Strain-induced creation and switching of anion vacancy layers in perovskite oxynitrides

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Perovskite oxides can host various anion-vacancy orders, which greatly change their properties, but the order pattern is still difficult to manipulate. Separately, lattice strain between thin film oxides and a substrate induces improved functions and novel states of matter, while little attention has been paid to changes in chemical composition. Here we combine these two aspects to achieve strain-induced creation and switching of anion-vacancy patterns in perovskite films. Epitaxial SrVO₃ films are topochemically converted to anion-deficient oxynitrides by ammonia treatment, where the direction or periodicity of defect planes is altered depending on the substrate employed, unlike the known change in crystal orientation. First-principles calculations verified its biaxial strain effect. Like oxide heterostructures, the oxynitride has a superlattice of insulating and metallic blocks. Given the abundance of perovskite families, this study provides new opportunities to design superlattices by chemically modifying simple perovskite oxides with tunable anion-vacancy patterns through epitaxial lattice strain.
In oxides, the introduction of anion vacancies brings about a diversity of chemical and physical properties, the most widely being studied in perovskite oxides1–3. If the anion-vacancy concentration (δ in ABO3, δ) is a rational fraction of the oxygen stoichiometry in the unit cell, the vacancies tend to aggregate to form linear or planar defects. For example, fast oxygen diffusion in BaInO2.5 (δ = 1/2) results from oxygen-vacancy chains4. In SrFeO2 (δ = 1), (001)p defect planes of the original perovskite cell allow metal-metal bonding between square-planar Fe(II) centers, or pressure5.

Concurrently, advances in the materials science of perovskite-based systems has been amplified with the development of single-crystal (epitaxial) thin films. In particular, lattice strain through a mismatch between the underlying substrate and the deposited film is a key parameter that has been extensively studied. Strain-driven phenomena has led to charge/orbital order in La1−xSrMnO3,13 improved ferroelectricity in BaTiO3,14 multiferroicity in EuTiO3,21, and superconductivity in La1+δSr1−δCuO4 (ref. 16). Furthermore, a ferroelectric response in tense-strained SrTaO2N films is ascribed to a change in local coordination geometry17. The lattice mismatch also allows for the introduction of random oxygen vacancies18–21. Controlling vacancy ordering of perovskite oxides have also been reported22–27, but these efforts are limited to controlling crystallographic orientation of the deposited films such as Ca2Fe2O5 brownmillerite.

In this study, we show a low-temperature reaction of SrVO3 (600 °C in NH3 gas) topochimically transforming to SrVO2.2N0.6 (δ = 0.2) with regular (111)p anion-vacancy planes. This is already a surprising observation as such anion-vacancy order has never been seen in oxynitrides. The crystal and electronic structure of SrVO2.2N0.6 is mainly two-dimensional, with conducting octahedral layers separated by insulating tetrahedral layers. Most surprisingly, the same ammonia treatment of an epitaxial SrVO3 film on different substrates can change the periodicity of the (111)p plane, or can even alter the direction of anion-vacancy plane to (112)p, which is distinct from the previous efforts22–27, where the crystallographic orientation of the film is altered depending on the substrates. This observation suggests that lattice strain can be used to induce and manipulate the anion-vacancy planes and provide a controllable parameter for the development of exotic structural and electronic states in perovskite films.

**Results and discussion**

A (111)p superlattice in nitridized SrVO3. Oxynitrides (oxide-nitrides) exhibit attractive properties including visible-light responsive photocatalysis28, but the highly reducing atmosphere of high-temperature reaction with ammonia (ammonolysis) often makes it difficult to obtain the desired structures29. Anion-vacancy order, which is common in oxides, has not been reported in oxynitrides. Recently, low-temperature ammonolysis (~500 °C) using oxhydroxides has been proven to be a useful approach to access highly nitridized BaTiO3 through topochemical O/N exchange (e.g., BaTiO2.4N0.4 from BaTiO2.4H0.6)30. Subsequently, ammonolysis at moderate temperatures (~800 °C) has been shown to promote topochemical O/N exchange (EuTiO2N from EuTiO2.8H0.2)31. The present study extends these approaches to a vanadium oxynitride32. When reacted at low temperature, 300 °C, in NH3, SrVO3 is topochimically converted into a cubic perovskite SrVO2.2N0.2 (Supplementary Note 1, Supplementary Figs. 1 and 2 and Supplementary Table 1). In contrast to the titanium case, even the pristine oxide SrVO3 can be partially nitridized at 500 °C resulting in SrVO2.8N0.1, while the nitrogen content is lower than that obtained from SrVO3H at 300 °C (Supplementary Note 1 and Supplementary Fig. 1). Both oxynitrides carry tetravalent vanadium ions.

With a moderate increase in the ammonolysis temperature to 600 °C, the ex situ X-ray diffraction (XRD) patterns of SrVO3 and SrVO3H become drastically different (Fig. 1a and Supplementary Fig. 1), although the sample color remains black. Since the XRD profiles are very similar, the data for the SrVO3-derivided sample will be shown in the main body of the manuscript. The resulting structure has a rhombohedral cell (a = 5.51 Å and c = 34.3 Å), similar to that of 15R-type perovskite SrCrO2.8 (Sr5Cr5O14) with oxygen-vacancy order along (111)p.33 The topochemical nature of

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**Fig. 1** Topochemical ammonolysis of perovskite vanadate SrVO3. **a** XRD patterns of precursor SrVO3 with the cubic perovskite structure (red, top) and the one ammonolized at 600 °C (blue, middle). A simulation pattern of 15R-SrCrO2.8 (a = 5.51 Å and c = 34.5 Å)33 is shown for comparison (black, bottom). **b**. The structural change from SrVO3 (b) to 15R-SrVO2.2N0.6 (Sr5V5O11N3) with anion vacancies in every fifth (111)p layer, leading to the (ooott)t stacking sequence (c). Sr atoms are omitted for simplicity. Black lines in each structure represent the unit cell.
the reaction is verified by ammonolysis reactions of Sr$_2$V$_2$O$_7$ above 600 °C, which yielded Sr$_3$V$_2$O$_8$ as the main product (Supplementary Fig. 1c). The 15R phase decomposes under NH$_3$ above 800 °C.

Rietveld refinement to the synchrotron XRD data was carried out assuming the 15R-structure for Sr(V(ON)$_2$)$_8$, within the R $-3m$ space group (Supplementary Note 1, Supplementary Fig. 2 and Supplementary Table 2). A subsequent neutron refinement enabled us to determine the anion distribution between N and O, where the site fractional occupancies ($g$) was constrained to $g_O + g_N = 1$. This analysis concluded that the isolated tetrahedral (6c) site is fully occupied by oxygen ($g_O = 1$), while nitrogen atoms are partially populated at the 18k sites ($g_{N2} = 0.325(8)$ $\approx 1/3$ and $g_{N3} = 0.173(5) \approx 1/6$), resulting in the average chemical formula SrVO$_2.203(8)$N$_{0.597(8)}$. X-ray and neutron refinement for the SrVO$_3$-H-derived sample gave similar results, with a composition of SrVO$_2.225(5)$N$_{0.585(5)}$ (Supplementary Note 1, Supplementary Fig. 2 and Supplementary Table 3). Combustion analysis validated the total nitrogen content (Supplementary Note 1).

We thus concluded that the composition is SrVO$_2.2N_0.6$ (Sr$_{14}$V$_{14}$(O,N)$_{2.71}$). 15R-SrVO$_{2.2N_0.6}$ contains one-third of the anion vacancies in every fifth SrO$_3$ (111) planes, and the residual oxide anions in the SrO$_2$ plane are re-organized to form a double-tetrahedral layer (Fig. 1c). Bond valence sum calculation for the tetrahedral (V1) site gave a value close to 5 (+5.1), while those for the octahedral (V2, V3) sites are +3.6 and +3.8 (Supplementary Table 4). The average valence of +4.2 well agrees with the value expected from the chemical composition. This valence assignment is fully supported by $^{51}$V-NMR as shown later. The transformation of SrCO$_3$ to SrVO$_3$ is exclusively limited to increasing random oxygen vacancies despite the 15R-structure for SrV(O,N)$_{2.71}$ (Sr$_{14}$V$_{14}$(O,N)$_{2.71}$). This is natural expected that the observed (111)p to (112)p switching on LaAlO$_3$ (111) (LAO) and SrTiO$_3$ (111) (STO) substrates and 15R-SrVO$_{2.2N_0.6}$ within the SrO$_2$N layer is not seen from the diffraction study. By using the SCAN metaGGA functional, which is more accurate than the SCAN functional, we used DFT to calculate the relative energies of the two SVON layers during the ammonolysis reaction at 600 °C.

Strain-induced defect layer switching. As demonstrated above, polycrystalline 15R-SrVO$_{2.2N_0.6}$ possesses (111)$_p$ defect planes with the fivefold periodicity (namely, the 000t sequence where “o” and “t” refer to octahedral and tetrahedral layers). In order to investigate the epitaxial strain effects on oxynitrides, we fabricated an epitaxial SrVO$_3$ thin film using a (111)-oriented substrate for subsequent ammonolysis. Surprisingly, thermal treatment (NH$_3$ gas, 600 °C) of the SrVO$_3$ film on an LSAT (111) substrate resulted in the creation of new anion-defect layers. Scanning transmission electron microscopy (STEM) clearly indicated a (112)$_p$ planar defect, as shown in Fig. 4a and Supplementary Fig. 4a for high-angle annular dark field (HAADF) and annular bright-field (ABF) images. The Fourier transform data shows sevenfold satellite peaks along [112]$_p$. Based on STEM and XRD along with simulation, we constructed a monoclinic structure 7M-Sr(V(ON)$_2$)$_7$ (Sr$_{34}$V$_{34}$(O,N)$_{21.2}$) with tetrahedra and pyramids around anion defects (Supplementary Note 3, Fig. 4a, c, e, Supplementary Fig. 4 and Supplementary Tables 5 and 6), meaning that the composition is slightly different from the bulk composition of SrVO$_2.2N_0.6$. A similar (112)$_p$ planar defect has recently been reported in BaFeO$_2.33F_{0.33}$ (Ba$_3$Fe$_3$O$_7F$) powder, but with a threefold periodicity. Nuclear reaction analysis (NRA) and elastic recoil detection analysis (ERDA), respectively, gave the nitrogen content of $x = 0.8$ (2) and 0.54(3) in SrVO$_{2.271-N_x}$. Note that the oxynitride films have threefold domain structures related by 120° rotation (Supplementary Note 3 and Supplementary Fig. 4h–j).

Despite extensive research on perovskite oxides, conversion of oxygen-vacancy planes via thin film fabrication has not been previously observed. Past studies on thin films have been exclusively limited to increasing random oxygen vacancies or controlling the crystallographic orientation of known defect perovskites such as Ca$_3$Fe$_2$O$_7$ brownmillerite. Given a lattice mismatch of ~0.7% between 15R-SrVO$_{2.2N_0.6}$ and LSAT (111), it is naturally expected that the observed (111)$_p$ to (112)$_p$ switching arises as a result of the compressive biaxial strain from the substrate. For a proof-of-concept, we grew epitaxial SrVO$_3$ films on LaAlO$_3$ (111) (LAO) and SrTiO$_3$ (111) (STO) substrates and nitridized under the same condition (Supplementary Note 4). For the LAO (111) substrate with a nominal strain of ~2.3%, although the film was partially relaxed to about ~1.0%, we observed (112)$_p$ defect planes with a sevenfold superlattice (Supplementary Fig. 5), as in the case of LSAT substrate. On the contrary, when an STO (111) substrate with 0.2% tensile strain was used, we observed (111)$_p$ defect planes (Fig. 4b). These results strongly support that the vacancy-plane switching originates from substrate strain (Fig. 4g).

To rationalize the formation of 7M-Sr(V(ON)$_2$)$_7$ on LaAlO$_3$ (SVON-112) versus 15R-SrVO$_{2.2N_0.6}$ in the bulk (SVON-111), we used DFT to calculate the relative energies of the two SVON orientations at various biaxial lattice strains. For these calculations, we used the SCAN metaGGA functional, which is more accurate than the SCAN functional.
temperatures. The ordered moment is estimated to be <0.01 at 0.

The spectra of SrVO₃ and Sr₃V₂O₈ are shown for comparison. The orange and red arrows indicate the positions at which 1/

the time constant. Tetrahedral data with

represents nuclear magnetization at a time t after a saturation pulse, at the tetrahedral (orange) and octahedral (red) sites. The lines are the fit to extract the time constant. Tetrahedral data with t<100 ms were not considered due to octahedral-site contribution (see yellow arrow in a).

Further insights are garnered from observation that the oxynitride film grown on SrTiO₃ (111) exhibits sixfold superlattice reflections in TEM and XRD (Fig. 4b and Supplementary Fig. 6), implying that the defect plane appears in every six SrO₃ layer, namely, the oooott sequence (Fig. 4d), in contrast to the (ooott)₃ sequence in the bulk (Fig. 1c). This observation suggests that even small strains (0.2%) may affect the structure, offering fine and extensive tuning of not only the direction but also the periodicity (density) of anion-defect layers (Fig. 4g), which will alter the chemical and physical properties. The slightly higher SDW transition temperature of 8 K for this film (Fig. 3d) compared with the bulk (5 K) might also be related to the periodicity change.

We carried out similar reactions to the SrVO₃ with the bulk (5 K) might also be related to the periodicity change.
octahedron is deformed greatly affects the vacancy-layer formation (or not). Recent first-principles study on LaAlO3 showed epitaxial strain in the (001) and (111) planes results in distinct phases with different octahedral rotation patterns.47

The observed periodicity change may also be subject to kinetic aspects. It is shown that brownmillerite CaFeO2.5 films with tetrahedral/octahedral layers stacked parallel and perpendicular to a substrate display distinct reactivities with anisotropic oxygen diffusions.25 Upon the reduction of CaFeO2.5 films to CaFeO2, oxide anions are prone to migrate perpendicular to the substrate. Our oxynitride films on STO (111) are overall epitaxial but the superlattice is slightly corrugated (Fig. 4b) unlike films with (112)p defect planes (Fig. 4a). Such corrugation might arise from faster oxygen extraction and nitrogen insertion perpendicular to the substrate and also be a cause for the elongated periodicity from five- to sixfold. If this is the case, the reaction temperature and time could also be parameters to tune anion-vacancy order patterns. It would be of further interest to see if the film thickness also plays a role in the resulting lattice periodicity/structure.

In the last two decades, there has been tremendous progress in the study of artificial perovskite superlattice of at least two sets of perovskite compositions (SrTiO3/LaAlO3, LaMnO3/SrMnO3, etc.), leading to the discovery of novel phenomena such as superconductivity and quantum Hall effects in 2DEG48–51.
the abundance of perovskite oxides forming linear and planar anion defects, it is clear that the present study offers exciting new opportunities to design perovskite superlattices by chemically modifying simple 3D perovskite oxides with controllable anion-vacancy planes through the lattice strain in order to obtain unique properties and phases such as 2DEG. Furthermore, in an even broader perspective not just limited to oxides, the vacancy engineering we demonstrated here might also be utilized for phonon control and to strongly modify thermal transport properties given less controlled approaches to yield record thermoelectric performance in commercial materials such as $\text{Ba}_2\text{Sr}_x\text{TiO}_3$ and PbSe$_{2/3}$.

**Methods**

**Preparation of powder samples.** $\text{Sr}_2\text{V}_2\text{O}_7$ was prepared by solid state reactions. Stoichiometric mixtures of $\text{SrCO}_3$ (99.99% High Purity Chemicals) and $\text{V}_2\text{O}_5$ (99.99%; Rare Metallic) were ground, pelletized, and preheated at 900 °C in air for 48 h with intermediate grindings. $\text{Sr}_2\text{V}_2\text{O}_7$ was obtained by annealing the $\text{Sr}_2\text{V}_2\text{O}_7$ pellet at 900 °C in flowing $\text{H}_2$–Ar (10:90 vol%) gas at a rate of 100 ml min$^{-1}$ for 24 h. $\text{Sr}_2\text{V}_2\text{O}_7$ was prepared by a topochemical reaction of $\text{SrVO}_3$ with CaH$_2$ (99.99%; Sigma-Aldrich) as described elsewhere. Ammonolysis reactions were performed for $\text{Sr}_2\text{V}_2\text{O}_7$, $\text{SrVO}_3$, and $\text{SrVO}_2\text{H}$; the powder samples on a platinum boat were placed in a tubular furnace (inside diameter of 26 mm) and were reacted under $\text{NH}_3$ flow (200 ml min$^{-1}$) at various temperatures (300–800 °C) for 12 h, at a heating and cooling rate of 100 °C h$^{-1}$. Before reaction, the tube was purged with dry $\text{N}_2$ gas at ambient temperature to expel oxygen and moisture.

**Characterization of powder samples.** We conducted XRD measurements using a D8 ADVANCE diffractometer (Buerker AXS) with a Cu Kα radiation. The nitrogen contents of the samples after different NH$_3$ treatments were determined by the combustion method (elemental analysis) at Analytical Services, School of Pharmacy, Kyoto University. Approximately 2 mg was used for each experiment, and 3 data sets were averaged. A high-resolution synchrotron XRD experiment for the nitrided samples was performed at room temperature using the large Debye–Scherer camera with a semiconductor detector installed at the beamline BL02B2 (JASRI, SPring-8). Incident beams from a bending magnet were monochromatized to $\lambda = 0.42073(1)$ and 0.78086(2) Å for the $\text{Sr}_2\text{V}_2\text{O}_7$ samples after NH$_3$ treatment at 300 and 600 °C, respectively. Finely ground powder samples were sieved and then a sample with a specific size and shape was packed into Pyrex capillaries with an inner diameter of 0.2 mm, which were then sealed. The sealed capillaries were rotated during measurements to improve randomization of the individual crystallite orientations. Powder neutron diffraction data were collected at room temperature using the high-resolution powder diffractometer BT-1 ($\lambda = 1.54060$ Å) at the NIST iMATERIA, and NOVA at the Japan Proton Accelerator Research Complex (J-PARC). The collected synchrotron and neutron profiles were analyzed by the Rietveld method using Rietan-FP program (SPring-8 and NIST) and Fullprof program (J-PARC).

**Preparation of thin film samples.** Epitaxial $\text{SrVO}_3$ thin films with a thickness of 100 nm were deposited on single crystalline substrates of $\text{SrTiO}_3$ (111), (LaAlO)$_3$ (SrAl$_2$Ta$_2$O$_9$), (LSAT) (111), LaAlO$_3$ (111), (LSAT) (100), and LaAlO$_3$ (100), using the pulsed laser deposition technique. We used a KrF excimer laser at $\lambda = 248$ nm, with a deposition rate of 2 Hz and an energy of ~2 J cm$^{-2}$. The substrate temperature was kept at 950 °C during the deposition, with an oxygen flow rate, and biaxial strain, are calculated using a thermodynamic grand potential, $\Phi$, as

$$\Phi_{\text{VO}_3N} = G_{\text{VO}_3N} - \mu_0\text{O} - \mu_0\text{N},$$

where the chemical potentials, $\mu_0$, of oxygen and nitrogen are determined from benchmarked nitrogen activities by Katsura; further details of this referencing is discussed in Supplementary Note 5. For both SVON (111) and (112) orientations, we first relax the unit cell until forces are converged to $10^{-6}$ eV Å$^{-1}$, and then we perform the slab transformation into (111) or (112) Miller indices and apply isotropic biaxial strain.

**DFT calculations.** Crystal structure optimization for 15R-$\text{Sr}_2\text{V}_2\text{O}_7$-$\text{N}_x$ was performed by using the PBE parameterization of the generalized gradient approximation and the projector augmented wave method (PAW) as implemented in the Vienna ab initio simulation package (VASP). In the PAW potentials used in this study, the following states are treated as core for each element: $\text{Sr}$ 3d$^{10}$ for Sr, $\text{Na}$ 3d$^{10}$ for Na, and $\text{H}$ for O and N, which is in common with the strain calculation described in the next paragraph and Supplementary Note 5. In order to obtain the electronic structure, we performed band structure calculation using the WIEN2k code and then extracted the vanadum-$d$ Wannier functions from the calculated band structures using the Wien2Wannier and Wannier90 codes. For this purpose, we also used the PBE functional. Further details of these calculations are discussed in Supplementary Note 2. For the biaxial strain calculations, ordered approximants for 7M-$\text{Sr}_2\text{V}_2\text{O}_7$-$\text{N}_{1/2}$ and 15R-$\text{Sr}_2\text{V}_2\text{O}_7$-$\text{N}_{1/2}$ were generated in pymatgen. Stability calculations were performed using VASP, with the SCAN metaGGA functional. The relative free energies of the 7M and 15R phase for a given temperature, ammonia flow rate, and biaxial strain, are calculated using a thermodynamic grand potential, $\Phi$, as

$$\Phi_{\text{VO}_3N} = G_{\text{VO}_3N} - \mu_0\text{O} - \mu_0\text{N},$$

where the chemical potentials, $\mu_0$, of oxygen and nitrogen are determined from benchmarked nitrogen activities by Katsura; further details of this referencing is discussed in Supplementary Note 5. For both SVON (111) and (112) orientations, we first relax the unit cell until forces are converged to $10^{-6}$ eV Å$^{-1}$, and then we perform the slab transformation into (111) or (112) Miller indices and apply isotropic biaxial strain.

**Data availability**

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Author contributions
T.Y. and H.K. designed the research. T.Y., N.I., T.N., and F.T. synthesized and characterization of the bulk samples. T.Y., A.C., N.I., H.T., T. Maruyama, M.N., T.N., and T. Hasegawa synthesized and characterization of the thin film samples. S.Y., T. Mori, and K. Kimoto performed STEM experiments. S.K. and K. Ishida performed NMR measurements. Y.S., Y.H., and D.S. performed ERDA. All the authors discussed the results. T.Y. and H.K. wrote the manuscript, with comments from all the authors.

Competing interests
The authors declare no competing interests.

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