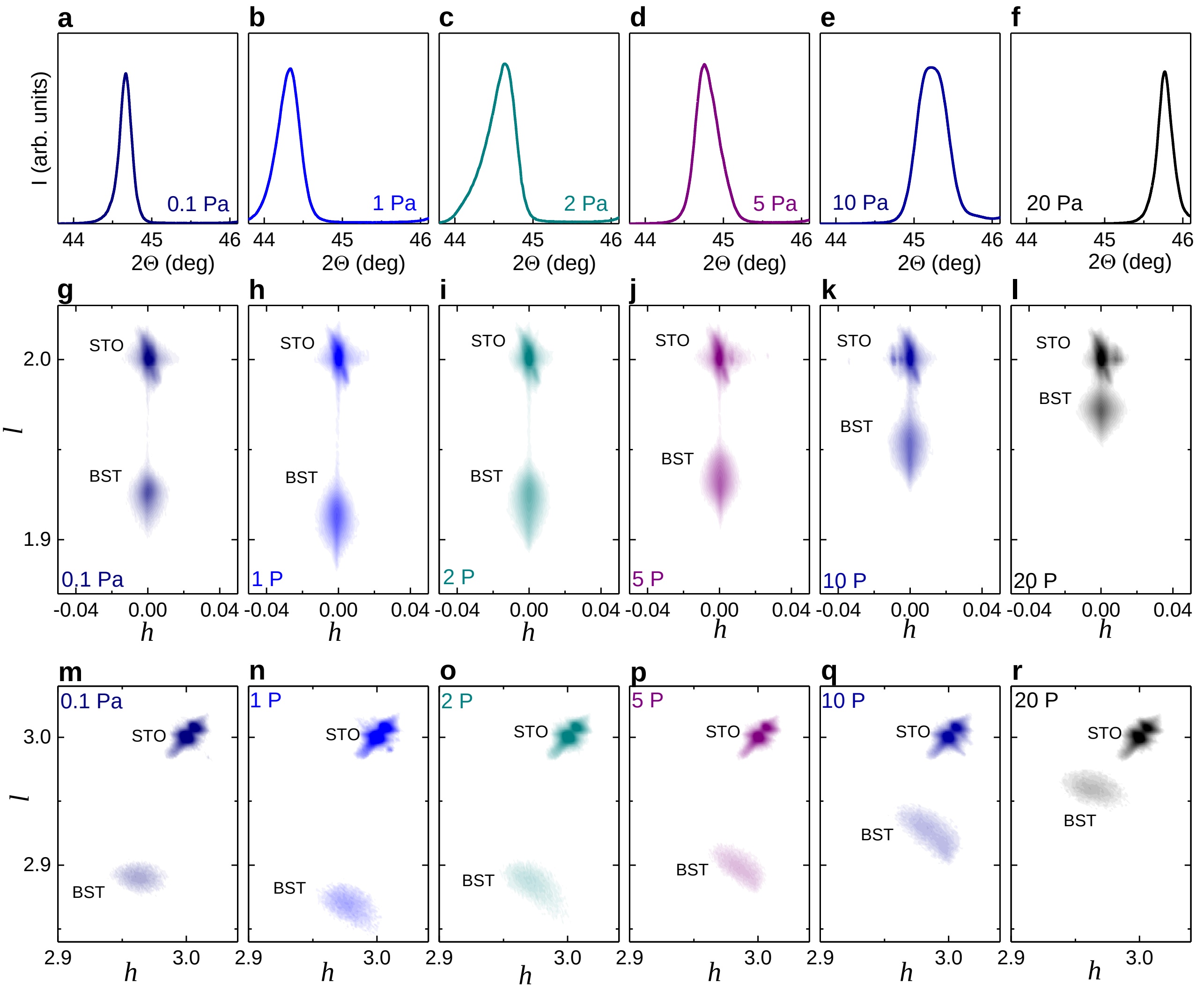

Fig. S12. XRD (a-f) Θ-2Θ scans around (002) peaks and (g-r) reciprocal space maps around (g-l) (002) and (m-r) (303) lattice points in the BSTO/STO films deposited at different pressures of oxygen. Coordinates in (g-r) are expressed in reciprocal lattice units of STO.

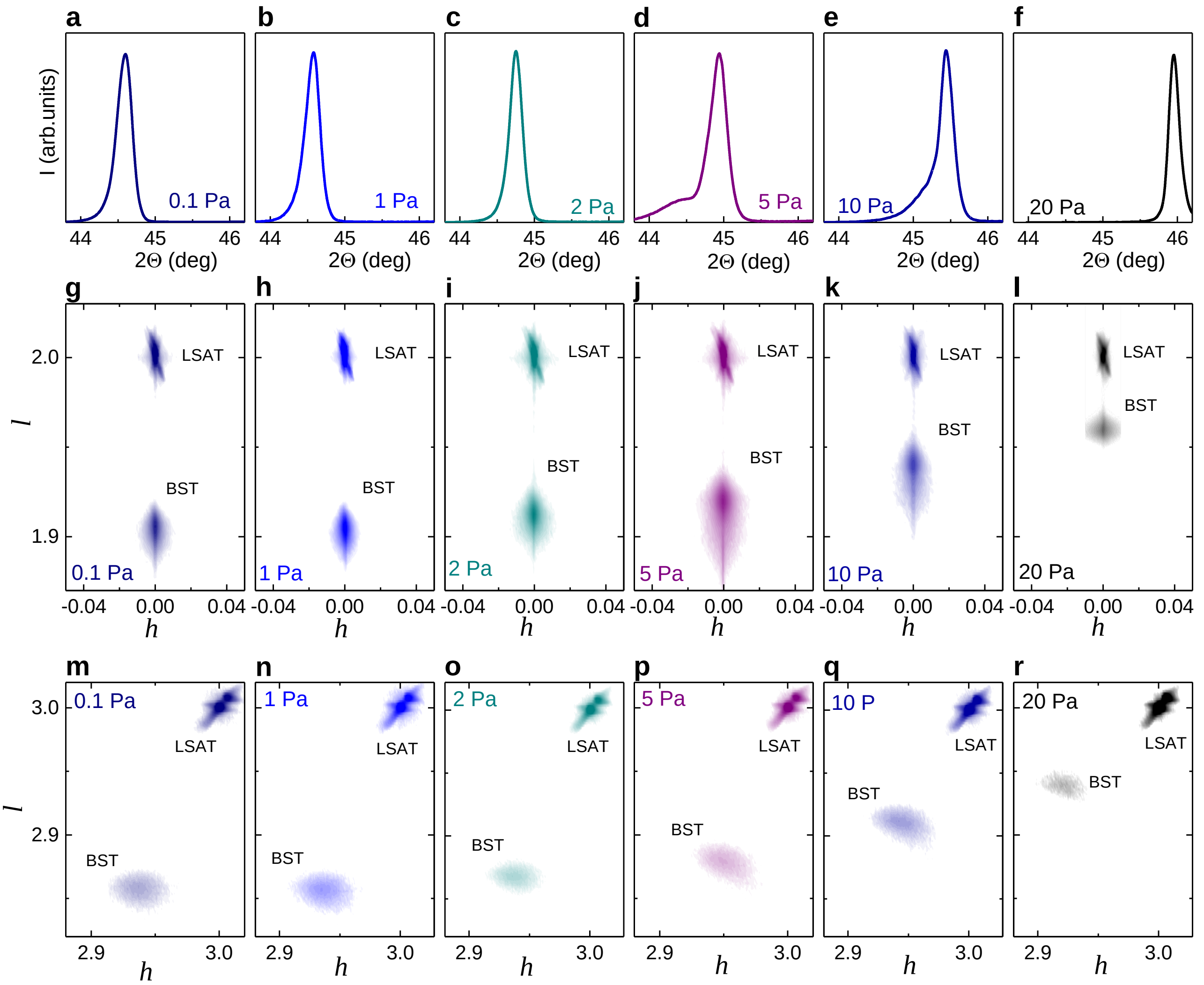

Fig. S13. XRD (a-f) Θ-2Θ scans around (002) peaks and (g-r) reciprocal space maps around (g-l) (002) and (m-r) (303) lattice points in the BSTO/LSAT films deposited at different pressures of oxygen. Coordinates in (g-r) are expressed in reciprocal lattice units of LSAT.

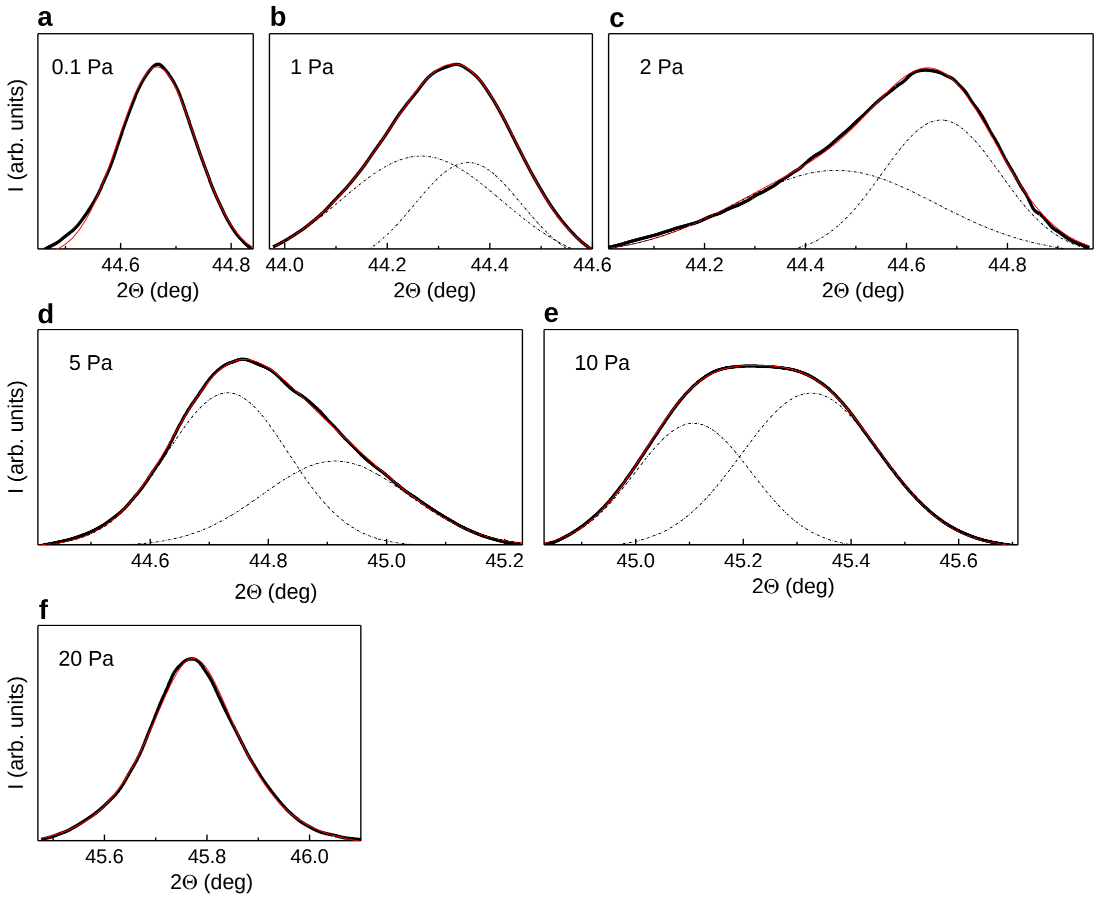

Fig. S14. XRD Θ-2Θ scans around (002) perovskite peaks in the BSTO/STO films. Deposition pressure is marked on the plots. Fits are shown by thin red curves. Dashed curves show fitting peaks.

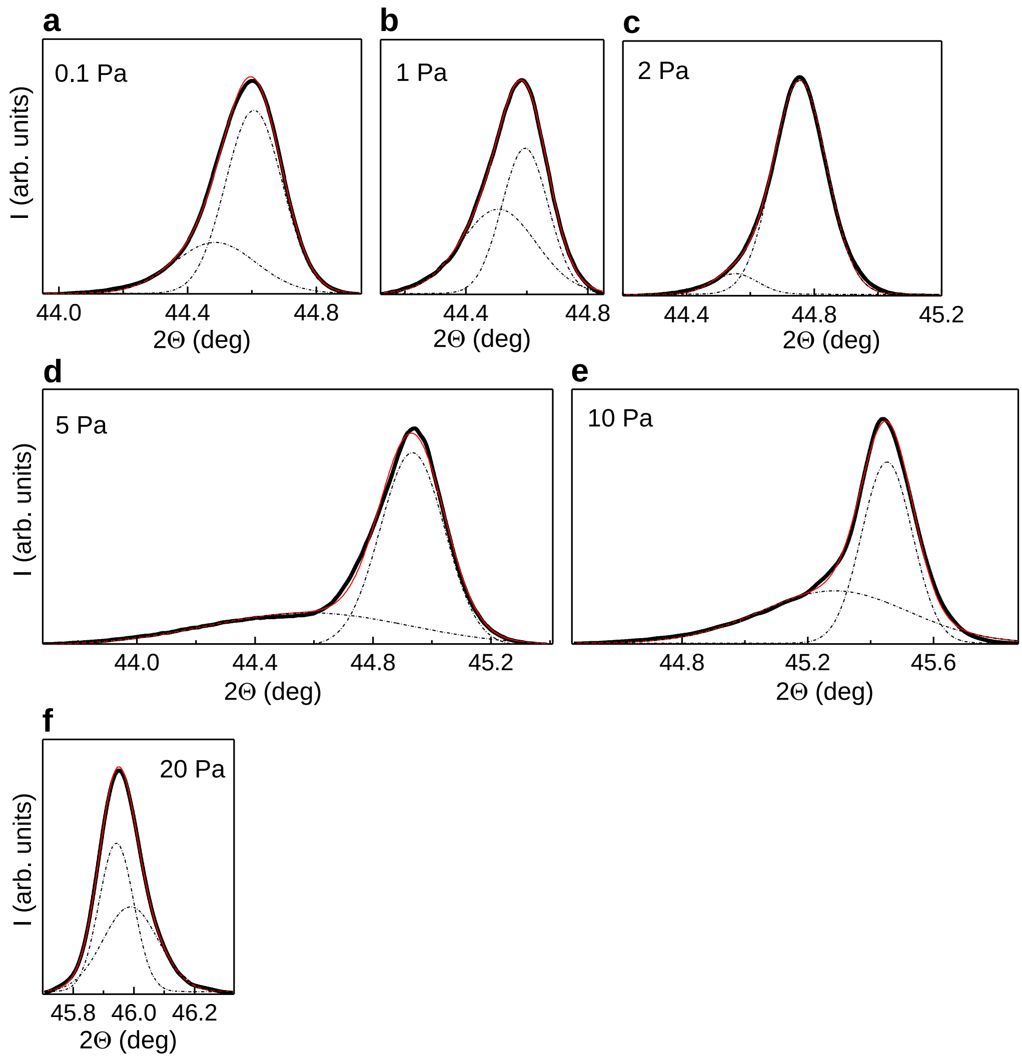

Fig. S15. XRD Θ-2Θ scans around (002) perovskite peaks in the BSTO/LSAT films. Deposition pressure is marked on the plots. Fits are shown by thin red curves. Dashed curves show fitting peaks.

Epitaxy

In epitaxial films, the observed increase of the parameter *c* and unit-cell volume *V* cannot be directly interpreted as a chemical expansion (or chemical strain) because both the chemical strain and misfit strain are present in the films. To extract the chemical strain from the measured parameters, we assumed a chemically expanded material, which is then subjected to a substrate-controlled stress for each film. We considered two cases: a conventional isotropic chemical expansion (material's cell is metrically cubic) and an unconventional specific anisotropic chemical expansion (material's cell is metrically tetragonal). Using the measured lattice parameters and epitaxial elastic relationships, we extracted the lattice parameters, chemical strain, and volumetric chemical expansion of the unstressed material as follows.

For a coherent cube-on-cube epitaxial film, the in-plane lattice parameters *a* are similar and equal to those of the underlying substrate, and the substrate-imposed stress leads to a new out-of-plane lattice parameter *c*, which differs from a_M in the material.

The theoretical material-substrate misfit strain is

$$s_a = \frac{a_{SUB}}{a_M} - 1. \tag{1}$$

The in-plane lattice parameters are similar:

$$a = b = a_{SUB} \tag{2}$$

The out-of-plane strain (s_c) and the out-of-plane lattice parameter (c) are elastically related to the in-plane strain (s_a):

$$s_c = -\frac{2c_{12}}{c_{11}} s_a \tag{3}$$

$$c = a_M(1 + s_c) = a_M\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \quad . \tag{4}$$

Here c_{11} and c_{12} are the elastic constants of the material.

The unit-cell volume *V* and tetragonality *t* of the strained film are, correspondingly:

$$V = ca^2 = a_0^3(1 + s_a)^2\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \quad , \tag{5}$$

$$t = \frac{c}{a} = \frac{\left(1 - \frac{2c_{12}}{c_{11}} s_a\right)}{(1 + s_a)} \quad . \tag{6}$$

The relationships (3-6) make it possible to determine the lattice parameter a_M of an unknown cubic material using the lattice parameters *a* and *c*, which are experimentally measured in the film made of such material. By comparing the parameter a_M with that of a prototype stoichiometric material, isotropic chemical strain (expansion) can be estimated.

To investigate anisotropic chemical expansion, it is assumed that the unit cell of a chemically expanded material, from which the film is made, is tetragonal with the lattice parameters (a_M, c_M), tetragonality (t_M), and unit-cell volume (V_M):

$$c_M = t_M a_M \tag{7}$$

$$V_M = t_M a_M^3 \tag{8}$$

The unit-cell volume in a coherent epitaxial film made of the chemically expanded material is *V* :

$$V = ca^2 = t_M a_M^3 (1 + s_a)^2\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \tag{9}$$

$$\frac{V}{V_M} = (1 + s_a)^2\left(1 - \frac{2c_{12}}{c_{11}} s_a\right) \tag{10}$$

Or in another form:

$$\left(\frac{V}{V_M} - 1\right) = \left(2 - \frac{2c_{12}}{c_{11}}\right) s_a + \left(1 - \frac{4c_{12}}{c_{11}}\right) s_a^2 - \frac{2c_{12}}{c_{11}} s_a^3 \tag{11}$$

The strain s_a can be found using expression (11) and assuming negligible changes of the chemically expanded material's unit cell volume compared to its pristine prototype. Then the tetragonality of the material is:

$$t_M = \frac{c(1+s_a)}{a\left(1-\frac{2c_{12}}{c_{11}}s_a\right)} \quad . \tag{12}$$

Consequently, the lattice parameters (a_M, c_M) of the chemically expanded material can be found from the measured lattice parameters of the film.