Oxynitrides have been explored extensively in the past decade because of their interesting properties, such as visible-light absorption, photocatalytic activity and high dielectric permittivity. Their synthesis typically requires high-temperature NH3 treatment (800–1,300 °C) of precursors, such as oxides, but the highly reducing conditions and the low mobility of N3− species in the lattice place significant constraints on the composition and structure—and hence the properties—of the resulting oxynitrides. Here we show a topochemical route that enables the preparation of an oxynitride at low temperatures (<500 °C), using a perovskite oxyhydride as a host. The lability of H− in BaTiO3−xHx (x ≤ 0.6) allows H−/N3− exchange to occur, and yields a room-temperature ferroelectric BaTiO3−xN2x/3. This anion exchange is accompanied by a metal-to-insulator crossover via mixed O−H−N intermediates. These findings suggest that this ‘labile hydride’ strategy can be used to explore various oxynitrides, and perhaps other mixed anionic compounds.

Mixed anion compounds, such as oxycarbides, oxysulfo-carbides, oxyridates and oxytrigades, are an emerging class of materials with intriguing properties unattainable in oxides. For instance, the incorporation of nitrogen into the oxide lattice results in a narrowing of the bandgap of d0 oxides by shifting the valence-band edge upwards, because nitrogen is less electronegative than oxygen. This region is responsible for the absorption of visible light and makes it possible to use these materials as visible-light photocatalysts (TiO2−xNx, Ga2−xZnxN2O3) for water splitting, the decomposition of organic compounds and dielectrics and other electronic properties. The lower electronegativity, higher electronic polarizability and higher formal charge of nitride relative to oxide species in the lattice place significant constraints on the composition and structure of these cations against reduction during high-temperature ammonolysis (that is, highly reducing). A large number of perovskite oxynitrides with the formulae AMO2N, AMON2, AMO3−xN1+x and AMO3−xN2−x (where A is an alkaline-earth or rare-earth element, 0 ≤ x ≤ 1) have been reported. However, once A and M are chosen, the anion composition is automatically set such that total charge neutrality is satisfied, for example (La3+)(Ti4+)(O2−x)(N3−x)2, (Sr2+)(Nb5+)(O2−x)(N3−x)2 and (Ca2+)(La3+)(Ta5+)(O2−x)(N3−x)2. Although anion vacancies may be present, in reality the amount appears to be small and difficult to control. Such a constraint severely limits compositional and structural variations of oxynitrides and thus calls for alternative approaches for the synthesis.

In coordination chemistry, a complex in which ligands can undergo a rapid exchange reaction is classified as a labile complex. In this study, we attempt to extend this concept in coordination chemistry to topochemical reactions of extended solids to access a new type of oxynitride using a recently reported perovskite oxyhydride, BaTiO3−xHx (0 ≤ x ≤ 0.6). As the hydride ion (H−) possesses a smaller mass and charge (relative to O2−) and is prone to reacting with oxidizers or acids, the H− in the TiO2H or TiO2H2 octahedron is quite reactive and thus can be considered to act in a similar manner to a labile ligand. The labile nature of the H− ligand is, indeed, seen in the hydride exchangeability of BaTiO3−xHx at low temperatures; under a D2 flow at 400 °C, such that it occurs only at the surface. Although several alternative methods, such as ammonothermal synthesis and a urea-based route, are reported, these methods only yield known oxynitrides.

Among oxynitrides, the most studied are perovskite-type compounds that contain d0 transition-metal ions (M, for example, Ti4+, Zr4+, Nb5+ and Ta5+), which is largely because of the tolerance of these cations against reduction during high-temperature ammonolysis (that is, highly reducing). A large number of perovskite oxynitrides with the formulae AMO2N, AMON2, AMO3−xN1+x and AMO3−xN2−x (where A is an alkaline-earth or rare-earth element, 0 ≤ x ≤ 1) have been reported. However, once A and M are chosen, the anion composition is automatically set such that total charge neutrality is satisfied, for example (La3+)(Ti4+)(O2−x)(N3−x)2, (Sr2+)(Nb5+)(O2−x)(N3−x)2 and (Ca2+)(La3+)(Ta5+)(O2−x)(N3−x)2. Although anion vacancies may be present, in reality the amount appears to be small and difficult to control. Such a constraint severely limits compositional and structural variations of oxynitrides and thus calls for alternative approaches for the synthesis.

In coordination chemistry, a complex in which ligands can undergo a rapid exchange reaction is classified as a labile complex. In this study, we attempt to extend this concept in coordination chemistry to topochemical reactions of extended solids to access a new type of oxynitride using a recently reported perovskite oxyhydride, BaTiO3−xHx (0 ≤ x ≤ 0.6). As the hydride ion (H−) possesses a smaller mass and charge (relative to O2−) and is prone to reacting with oxidizers or acids, the H− in the TiO2H or TiO2H2 octahedron is quite reactive and thus can be considered to act in a similar manner to a labile ligand. The labile nature of the H− ligand is, indeed, seen in the hydride exchangeability of BaTiO3−xHx at low temperatures; under a D2 flow at 400 °C, such that it occurs only at the surface. Although several alternative methods, such as ammonothermal synthesis and a urea-based route, are reported, these methods only yield known oxynitrides.
BaTiO$_2.4$H$_{0.6}$ is converted completely into BaTiO$_2.4$D$_{0.6}$ (ref. 16). The present work demonstrates that the hydride thermolability in BaTiO$_{3-x}$H$_x$ allows H$^+/\text{N}_3^-$ exchange through low-temperature ammonolysis (<500 °C) to yield oxynitride BaTiO$_{3-x}$N$_{2x/3}$ via oxyhydride–nitride intermediates, as illustrated in Fig. 1. This H$^+/\text{N}_3^-$ exchange is an oxidative reaction that involves a crossover of metal-to-insulator behaviour as well as a cubic-to-tetragonal transition, and the final tetragonal product BaTiO$_{2.4}$O$_{3-x}$N$_{2x/3}$ shows ferroelectric properties at room temperature.

Results and discussion

Sample preparation and characterization. First, a powder sample of BaTiO$_{3-x}$H$_x$ with $x = 0.60$ ($a = 4.0321(1)$ Å) was synthesized by the CaH$_2$ reduction of BaTiO$_3$ (100–200 nm), as reported previously$^{16}$. The BaTiO$_{2.4}$H$_{0.60}$ powder, which contained a tiny amount of TiH$_2$ impurity (Supplementary Fig. 1 and Supplementary Table 1), was pelletized and heated at various temperatures (reaction temperature $T_R$, 375–500 °C) for three hours under flowing dry NH$_3$, and the resulting materials were characterized...
Room-temperature laboratory powder X-ray diffraction (PXRD) profiles of samples after the low-temperature ammonolysis (Supplementary Fig. 2) revealed that the cell volume decreased with increasing \( T_R \) (Fig. 2b), which implies a gradual increase in the valence of Ti. A continuous colour change from dark blue to green accompanied the reaction. As shown in Fig. 2a, the temperature dependence of the magnetic susceptibility of the sample reacted at \( T_R = 500 \text{ °C} \) (sample 1) exhibited a non-magnetic nature throughout the temperature range examined, which indicates an almost complete oxidation to Ti\(^{4+}\) (\( d^0 \)), in stark contrast to the paramagnetic behaviour of the precursor oxyhydride, which consisted of Ti\(^{4+}\) (\( d^0 \)) (ref. 16). It is rare that NH\(_3\) acts as an oxidizing agent. This unusual reaction probably arises because only the hydrides, and not the oxides, can leave or be abstracted from the lattice at low temperatures. Such oxidation reactions with NH\(_3\) or other gaseous species can be observed with Ta or Ti in reduced oxidation states, or from other systems in coordination chemistry. For example, Ti metal or TaN react with NH\(_3\) to yield Ti\(^{3+}\)N or Ta\(^{5+}\)N\(_2\), and the oxidative addition of H\(_2\) to Rh\(^{1+}\)Cl(PPh\(_3\))\(_3\) leads to Rh\(^{3+}\)ClH\(_2\)(PPh\(_3\))\(_3\).

We also performed NH\(_3\) reactions (reaction temperature \( T_R = 450–550 \text{ °C} \), three hours) with an oxyhydride of lower hydride content (BaTiO\(_2\)\(_{1.62}\)H\(_{0.38}\), \( a = 4.01411(6) \text{ Å} \) (see Supplementary Fig. 3 and Supplementary Table 1 for a structural analysis)), which also revealed the lattice expansion as a function of \( T_R \) (Supplementary Fig. 4). Measurements with a superconducting quantum interference device showed that almost all of the Ti\(^{3+}\) in the precursor was oxidized to Ti\(^{4+}\) at \( T_R = 550 \text{ °C} \). The green colour of the product comes from the low-energy photon absorption of intervalence charge transfer and implies a tiny amount of Ti\(^{3+}\).

Several chemical analyses were conducted to determine the anion composition in the terminal non-magnetic compounds (samples 1 and 2). Quadrupole mass spectroscopy (QMS) for samples 1 and 2 showed the absence of hydrogen. Elemental analysis (combustion analysis) revealed the presence of a considerable amount of nitrogen, 2.8 wt% (sample 1) and 1.3 wt% (sample 2). Furthermore, in situ QMS during the NH\(_3\) reaction exhibited no trace of H\(_2\)O. This means that the oxygen content remained the same because O\(^{2–}\) is more strongly bound to the metal centre than H\(^{–}\). Thus, nitride anions should replace only the labile hydride ions. The elemental analysis gave compositions of BaTiO\(_2\)\(_{2.40}\)N\(_{0.43}\) (sample 1) and BaTiO\(_2\)\(_{2.62}\)N\(_{0.21}\) (sample 2), with corresponding Ti valences of +4.09 and +3.87, both of which are in fairly good accordance with the non-magnetic nature.

We also found a tetragonal distortion of the unit cell in the samples (\( x = 0.60 \)) ammonolysed at \( T_R \geq 425 \text{ °C} \) (Fig. 2b). As described later, the tetragonal distortion is associated with the absence of conduction electrons in a Ti 3d\(^*\) 1g band. The room-temperature lattice constants of sample 1 (ammonolysed at 500 °C) were estimated to be \( a = 4.0057(7) \) Å and \( c = 4.0292(7) \) Å (\( c/a = 1.0059(3) \)). Similarly, the \( x = 0.38 \) samples reacted at 500 °C and 550 °C exhibited a tetragonal distortion (Supplementary Fig. 4). An in situ synchrotron PXRD study on sample 1 revealed a tetragonal-to-cubic transition at around 100–150 °C (Fig. 2c), which was accompanied by a paraelectric-to-ferroelectric phase transition, as is discussed later in the section Ferroelectricity in BaTiO\(_2\)\(_{1.62}\)N\(_{0.38}\).

Despite the low-temperature reaction, no appreciable peak broadening was seen in the PXRD and powder neutron diffraction (PND) profiles for sample 1. This indicates a compositional uniformity and we performed a Rietveld structural refinement as another verification of the anionic composition. Given the tetragonal symmetry (\( c/a > 1 \)) and the similarity in Ti\(^{3+}\) with the ferroelectric BaTiO\(_3\) (150 °C), it is natural to build a structural model on the basis of BaTiO\(_3\) (P\( 4\text{mm} \) space group), in which Ba atoms are placed at the 1a site, Ti atoms at the 1b site and O/N atoms at the 1b and 2c sites with a random distribution of the anions. An oxygen-deficient BaTiO\(_2\)\(_{1.62}\)N\(_{0.38}\) was assumed for the PXRD refinement because of the negligible X-ray scattering contrast between O and N, and the composition of BaTiO\(_2\)\(_{1.62}\)N\(_{0.38}\) was assumed for the PND refinement. The ammonolysis causes the small TiH\(_3\) impurity in the oxyhydride precursor to convert into TiN, which was included in both refinements as a secondary phase.

As shown in Fig. 3a and Table 1, the XRD refinement converged successfully, with the anion-vacancy content refined to \( \delta = 0.14(1) \) (meaning BaTiO\(_2\)\(_{2.40}\)N\(_{0.46}(1)\)). The PND refinement also converged (Fig. 3b), and the nitrogen content \( y \) was refined to 0.39(7) (BaTiO\(_2\)\(_{2.40}\)N\(_{0.38}(7)\)). Given that the terminal oxyxinitrides are non-magnetic, the composition of sample 1 should be BaTiO\(_2\)\(_{2.40}\)N\(_{0.40}\). The PXRD and PND refinements for sample 2 using the BaTiO\(_2\)-type structure (Supplementary Fig. 5 and Supplementary Table 1), respectively, gave BaTiO\(_2\)\(_{2.75}\) (meaning BaTi\(^{3.99+}\)O\(_{2.62}\)N\(_{0.25(3)}\)) and BaTi\(^{3+}\)O\(_{2.62}\)N\(_{0.24(1)}\) with the Ti valence very close to +4. Therefore, we conclude in general that the hydride lability in BaTiO\(_2\)\(_{1.62}\)H\(_4\) allows low-temperature oxidative nitridization to give the non-magnetic tetragonal phase of BaTiO\(_2\)\(_{3.9}\)N\(_{2.5}\).
Table 1 | Refined PND (PXRD) structural parameters of BaTiO2.4N0.4.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>Z</th>
<th>Occupancy</th>
<th>100Uiso (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>1a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.0 (1)</td>
<td>2.4(1)</td>
</tr>
<tr>
<td>Ti</td>
<td>1b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.48(1)</td>
<td>1.0 (1)</td>
<td>2.4(1)</td>
</tr>
<tr>
<td>O(1)</td>
<td>1b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.004(10)</td>
<td>0.8</td>
<td>0.9(6)</td>
</tr>
<tr>
<td>O(1)</td>
<td>2c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.004(10)</td>
<td>0.13(4)</td>
<td>0.9(6)</td>
</tr>
<tr>
<td>O(2)</td>
<td>2c</td>
<td>0.5</td>
<td>0.5</td>
<td>0.500(9)</td>
<td>0.8</td>
<td>0.93</td>
</tr>
</tbody>
</table>

Space group Pmnm, α = 4.0087(2) Å (4.00883(6) Å), c = 4.0223(4) Å (4.02058(10) Å), R_wP = 5.2% (3.86%), R_f = 3.78% (3.05%), R_p = 1.20 (2.7%). Supplementary Note 1 gives the definitions of R_wP, R_f, and R_p. Isotropic temperature factor. The PND and PXRD patterns are shown in Fig. 3.

However, it exists as a two-phase mixture and its nitrogen amount is much smaller. (Ba,Sr)1−yTi1−xOyNz thin films synthesized by a molecular beam epitaxy technique have a negligible amount of nitrogen (N/O ratio < 0.001)\(^{18}\). As shown below, in addition to this significant quantitative difference, our labile hydride strategy enables a versatile control of the nitrogen content by the ammonolysis temperature (and possibly reaction time) and by precursors with different hydride concentrations.

Metal-to-insulator crossover via mixed O–H–N intermediates. Oxyhydride–nitrides BaTiO3−xHxNy (where x + y + z) can also be formed at lower reaction temperatures with NH3. The amount of hydride/nitride was examined by elemental analysis and thermal desorption spectroscopy (TDS). The x = 0.6 sample at TR = 400 °C was determined to be BaTiO3−0.4H0.14N0.22. Figure 2d illustrates a correlation between the hydride and nitride concentration. As TR is increased, the N content (y) increases and the H content (z) decreases. The PXRD profiles of the intermediate oxyhydride–nitride samples (including BaTiO2.4H0.34N0.10 obtained at TR = 375 °C) consist of relatively sharp peaks (Supplementary Fig. 2), which suggests a uniform anion composition. Apparently, trivalent N\(^3\) ions are mobile even at low temperatures during the NH3 reaction. Although there are very few vacancies in BaTiO3−xHxNy (ref. 16), the vacancy amount (x + y + z in BaTiO3−xHxNy) must increase on ammonolysis, given that the final composition of BaTiO3−xHxNy has a vacancy amount of x/3 (10% in BaTiO2.4H0.3). We speculate that the reduced H\(^+\) amount, which is unfavourable for anion diffusion, is compensated by the increased vacancy amount, which is favourable for anion diffusion, and thereby helps the reaction to reach the terminal oxynitride.

A few oxynitrides, such as layered Li0.88Vb3(O0.13N0.87) and anatase TaON, are known to exhibit electric conductivity or superconductivity\(^{19,20}\), but the precise and extensive tuning of carrier concentration is rather difficult, which notably limits the extensive investigation of physical properties of oxynitrides. From the metallic and insulating behaviour in SrTiO3−xHxNy (x ≈ 0.3)\(^{21}\) and BaTiO2.4N0.4, respectively, one can expect controlled transport properties by continuous oxidative nitridization of the oxyhydride to the oxynitride via oxyhydride–nitriles. To demonstrate this, epitaxial thin films of SrTiO2.75H0.25 on a (La,Sr)(Al,Ta)O3 (LSAT) substrate were grown as described in Yajima et al.\(^{22}\) and reacted with NH3 at various temperatures up to 550 °C. The presence of nitrogen and the absence of hydrogen for the terminal film (with T_R = 550 °C) was checked, respectively, by X-ray photoemission spectroscopy (XPS) (Supplementary Fig. 6) and TDS. With increasing T_R, the electrical resistivity showed an increase by four orders of magnitude, accompanied by a drastic reduction in carrier density (Fig. 4). A semiconducting or insulating temperature dependence was seen for the films treated above 450 °C.

Ferroelectricity in BaTiO2.4N0.4. Recently, it was highlighted that AtaO2N (A = Ba, Sr) is tetragonal and has an unusual anion order that originates from a cis coordination within the TaO2N2 octahedron\(^ {23,24}\). However, this tetragonal phase is stable at much higher temperatures (up to 700 °C) and its tetragonality is not significant. The dependence of T_F on the nitrogen content (1.0069 in BaTiO3 (140 nm))\(^ {25}\), 1.0039 in BaTiO2.62N0.24 and 1.0034 in BaTiO2.4N0.4) shows that the solid-solution BaTiO3−xN2x/3 probably belongs to the same ferroelectric phase. Optical second-harmonic generation (SHG) and piezoresponse force microscopy (PFM) are powerful tools for probing non-centrosymmetry and ferroelectricity in materials. Figure 5a shows the temperature dependence of SHG intensity for a BaTiO2.4N0.4 bulk sample, measured in reflection geometry with an 800 nm fundamental beam (Tissapphire laser, 80 fs pulses, 1 kHz repetition rate). A finite SHG signal is clearly observed at room temperature, which indicates that the tetragonal BaTiO2.4N0.4 has a non-centrosymmetric structure. On heating, the SHG intensity steeply decreases and diminishes at about 150 °C, at which the...
The temperature dependence of the lattice parameters shows the tetragonal-to-cubic transition (Fig. 2c). This transition temperature is close to that of BaTiO$_3$.

To confirm the point-group symmetry of tetragonal BaTiO$_2$$_\text{.4}$N$_{0.4}$, we performed SHG polarimetry at room temperature using a thin film. The presence and composition of nitrogen in the BaTiO$_2$$_\text{.4}$N$_{0.4}$ film was checked with XPS (Supplementary Fig. 7) and TDS. Figure 5b shows the dependence of SHG intensity on the direction of polarization of the fundamental light for the BaTiO$_2$$_\text{.4}$N$_{0.4}$ thin film collected in the transmission geometry (Supplementary Fig. 8). The polar plots for both $p$ and $s$ polarizations, $I_{2\omega}^p$ and $I_{2\omega}^s$, respectively, are reproduced well by curves derived by $4mm$ symmetry with a four-fold axis perpendicular to the film, in good agreement with the PXRD results.

Figure 5c–f presents vertical (V) and lateral (L) in-phase and out-of-phase PFM scanning images for the BaTiO$_2$$_\text{.4}$N$_{0.4}$ film, taken after being electrically polarized (Supplementary Fig. 9). One can clearly see PFM signal contrasts in the region where the poling was applied.

Figure 5 | Ferroelectric properties of BaTiO$_2$$_\text{.4}$N$_{0.4}$. a, The temperature dependence of SHG intensity for the BaTiO$_2$$_\text{.4}$N$_{0.4}$ bulk sample reveals a centrosymmetric-to-non-centrosymmetric phase transition around 150 °C. b, Variation of $p$- and $s$-polarized SHG intensities, $I_{2\omega}^p$ and $I_{2\omega}^s$, for the BaTiO$_2$$_\text{.4}$N$_{0.4}$ thin film as a function of rotation angle of the electric field of the fundamental light, $\theta$, measured in the transmission set-up (Supplementary Fig. 8). The polar plots fitted well using a $4mm$ model with a four-fold axis perpendicular to the film. c–f, In-phase PFM (c), out-of-phase PFM (d), in-phase LPFM (e) and out-of-phase LPFM (f) images taken after the electric-field poling (Supplementary Fig. 9), which clearly demonstrate polarization switching. g,h, Corrected PFM (g) and LPFM (h) images obtained by poling in a different way (Supplementary Fig. 10). i,j, Averaged line profiles of the dashed rectangle areas in g and h, respectively. Also shown is the in-plane piezoelectric displacement simulated by FEM. Here the in-plane displacement is the piezoelectric displacement in the scanning direction when a tip is scanned across 180° up and down domain walls (Supplementary Fig. 11). The PFM response is contributed not by out-of-plane piezoelectric displacements, but by a buckling effect of the PFM tip. a.u., arbitrary units.
was done, which demonstrates the ferroelectric nature. We also performed PFM imaging after poling in a different way. The corrected VPFM and LPM images are shown in Fig. 5g,h. To understand the PFM patterns, piezoelectric displacements were calculated using finite-element methods (FEMs). Figure 5i,j show line profiles of the VPFM and LPM signals averaged within the dotted rectangles in Fig. 5g,h, respectively, along with the calculated piezoelectric displacements. Both the VPFM and LPM line profiles are very similar to a simulated curve for the in-plane displacement. The VPFM responses at 580 °C for five days (x = 0.38) and seven days (x = 0.5) before the hydroxide reaction accounted for the in-plane displacement rather than to the out-of-plane displacement (Supplementary Fig. 10). This is because the PFM tip used in the present experiments is sensitive to buckling, which is detected as a VPFM response.34. Thus, the PFM responses of the BaTiO3-N0.4 film, together with the SHG observation, corroborate its ferroelectricity.35.

Perspectives. A growing number of transition-metal oxyhydrides have been discovered since 2002, and especially within the past few years, namely ATO3–xHx (A = Ca, Sr, Ba)36, LaSrCoO3H0.7 (ref. 26), SrVO3H (ref. 27), Sr1+yOyZr2+Hx (n = 1, 2)28,29, SrTiO3H (ref. 30). However, most studies have focused on their synthesis and physical properties. What we show here is that the lability of the hydride makes an oxyhydride useful for a preparatory reaction. We believe that this reactivity applies to oxyhydride systems more generally, and that it should be possible to prepare, through this topochemical route, a large number of new transition-metal oxynitrides with interesting transport and magnetic properties. Such studies are in progress in our laboratory and will be reported elsewhere in due course. For example, although BaTiO3–xHx with 0.1 M NH4Cl/methanol to remove excess CaH2 and CaO and were dried at 550 °C for one day as reported31. The nitridation reaction of the BaTiO3–xHx films with NH3 gas was conducted in a sealed, evacuated Pyrex tube in a temperature range of 375–500 °C for three hours. As the NH3 gas source, a 1:1 mixture of NaNH2 and NH4Cl (40 mg) was used, which was placed separately from the film. Out-of-plane XRD and reciprocal space mapping of the oxynitride films were measured to check the epitaxy, and XPS and TDS were conducted to probe and quantify the nitrogel (Supplementary Figs 6 and 7). In XPS measurements, the N 1s peaks were observed around 396 eV, which suggests Ti–N bonding32. The nitrogen amount was determined as 2.9 wt% from TDS, which is very close to that in the bulk BaTiO3–xHx sample (2.8 wt%). The temperature dependence of electric resistivity was measured by a standard four-probe method along the in-plane direction where Au(30 nm)/Ti(5 nm) electrodes were deposited by electron-beam evaporation. The carrier density of the films was estimated from Hall measurements.33. Optical SHG was measured for BaTiO3–xHx bulk and thin-film samples using an 800 fs, 1 Hz, Ti:sapphire laser at 780 nm, 80 fs pulses, 1 kHz repetition rate. The SHG signals from the bulk sample were collected in reflection geometry between 30 and 250 °C. The SHG polarimetry measurements were performed at room temperature for the thin film on an LSAT substrate in transmission geometry. Supplementary Fig. 8 illustrates the experimental geometry in the transmission geometry. PFM measurements were performed for the BaTiO3–xHx thin film on an LSAT substrate with SrRuO3 conducting buffer layer by using atomic force microscope (AFM) system (Bruker, Dimension Icon). A chromium/gold-coated AFM tip (HQCNSC19/15-Au, MikroMasch) was utilized. The experimental geometry and poling process are shown in Supplementary Fig. 9. A background correction was done according to the methods described in Jung et al.32 and Lei et al.33 (Supplementary Fig. 12). An SEM simulation was conducted to calculate the piezoelectric displacements by using the commercial software ANSYS. A domain-structure model used in this study is illustrated in Supplementary Fig. 10. More details about the PFM simulations are described in Lei et al.34.

Received 12 June 2015; accepted 8 September 2015; published online 19 October 2015

References


ARTICLES

NATURE CHEMISTRY | VOL 7 | DECEMBER 2015 | www.nature.com/naturechemistry


Acknowledgements
This work is supported by FIRST and CREST programmes of the Japan Science and Technology Agency. H.A., S.L. and V.G. acknowledge support from the National Science Foundation grant numbers DMR-1420620 and DMR-1210588. H.A. acknowledges support from Japan Society for the Promotion of Science for Research Abroad (No. 25-185). The synchrotron radiation experiments were performed at the BL02B2 of SPring-8 with the approval of the JASRI.

Author contributions
T. Yajima and F.T. contributed equally. T. Yajima, F.T. and H.K. conceived and designed the study. F.T., K.A., M.O., W.Y. and T. Yajima performed the synthesis, laboratory PXRD, synchrotron PXRD, XPS and elemental analysis. T.Yam., C.M.B., M.A.G. and H.K. obtained the neutron data. The structural refinement was performed by K.A., T. Yamamoto and T. Yajima. W.Y. and T. Yajima fabricated the thin films. H.A., K.F., S.L., V.G. and K.T. conducted the SHG and PFM measurements and FEM simulations. All authors discussed the results. F.T. and H.K. wrote the manuscript, with contributions and feedback from all the authors, mainly T. Yajima, Y.K., H.A. and K.F.

Additional information
Supplementary information is available in the online version of the paper. Reprints and permissions information is available online at www.nature.com/reprints. Correspondence and requests for materials should be addressed to H.K.

Competing financial interests
The authors declare no competing financial interests.