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Author(s)	Masubuchi, Yuji; Koyama, Kyohei; Hosono, Akira et al.
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Average cubic BaTaO₂N crystal structure formed by 50 nm size domains with polar nano regions consisting of *cis*-TaO₄N₂ octahedral chains

Yuji Masubuchi^{*a}, *Kyohei Koyama*^b, *Akira Hosono*^{b†}, *Mikio Higuchi*^a, *Masaki Takesada*^c, *Kazuki Shitara*^d, *Hiroki Moriwake*^{d, e}, *Shinichi Kikkawa*^a

a Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan

b Graduate School of Chemical Sciences and Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan

c Graduate School of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo 060-0810, Japan

d Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 456-8587, Japan

e International Research Frontiers initiative (IRFI) MDX Research Center for Element Strategy (MDXES), Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama, 226-8503 Japan

*Corresponding Author: Yuji Masubuchi, yuji-mas@eng.hokudai.ac.jp

ABSTRACT

Non-centrosymmetric polar structure in ferroelectric BaTaO₂N having cubic perovskite-type structure was investigated both in theoretical calculation and experimental observations. Most probable coordination around Ta was confirmed to be *cis*-TaO₄N₂ in exhaustive energy calculation about O and N atomic distribution. The *cis*-TaO₄N₂ octahedra formed their local stackings during cooling of BaTaO₂N melt at 1183 K. Their linkages precipitate as nano-size units forming domains in approximately 50 nm individually having spontaneous polarization as observed in integrated differential phase contrast-scanning transmission electron microscopy. They were observed in non-centrosymmetric with polar space group *Pmc*2₁ detected in Raman spectroscopy and supported by the theoretical calculations to form nano polar regions. The polar nano regions were three-dimensionally averaged as a centrosymmetric crystal structure in cubic space group *Pm* $\bar{3}$ *m* observed in neutron diffraction. The nano regions in *Pmc*2₁ were quenched at room temperature to show their relaxor-type ferroelectricity in the average *Pm* $\bar{3}$ *m* structure.

Introduction

Mixed anion compounds with multiple anions attract attention for their unique electrical and optical properties.¹⁻⁴ Their functionality is related not only to the combination of multiple anions, but also to the arrangement of anions in the crystal structure. Metal oxynitrides containing both oxide and nitride anions are expected to have a wide variety of applications as photocatalysts, inorganic pigments, dielectrics and magnetoresistance.⁵⁻¹² Their band structure can be tuned by the combination of oxygen and nitrogen, allowing the absorption of visible light,

and leading to the development of visible light responsive photocatalyst and inorganic pigments.^{13,14} Oxynitrides are very special among mixed anion compounds because of the similarity in size and difference in electronegativity between the oxide and nitride anions. Both anions coordinate to the same cation together to form a coordination polyhedron. It is suggested that the perovskite-type oxynitrides exhibit a *cis*-type anion ordering around the d^0 transition metal at the B site to obtain chemical stability similarly to MoO_2^{2+} .¹⁵⁻¹⁸ The polar octahedra of *cis*- TaO_4N_2 were connected in several ways. They have assumed to form two kinds of -Ta-N- linkage in topologically different cubic lattice of BaTaO_2N_A and B and in tetragonal SrTaO_2N crystal structure (Fig. 1)^{15,17}. The two structures of BaTaO_2N are sensibly different and almost degenerate accidentally. Long-range order breaking was expected between them with two kinds of different -Ta-N- linkages. Switching of the linkages was expected as the boundary of 4 kinds of the sublattice which are the polar nano regions. It can induce relaxor-type ferroelectricity locally, but it has not been directly related to the long range, i.e. averaged, crystal structure.

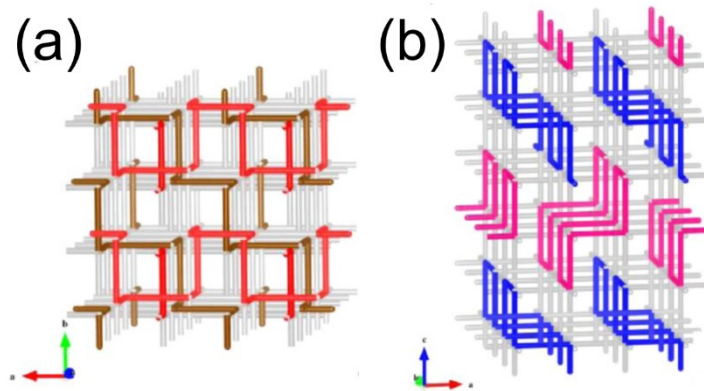


Figure 1. -Ta-N- linkages suggested for cubic BaTaO_2N structure. (a) -Ta-N- in BaTaO_2N_A and (b) in BaTaO_2N_B structure models. Red/brown lines in (a) and pink/blue lines in (b) correspond to two kinds of -Ta-N- linkages in BaTaO_2N_A and $_B$, respectively¹⁷. Straight Ta-

N-Ta bond bend 90° at each Ta atom forming Ta-N- chain motifs. Reproduced with permission from ref. 17. Copyright 2012 American Chemical Society.

Classical crystal structure analyses showed that perovskite-type oxynitrides crystallize in centrosymmetric structures with $Pm\bar{3}m$ and $I4/mcm$ space groups for $BaTaO_2N$ and $SrTaO_2N$, respectively.¹⁹⁻²² Dielectric properties of the perovskite-type oxynitrides was preliminarily studied in relation to local *cis*-type O/N ordering instead of an average crystal structure with a static O/N distribution.^{23,24} It was not clarified how the ordering is described in the whole crystal structure. It was also not clear whether the dielectric behavior was paraelectric nor relaxor-type ferroelectric behavior in the preliminary studies. Then electrical characterization of sintered $BaTaO_2N$ and $SrTaO_2N$ thin ceramics revealed a piezoelectric response.^{9,25} A butterfly-like piezoresponse along with a reversal of polarization direction under applied high voltage was observed in the electrical characterization of micrometer sized $BaTaO_2N$ single crystals to clearly prove their ferroelectricity.²⁶ Second harmonic wave generation (SHG) was also observed for the aggregate of the $BaTaO_2N$ microcrystals, indicating the presence of a locally polar structure. It should not appear in the centrosymmetric structures observed in powder diffraction studies. The ferroelectricity may be conjunction to polar nano regions (PNRs) originating from the local *cis*- TaO_4N_2 chains precipitated in the cubic crystals, although unveiling of the relaxor-type dielectric behavior is still a significant challenge due to a lack of well-defined samples in large scale.

The lower symmetry of perovskite-type oxynitrides than a cubic structure of $BaTaO_2N$ was suggested for $LnTaON_2$ ($Ln = La, Ce, Pr$) perovskites by Porter et al.²⁷ based on powder neutron diffraction data. Perovskite-type structures with the *Imma* and *Pnma* space groups were reported for $LaTaON_2$ and $CeTaON_2$, respectively, with *cis*-type O/N ordering in TaO_2N_4

octahedra. However, the reported *Imma* and *Pnma* space groups are centrosymmetric, which does not match with the previous observations of the ferroelectricity confirmed by piezoresponse force microscopy and SHG signal for the BaTaO₂N perovskite.²⁶ Only four space groups, *C2*, *Ima2*, *Pmc2₁*, and *Pmn2₁*, have polarities among 18 space groups suggested for the perovskite-type oxynitrides in conjunction with the octahedral tiltings and anion orderings (*trans*-, and *cis*-ordering).²⁷ The polarity is inevitable for showing the ferroelectricity and SHG on BaTaO₂N observed in our previous study.²⁶

The *Pnma* orthorhombic perovskite structure was suggested to be more stable crystal system of BaTaO₂N than the *Pm $\bar{3}$ m* cubic and *I4/mcm* tetragonal perovskites in the early Ab-initio study.²⁸ Among orthorhombic candidates, the perovskite-type structure with *Pmc2₁* space group is the most energetically stable in conjunction with *cis*-type anion-ordering. It has the polarity along its *c*-axis as shown in Fig. 2. However, the observed crystal structure in any diffraction methods was not in *Pmc2₁* but *Pm $\bar{3}$ m*.²⁹ It is a problem whether the *Pmc2₁* perovskite with *cis*-configuration can extend infinitely as a crystal structure or is in nano meter size crystallites forming an apparent crystal from a kinetic reason in its preparation.

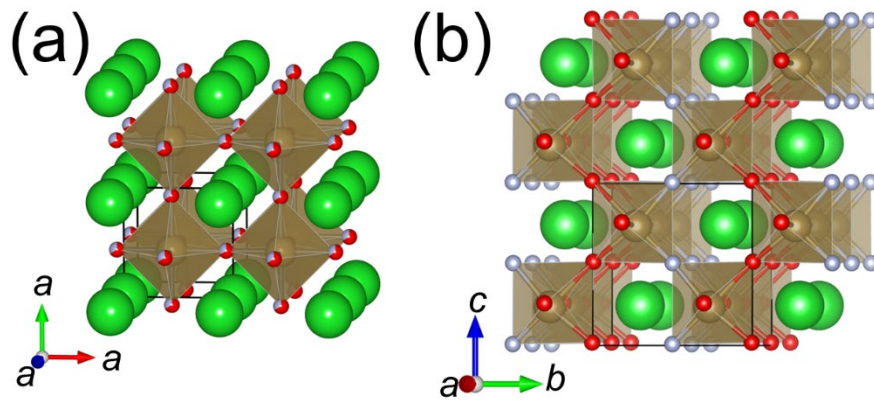


Figure 2. Crystal structure images of BaTaO₂N in (a) cubic $Pm\bar{3}m$ and (b) orthorhombic $Pmc2_1$ perovskites. Atomic positions in the $Pmc2_1$ BaTaO₂N adopt the theoretically predicted structural parameters discussed later. Green, brown, red, and gray spheres correspond to Ba, Ta, O, and N atoms, respectively.

A combination of neutron diffraction and pair distribution function analyses of neutron total scattering data suggested *cis*-type O/N ordering was locally present in BaTaO₂N.^{30,31} X-ray absorption fine structure (XAFS) analysis has been used to examine the O/N distortion around the Ta⁵⁺ cations in BaTaO₂N.^{11,32} The local distortion caused by *cis*-type O/N ordering was suggested for the cubic BaTaO₂N in the above reports, however the polar crystal structure was not confirmed experimentally in the oxynitride perovskite. Polar nano regions (PNRs) were assumed to be incoherently present in its centrosymmetric average crystal structure forming ferroelectric domains to provide relaxor-type dielectric behavior in the perovskite oxynitrides¹⁷. However, it remains unclear on the atomic arrangement in the PNRs, their size and the way of distribution in relation to the average centrosymmetric structure. It is very important to understand the relaxor-type ferroelectricity in relation to the PNR mechanism. Differential phase contrast-scanning transmission electron microscopy (DPC-STEM) analysis in comparison to HAADF image may provide a direct observation of the polar domains.³³⁻³⁵ Characterization of the PNRs is important to understand and control the ferroelectric properties of perovskite-type oxynitride similar to the relaxor-type ferroelectric oxides.

Raman spectroscopy is widely used to investigate incoherent local crystal structures that cannot be detected using X-ray nor neutron diffraction studies. It is useful to clarify preliminary steps in crystallization, precipitations of quantum dots and molecular assemblies of organic and biomolecules.³⁶⁻⁴¹ Angle-dependent Raman spectroscopy was applied to single crystals or

epitaxially grown thin films to clarify anisotropic polarization induced by the local symmetry of Raman modes.⁴²⁻⁴⁵ The micro-Raman scattering technique in micrometer-scale spatial resolution was useful to detect the local symmetry of the nano-size region and the ferroelectric domains present in a BaTaO₂N microcrystal as in a SrTiO₃ single crystal.⁴⁶

Here we experimentally report the domain structure formed with PNRs in the ferroelectric BaTaO₂N perovskite having the cubic $Pm\bar{3}m$ average structure with a help of theoretical calculation. DPC-STEM images showed the domain structure with the PNRs caused by the different stacking of *cis*-TaO₄N₂ octahedra with a help of HAADF image. Angle-dependent Raman spectra was applied on the BaTaO₂N single crystal using polarized micro-Raman spectroscopy. The change in Raman scattering intensity with crystal rotation angle supported that the local polar crystal symmetry was in $Pmc2_1$ space group. The PNRs in space group of $Pmc2_1$ randomly distribute forming electric domains in their average size of 50 nm. Their aggregates were observed as a centrosymmetric $Pm\bar{3}m$ structure of BaTaO₂N in any diffraction methods showing its relaxor-type ferroelectricity.

Experimental

Sample preparation

Single-crystal BaTaO₂N grains up to several micrometers in size were grown in a BaCN₂ flux using a BaTaO₂N precursor powder, as in our previous study.²⁶ The BaTaO₂N powder and BaCN₂ flux were obtained from a mixture of BaCO₃ (99.9%, Fujifilm Wako Pure Chemical Corp.) and Ta₂O₅ (99.9%, Fujifilm Wako Pure Chemical Corp.) with a molar ratio Ba:Ta=1.03:1

and BaCO_3 , respectively, using an ammonolysis reaction.²⁶ The BaTaO_2N powder product was mixed with 46 mol% BaCN_2 in a N_2 -filled glove box. The powder mixture was transferred to an alumina crucible and then enclosed in a custom-made tantalum capsule (>99%, Nilaco) in a N_2 atmosphere. The mixed powder in a tantalum capsule was heated at 1183 K for 30 min and slowly cooled at a rate of -1.8 K/h in a N_2 gas. After the mixture was cooled to room temperature, it was washed with 1 M nitric acid and then with distilled water. After drying in air, the product was used in further characterization.

Crystalline phase analysis

Crystalline phases in the product were characterized using powder X-ray diffraction (XRD; Ultima-IV, Rigaku) with $\text{Cu-K}\alpha$ radiation operated at 40 kV and 40 mA. XRD patterns were obtained at room temperature over the range $2\theta = 20^\circ - 90^\circ$ with scanning speed and step size of $10^\circ/\text{min}$ and 0.02° , respectively.

Neutron diffraction

The neutron diffraction (ND) data of the BaTaO_2N powder synthesized by ammonolysis of a mixture of BaCO_3 and Ta_2O_5 was collected at BL20 (iMATERIA) beamline of Japan Proton Accelerator Research Complex (J-PARC)⁴⁷ at 298 K and analyzed with the software Z-Rietveld (Windows ver. 1.1.1.0914).⁴⁸ Crystal structure images were visualized by using a software VESTA.⁴⁹

Microstructure observation

Microstructure of the acid washed product was observed using both optical (VHX-2000, KEYENCE) and scanning electron microscopies (SEM; JSM-6500F, JEOL). The crystalline

plane indexing based on the crystal habit in cubic grains was performed using high-voltage transmission electron microscopy (HV-TEM; JEM-ARM-1300, JEOL). Electron diffraction patterns were obtained to confirm the crystal orientation at an accelerating voltage of 1250 kV for several hundred nanometer-scale BaTaO₂N cubic single crystals.

Differential phase contrast (DPC) image

A thin slice of the BaTaO₂N microcrystal was prepared for the STEM observation using a focused ion beam (FIB) of gallium ion (SMI 3050SE, Hitachi High-Technologies). Its thickness was less than 100 nm. The annular bright field (ABF) and the high angle annular dark field (HAADF) STEM images were acquired using a STEM instrument equipped with a spherical aberration corrector (Titan3 G2 60-300, FEI Co.) operated at 300 kV. The DPC signals were recorded using a quadrant detector. Two perpendicular DPC images were then processed to produce a color map showing both strength and direction of the DPC signal, according to a color wheel. The color images obtained is related directly to the magnitude and direction of the polarization in specimen. The schematic image to produce the color map is shown in Fig. S1.

Angular-dependent Raman scattering

Confocal micro-Raman spectroscopy measurements were conducted on a BaTaO₂N microcrystal ($\sim 1.5 \times 1.5 \times 1.5 \mu\text{m}^3$) by irradiating a linearly polarized laser beam generated in a diode-pumped solid-state laser system (continuous wave Nd:YVO₄ laser; wavelength: 532 nm). The microcrystal was placed on a sample holder at room temperature under flowing N₂ gas on an xyz stage. The angle dependence of Raman spectra was measured in both optical settings of parallel and crossed polarizations using an analyzer as shown in Fig. S2. The polarized laser beam was irradiated to the microcrystal along the optical axis of an objective lens. The laser

power and beam diameter were approximately 0.1 mW and 1 $\mu\text{m}\phi$, respectively. Decomposition and oxidation of the BaTaO_2N microcrystal during the Raman spectroscopy measurements were avoided by the operation in N_2 atmosphere. The original reddish brown color was preserved even after the present measurement although it was reported to change to dark brown in the decomposition in a previous report.²⁵

Raman spectra changing with the crystal rotation angle φ ($= 2\theta$) were measured by rotating a half-wave plate (rotation angle, θ) placed above the objective lens in a backscattering geometry (see Fig. S2).^{50,51} Scattered light from the sample was collected using the objective lens and focused into a spectrometer (PHOTON Design PDPX, focal length: 64 cm) through a slit (width: 100 μm). The incident light was separated from the Raman scattered light component using a notch filter mounted in front of the spectrometer. The Raman spectrum was obtained in a frequency range of 63-469 cm^{-1} centered at 270 cm^{-1} and converted into spectral lines using a charge-coupled device (CCD) detector cooled by liquid nitrogen. The background intensity was measured in the same frequency range without a laser irradiation to subtract from the observed spectrum. The polarization angle θ changed in the crystal rotation angle φ ($=2\theta$) of the microcrystal, as illustrated in Fig. S2. The angular dependence was obtained in 6° step for the crystal rotation angle φ (240 seconds for each step). The total 360° measurement was repeated 30 times (120 hours) and 35 times (140 hours) for the parallel and crossed polarization set-ups, respectively, to improve the signal-to-noise ratio. The obtained spectra were deconvoluted into Lorentzian peaks using the software OriginPro 2021 (OriginLab Corp.). The details of the Raman tensor analysis for the Raman peaks are described in supporting information.

Theoretical calculation

Energies for all the O and N atomic distributions were estimated in $2 \times 2 \times 2$ supercell of BaTaO₂N perovskite structure to obtain insights about atomic configurations. To remove all symmetry constraints, all atoms in the expanded special structure were displaced randomly within 0.1 Å. There are 2664 symmetrically independent configurations in the cell. Energies of all the independent structures were calculated. First-principles calculations based on density functional theory were performed using projector augmented-wave (PAW) method implemented in the VASP code.^{52,53} The exchange correlation term was treated with the GGA-PBE for solid.⁵⁴ The valence electron configuration of the potentials was taken as $5s^2 5p^6 6s^2$ for Ba, $5p^6 5d^3 6s^2$ for Ta, $2s^2 2p^4$ for O, and $2s^2 2p^3$ for N. The plane-wave cutoff energy was set to 520 eV. Integration in reciprocal spaces was performed with the grid of 0.2 Å^{-1} . Crystal structures were fully relaxed until all residual forces acting on each atom were less than 0.02 eV/Å .

Inversion energy barrier was theoretically calculated for BaTaO₂N with $Pmc2_1$ non-centrosymmetric crystal structure. There are two Ba, two Ta, four O and two N atoms in the calculated cell. Candidates for centrosymmetric crystal structures were searched by using the PSEUDO algorithm.^{55,56} Centrosymmetric crystal structures were calculated using climbing Nudged elastic band methods with seven intermediate images,⁵⁷ considering the non-centrosymmetric crystal structure and the inversed one as initial and final structures, respectively. Spontaneous polarization was determined by the berry phase calculations.⁵⁸

Results and discussion

Extended linkage of polar octahedra in BaTaO₂N perovskite structure

The energy was estimated in $2 \times 2 \times 2$ supercell of BaTaO₂N perovskite on various kinds of O and N atomic distribution to obtain insight of O and N configurations. The structure with *cis*-configuration of two N atoms in an octahedron around Ta is more stable energetically than any other configurations, such as *trans*-configuration or with more N atoms. Considering the multiplicity, the relative energy for completely random configurations of O and N was estimated as 11.6 kJ/mol to the most stable configuration. This energy value corresponds to 275 K, almost room temperature, in the Boltzmann distribution. It suggests that the almost random distribution of O and N is stable at around room temperature in macroscopic view.

Then we estimated probabilities for the number of N atoms and *cis/trans*-configurations at 1183 K, where the present microcrystal was grown, assuming the Boltzmann distributions. They are 0.19, 0.61 and 0.19 for the cases that the number of N atoms in Ta octahedron is one, two and three, respectively. Two N atoms are mostly present in an octahedron and some of the octahedra containing one or three N atoms are also present. The minor TaO₅N and TaO₃N₃ octahedra restrict the growth of *cis*-TaO₄N₂ chains and disturb a long-range order crystal structure. The probabilities of *cis*- and *trans*-configurations in the TaO₄N₂ octahedron are estimated as 1.19 and 0.006, respectively, suggesting a preference for *cis*-configuration in the octahedron. It is noted that the sum of these values is more than 1 because *cis*-configurations are multiply counted in the cases of octahedron with three or more N atoms. Focusing on only the octahedron with two N atoms, the probabilities of *cis*- and *trans*-configurations are calculated again to be 0.998 and 0.001, respectively, suggesting rare *trans*-configuration. The boundary between *cis*-type TaO₄N₂ should contain TaO₅N and TaO₃N₃ octahedral units forming random O/N distribution and non-polar matrix between the PNRs.

The crystal structure in space group $Pmc2_1$ was the most stable in the energetic estimation among the 2664 independent O and N configurations as already expected in the previous publications^{27,28}, which also corresponds to the Raman spectroscopy result mentioned below. Inversion barrier for electric field induced phase transition of ferroelectrics was therefore, evaluated for $Pmc2_1$ non-centrosymmetric crystal structure of $BaTaO_2N$ which having *cis*-configuration of N atoms. The lattice parameters of a reduced cell for $Ba_2Ta_2O_4N_2$ are calculated as $a = 4.048 \text{ \AA}$, $b = 5.872 \text{ \AA}$, and $c = 5.848 \text{ \AA}$. Using PSEUDO algorithm, four kinds of candidates are generated as the intermediate; $Pmm2$, $Amm2$, $Pmma$ and $Pbam$. The calculation converged only in the case of $Pmma$. The inversion barrier was estimated to be 1.8 kJ/mol and spontaneous polarization of $Pmc2_1$ phase was $36 \text{ \mu C/cm}^2$ assuming $Pmma$ as the intermediate in inversion process (Fig. S3).

Small inversion barrier suggests the possibility of polarization inversion in the cases such as $Pmc2_1$ having *cis*-configuration in the octahedron. Ta atoms slightly displace along two nitrogen atoms in an octahedron with the applied electric fields. The linkages of *cis*- TaO_4N_2 octahedra precipitate in various length and direction from the melt at 1183 K. They are present as PNRs within the domains in random direction forming cubic average crystal structure. They show electric polarization along the *cis*-arrangement of N atoms. The boundary between the polar nano regions consisting of TaO_5N and TaO_3N_3 units breaks down the linkage of *cis*- TaO_4N_2 chain to non-polar matrix. Relaxor-type ferroelectric behavior can be observed in the average cubic crystal structure.

Observation of domain structure formed with the polar nano regions

The above linkages extend forming nano size regions which are not coherent each other in a whole cubic crystal structure as expected in the previous theoretical paper¹⁷. The PNRs are not so homogeneous in their shape and size as expected in the above manuscript because there are some possible distributions both in the N numbers and *cis/trans* in Ta octahedron as mentioned in the theoretical calculation in this paper. It is important to observe the way how these nano regions and domains are present in a whole crystal structure.

Powder XRD pattern for the BaTaO₂N microcrystals indicated the cubic perovskite-type crystal structure as reported in the previous papers on as-synthesized powder sample (Fig. 3(a))^{19,20}. Neutron diffraction pattern was also analyzed based on a single phase of the cubic perovskite-type structure as shown in Fig. S4. There were no additional diffraction lines coming from its superlattice related to the different stacking of TaO₄N₂ octahedra with *cis*-type O/N ordering in the XRD nor ND patterns. SEM image depicted in Fig. 3(b) shows that the cubic-like grains having approximately 1 μm or more were obtained in the product. Red-brown crystal was observed under the optical microscope (Fig. 3(c)). High voltage electron beam was irradiated directly on a BaTaO₂N microcrystal in 500 nm of the edge size (Fig. S5). Diffraction indexes suggest the crystal outer surfaces are {001} planes of the cubic structure. Polarization switching had been observed on BaTaO₂N microcrystals by using a piezoresponse microscopy. Also, SHG was clearly observed from the aggregate of the microcrystals.²⁶ Therefore, polar non-centrosymmetric regions must be present in the microcrystals, whilst there are no clear diffraction spots related to the non-centrosymmetric structure.

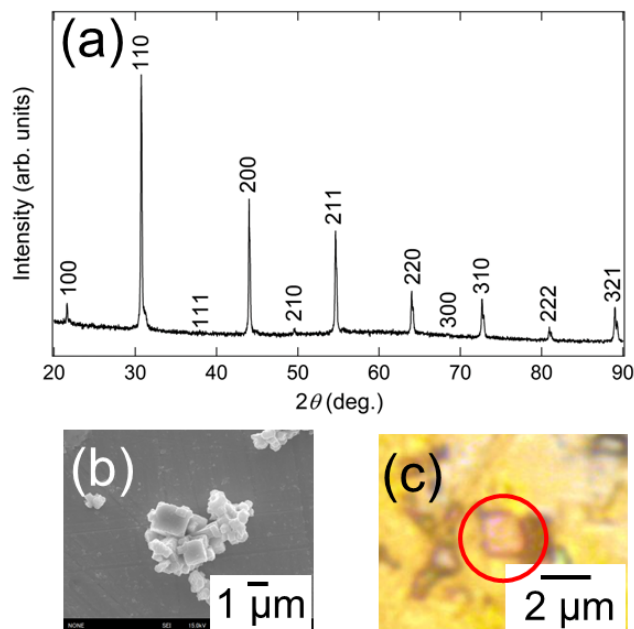


Figure 3. (a) Powder XRD pattern of BaTaO₂N microcrystals after acid washing, (b) SEM and (c) optical images of the as-grown BaTaO₂N microcrystals.

Figure 4 shows a thin slice of the BaTaO₂N single crystal used in the STEM observation. ED pattern indicates the crystal is surrounded by (100) and (010) planes of the cubic structure as observed in HV-TEM. The HAADF images for two different parts (yellow and red squares) in the same crystal are shown in Figs. 5(b) and 5(d). Bright spots indicate the positions of Ba and Ta atomic columns along the $\langle 001 \rangle$ direction as shown in Fig. 5(b). The brightness of the HAADF image is proportional to the square of atomic number, Z .⁵⁹ Both Ba and Ta atomic columns are clearly observed in the HAADF image. Light elements O and N are emphasized in ABF image in comparison to the HAADF one because its contrast is roughly proportional to $Z^{1/3}$.⁶⁰ The HAADF image in Fig. 5(b) shows homogeneous distribution of the atomic column, and the corresponding ABF one in Fig. 5(c) is also clear but not homogeneous in part. However,

both HAADF and ABF images for another part of the same crystal shows the blurred contrast even in lower magnified images than those above (Figs. 5(d) and (e)). The crystal structure in this part is obviously disturbed in its periodicity. The periodical atomic arrangement has already been slightly disturbed in ~ 5 nm size regions. There are some distributions on the various kinds of octahedra around Ta as suggested in the above theoretical calculation. Different PNRs coexist either coherent or incoherent each other.

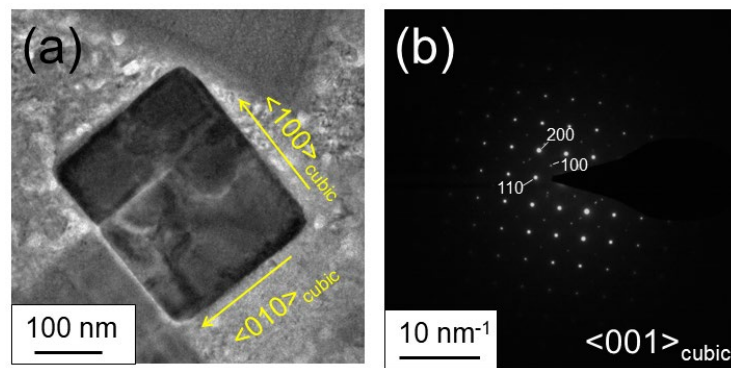


Figure 4. (a) STEM image of BaTaO_2N microcrystal after FIB thinning. ED pattern (b) indicates the crystal edges are $\langle 001 \rangle$ directions of cubic perovskite.

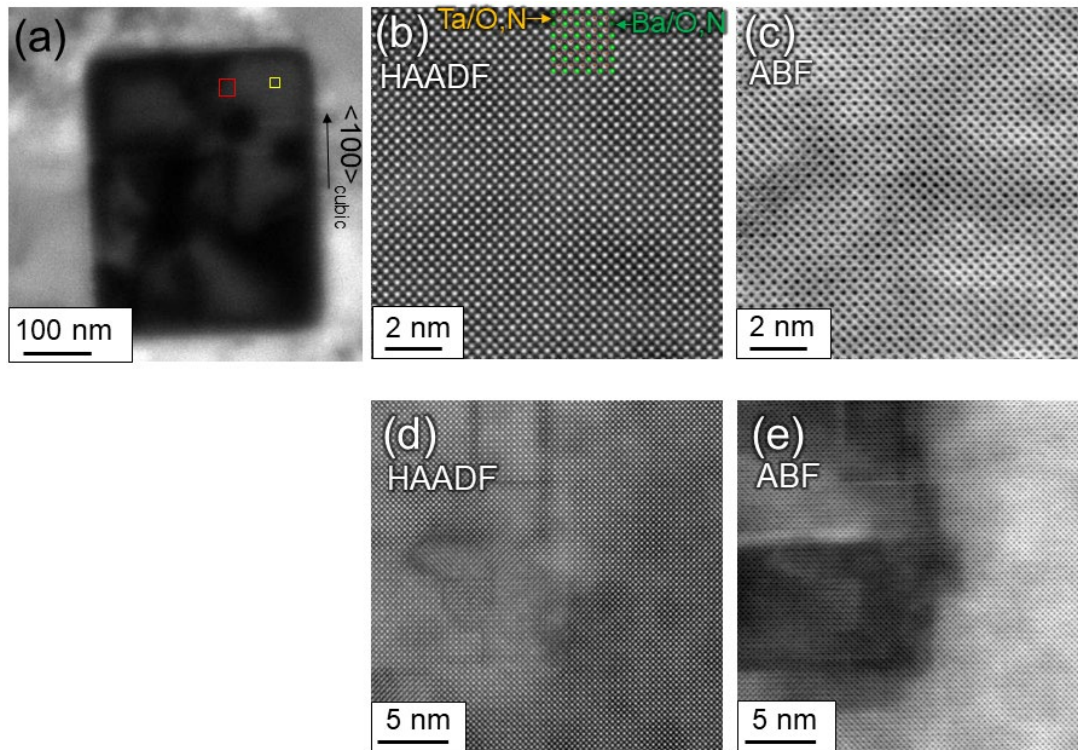


Figure 5. HAADF (b, d) and ABF (c, e) images of the BaTaO₂N microcrystal. The atomic scale images (b, c) and (d, e) were obtained from the regions of yellow and red squares in Fig. (a), respectively. The schematic cubic structure image of BaTaO₂N is drawn on the top of HAADF image (b).

Differential phase contrast (DPC) images were obtained from the same area to study the effect of domain polarization (Fig. 6). Figs. 6(c) and (d) show the differential signals between the opposite segments (A–C) and (B–D) of the detector in Fig. S1, respectively. Spontaneous polarization direction produced from these DPC images was indicated as electric field color map in Fig. 6(e) and both direction and strength of the electric field is depicted in a color wheel in its upper right. Purple and green areas which have the opposite polarization directions toward the lower-left and upper-right directions, respectively, were observed in whole area of the image. The brightness of purple and green color was inhomogeneous in each area. Between the purple

and green areas, black regions with a thickness of less than 5 nm were observed. The DPC image indicate BaTaO₂N has polar domains of approximately 50 nm size in the crystal structure with opposite orientations and the strength of the polarization in each domain is not uniform. The tiny periodic regions in ca. 5 nm size observed in HAADF image (Figs. 5(d) and (e)) cooperatively respond to the electric field induced by the electric domains in size of 50 nm. They are formed with *cis*-TaO₄N₂ stackings as predicted in our theoretical calculation. Angle dependent Raman spectroscopy was applied on a BaTaO₂N single crystal to analyze the crystal structure at the locally polar regions observed in electron microscopy.

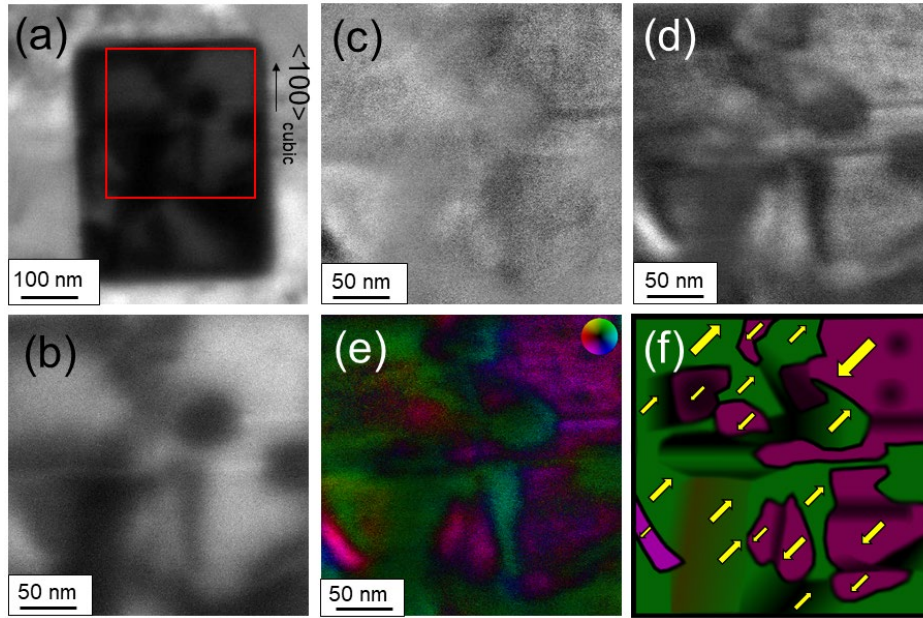


Figure 6. HAADF of the BaTaO₂N microcrystal (a) and its magnified image (b) obtained from its red squared region. Differential signals from the same area observed in opposite segments (A–C) and (B–D) of the detector (Fig. S1) are shown in (c) and (d), respectively. The polarization distribution in this area and its polarization direction are represented as the color map in (e). The inset color wheel on its upper right indicates the electric field direction in this

map. Schematic image of the DPC-STEM image is re-drawn in (f) together with the polarization directions as yellow arrows.

Raman spectroscopy

Micro-Raman spectroscopy measurement was performed on a red brown BaTaO₂N micro single crystal in Fig. 3(c) to study crystal symmetry in the PNR. The Raman spectra obtained at the BaTaO₂N crystal in rotation angle $\varphi = 0^\circ$ for both parallel and crossed polarization settings were similar each other as shown in Figs. 7 and S6. There are several peaks in the observed frequency range similarly in these spectra, although no Raman active mode for the average cubic perovskite structure ($Pm\bar{3}m$) should appear with Wyckoff positions of $1a$ (Ba), $1b$ (Ta), and $3c$ (O/N) sites according to the selection rules for $Pm\bar{3}m$ space group. The spectrum in 80 to 420 cm⁻¹ frequency range was deconvoluted into eight Lorentzian curves with peaks at 83, 114, 164, 196, 207, 252, 293, and 391 cm⁻¹, as shown in Figs. 7 and S6. This supports the BaTaO₂N crystal lattice could have the lower symmetry than the cubic perovskite-type structure of $Pm\bar{3}m$. Similar Raman spectra have been reported for the perovskite oxynitride SrTaO₂N under high pressure. It was suggested to have lower symmetry than that of the average tetragonal $I4/mcm$ centrosymmetric structure but there had been no practical explanation for the contradiction.⁶¹

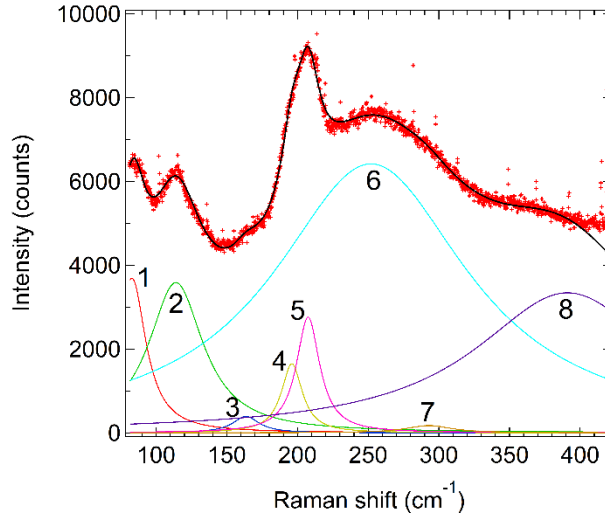


Figure 7. Raman spectrum obtained from a BaTaO₂N micro single crystal under the parallel polarization optical setting at the crystal rotation angle $\varphi = 0^\circ$. The spectrum intensity is shown by red dots. The spectrum was deconvoluted to eight Lorentzian peaks in different color (peak 1: red, 2: green, 3: dark blue, 4: yellow, 5: pink, 6: blue, 7: orange, 8: purple, sum: black) between 80 and 420 cm⁻¹.

The angular dependences of the present Raman spectra were obtained under the parallel and crossed polarization settings as shown in Fig. 8. The Raman peaks at 114, 207 and 251 cm⁻¹ (denoted as peaks 2, 5 and 6 in Fig. 7) showed 180° rotational symmetry in the contour color map under the parallel polarization setting (Fig. 8(a)). Their polar plots shown in Figs. 9(a) and S7 strongly suggest that the symmetry of the BaTaO₂N perovskite is reduced from the average cubic structure to a lower symmetry with 2-fold rotational symmetry. For the crossed polarization, these peaks showed nearly 90° rotation symmetry in both contour color map (Fig. 8(b)) and polar plots in Figs. 9(b) and S8. The optical condition between the incident and scattering beam through the half-wave plate converted the above 180° rotation symmetry to the 90° one. The maximum intensity appeared at $\varphi = 45^\circ$ off from the origin $\varphi = 0^\circ$ in both parallel

and crossed polarization optical settings. This suggests the polarization direction is tilted in 45° from $\langle 100 \rangle$ in the cubic lattice appearance.

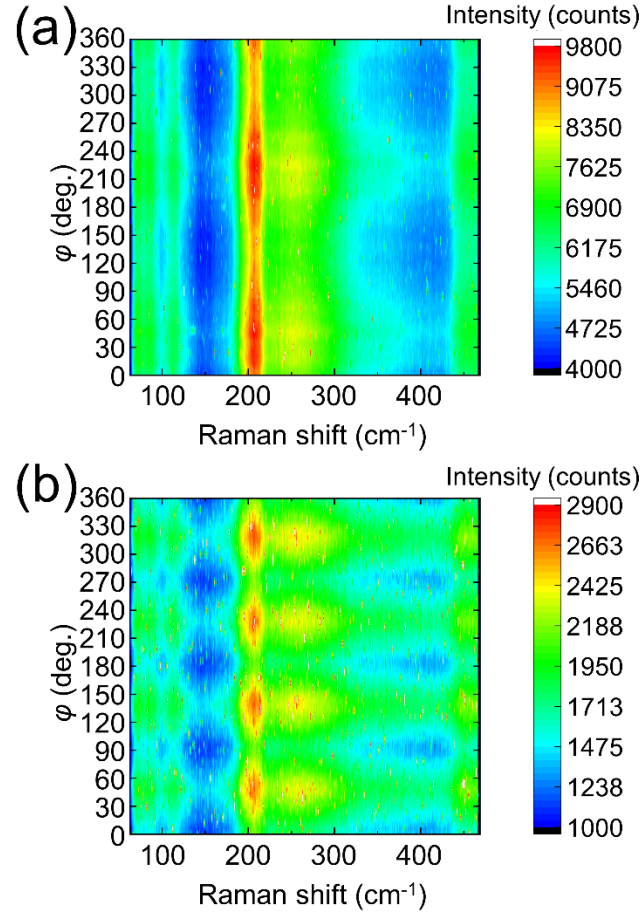


Figure 8. Contour color maps of Raman spectrum intensity observed for BaTaO₂N microcrystal with (a) parallel and (b) crossed polarization optical setting. The vertical and horizontal axes are the crystal rotation angle ϕ and Raman shift, respectively. Spectrum intensity is shown in color as depicted in the right bar.

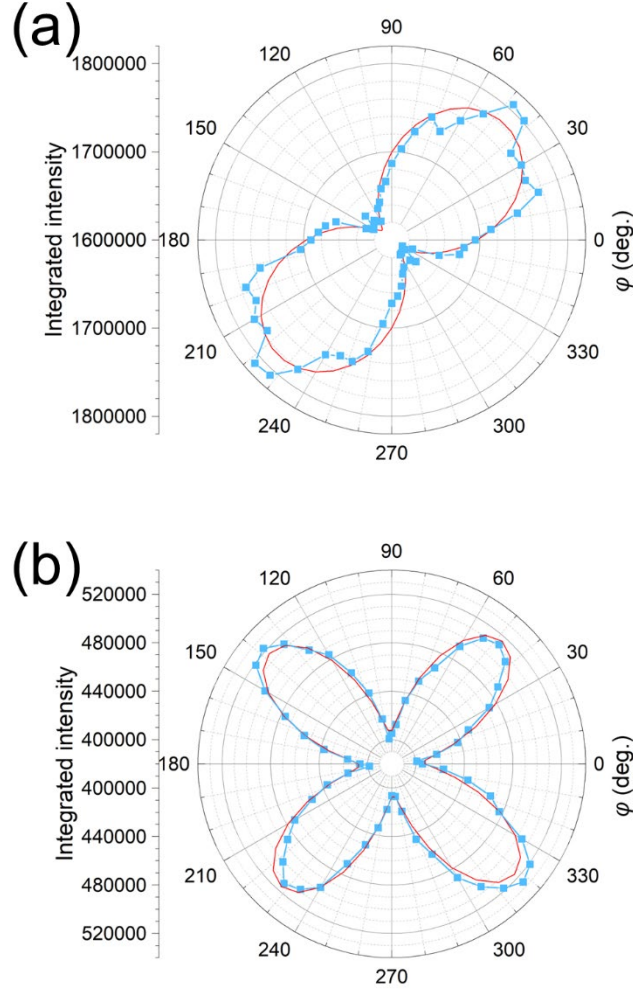


Figure 9. Crystal rotation angle φ dependence of Raman peak at 252 cm^{-1} (peak 6 in Fig. 7 and S6) observed for (a) the parallel and (b) crossed polarization optical setting. The crystal rotation angle $\varphi = 0$ corresponds to the ridgeline of the BaTaO_2N microcrystal shown in Fig. 3(c). The solid red lines represent the best fit for the Raman intensity obtained using the calculation angular dependence of the Raman mode. The details of the calculation are described in the supporting information.

The angular dependence of the spectrum led to the $mm2$ point group, which provides $Pmc2_1$ space group, as the non-centrosymmetric BaTaO_2N crystal structure confirmed by the

STEM observation and theoretical calculation in this study. Raman tensor analysis is performed in the point group with four Raman active modes in A_1 , A_2 , B_1 , and B_2 modes for all Wyckoff positions. The two-fold symmetry observed in the present Raman spectra is understood by these modes in the orthorhombic $Pmc2_1$ perovskite structure with *cis*-type anion ordering. It is well explained together with the four-fold symmetry as the detailed discussion on Raman tensor analysis in supporting information. The $BaTaO_2N$ crystallizes locally in space group $Pmc2_1$ in Raman spectroscopy and it appears as cubic $Pm\bar{3}m$ in diffraction methods as its average.

The $BaTaO_2N$ microcrystals have crystal planes of $\{100\}$ in the average cubic perovskite structure, which was confirmed in the ED pattern (Fig. 4(b)) and HAADF image (Fig. 5(a)). The polarization direction is tilted approximately 45° from the crystal habit plane as observed in Fig. 6. The polarization direction in orthorhombic perovskite with a possible $Pmc2_1$ space group is parallel to the orthorhombic *c*-axis. It is tilted 45° from the primitive cubic perovskite cell and is along the N-N direction as expected in the theoretical calculation in this study. The angular dependence observed in Raman spectra also showed the 45° tilting in polarization direction as mentioned above. The PNRs in Raman spectroscopy are also polarized cooperatively in the same direction as those in domains observed in the DPC image. $BaTaO_2N$ perovskite in orthorhombic $Pmc2_1$ has its TaO_4N_2 octahedra mostly in *cis*-type N configuration and their polarization direction in the *bc* plane is thought to be along *c*-axis in the orthorhombic cell as shown in Fig. 10. The apparent cubic crystal structure of $BaTaO_2N$ in powder diffraction^{19,21} is made of the PNRs, which are the assemblies of *cis*- TaO_4N_2 linkages, in orthorhombic $Pmc2_1$.

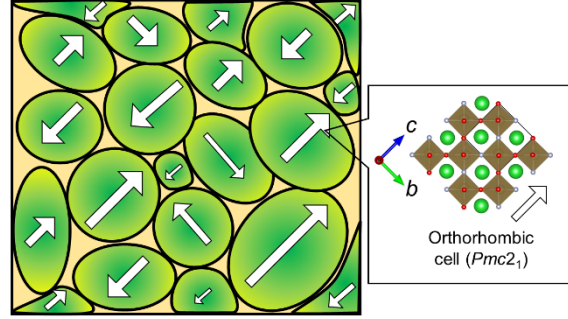


Figure 10. Schematic representation of PNRs (black circles) present in a domain (black square, ~50 nm) and they crystallize in various size (~5 nm) with orthorhombic $Pmc2_1$ space group. The yellow area consists of non-polar matrix made with statistic O/N distribution. White arrows indicate the polarization directions.

The ferroelectricity and SHG signal for the perovskite oxynitride $BaTaO_2N$ are ascribed to the tiny domains probably related to PNRs induced by the local *cis*-type O/N ordering in TaO_4N_2 octahedral chains. The chain linkage of *cis*- TaO_4N_2 octahedra was divided and terminated by a statistical distribution of the disorder such as TaO_5N and TaO_3N_3 as theoretically predicted. Based on the present Raman spectroscopy results and theoretical calculation, the local structure of $BaTaO_2N$ is in orthorhombic $Pmc2_1$ system. The domains in size of approximately 50 nm made of the local PNRs showed their polarization directions in the opposite directions each other as observed in the DPC-STEM image. The size of local PNRs is smaller than that in the perovskite-type $Pb(Mg_{1/3}Nd_{2/3})O_3$ (PMN) relaxor-type ferroelectric oxide.⁶³ In the PMN structure, PNRs arises from the ordering of B-site cations in cubic matrix. The present PNRs caused by the local O/N ordering in *cis*- TaO_4N_2 chain linkage terminated by O/N disorder, which is characteristic for the oxynitride perovskites. The polarization is totally averaged in the as-grown $BaTaO_2N$ crystal, and its cubic perovskite structure is falsely observed in the diffraction

studies. The 180° domains are separated with approximately 5 nm of domain walls shown as black regions in Fig. 6(e).

The linkages of *cis*-TaO₄N₂ octahedra start to precipitate during cooling of the melt of BaTaO₂N in BaCN₂ flux at 1183 K. They are formed in certain length because of the complicated nature of the linkage and its statistical nitrogen distribution in the crystal. They get together to form polar domains in size of approximately 50 nm consisting of PNRs with space group *Pmc*2₁ detected in Raman spectroscopy. Assemblies of the PNRs were observed as a cubic crystal structure in neutron diffraction and showed relaxor-type ferroelectricity with domain structure. In the previous piezoresponse measurement on BaTaO₂N microcrystals precipitated from BaCN₂ flux, electrical field necessary to saturate polarization varied depending on individual grain.^{26,64} This difference may be assumed as a result of a slight inhomogeneity of local linkages of octahedra and nitrogen distribution to induce some covalent interaction with cation, resulting in a variation of coercive field and domain pinning.

The present manuscript suggests mixed anion compounds especially oxynitrides have a possibility to show a variety of ferroelectric properties in relaxor-type. Their texture is controlled in their preparation conditions such as temperature, duration, atmosphere, and so on. The ferroelectricity strongly depends on their nano structure. Both *cis*-TaO₄N₂ octahedra and its linkages are the results of different chemical bond nature between oxygen and nitrogen. The ferroelectricity in oxynitride is a characteristic that appears from the covalent chemical bond nature of nitride in oxide matrix. It is induced by the more covalent nitrogen than oxygen similarly to high temperature sialon ceramics, visible light photocatalysts and red-light emitting diodes.

Conclusion

Domain structure made of nano sized polar $Pmc2_1$ regions in the cubic perovskite $BaTaO_2N$ was directly observed in DPC-STEM image and characterized by polarized-Raman spectroscopy of the micro single crystal. The spontaneous polarization with approximately 50 nm domain size was visualized in the DPC-STEM image and its direction was 45° off from the apparent cubic lattice. The Raman spectra depending on the crystal rotation angle showed two-fold symmetry with the polarization direction tilted 45° from the primitive cubic perovskite cell. The $Pmc2_1$ perovskite structure is plausible as a non-centrosymmetric polar structure in the polar nano regions, and they were averaged as the cubic $Pm\bar{3}m$ structure observed in the previous diffraction studies. The domain made of PNRs is attributed to the linkages of *cis*- TaO_4N_2 octahedra and they were quenched in the high temperature synthesis. The ferroelectricity of $BaTaO_2N$ is a characteristic from its nitrogen and oxygen configuration. Their coordination and distribution around the cation can be tuned by changing the formation temperature, atmosphere, and duration.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/*****:

Schematic representation of differential phase contrast technique, optical geometry of angular dependence Raman spectroscopy, polarization inversion process, neutron diffraction profile for

BaTaO₂N, HV-TEM image of BaTaO₂N microcrystal, Raman spectrum of BaTaO₂N microcrystal observed under crossed polarization optical setting, crystal rotation angle dependence Raman intensity, Raman tensor analysis (PDF)

AUTHOR INFORMATION

Corresponding Author

* **Yuji Masubuchi** – Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan. orcid.org/0000-0003-3601-7077; E-mail: yuji-mas@eng.hokudai.ac.jp

Authors

Kyohei Koyama – Graduate School of Chemical Sciences and Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan. E-mail: koy.koyama719@gmail.com

Akira Hosono – Graduate School of Chemical Sciences and Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan. orcid.org/0000-0002-8491-2941; E-mail: akira.hosono.a7@tohoku.ac.jp

Mikio Higuchi – Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan. E-mail: hig@eng.hokudai.ac.jp

Masaki Takesada – Graduate School of Science, Hokkaido University, N10 W8, Kita-ku, Sapporo, 060-8610, Japan. orcid.org/; E-mail: mt@phys.sci.hokudai.ac.jp

Kazuki Shitara – Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 464-8587, Japan. orcid.org/0000-0002-9744-8578; E-mail: kazuki_shitara@jfcc.or.jp

Hiroki Moriwake – Nanostructures Research Laboratory, Japan Fine Ceramics Center, 2-4-1 Mutsuno, Atsuta-ku, Nagoya 464-8587, Japan. orcid.org/ ; E-mail: moriwake@jfcc.or.jp

Shinichi Kikkawa – Faculty of Engineering, Hokkaido University, N13 W8, Kita-ku, Sapporo, 060-8628, Japan. orcid.org/0000-0002-3498-0735; E-mail: kikkawa3shinichi@gmail.com

Present Address

†**Akira Hosono** – Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan orcid.org/0000-0002-8491-2941; E-mail: akira.hosono.a7@tohoku.ac.jp If an author's address is different than the one given in the affiliation line, this information may be included here.

Author Contributions

Y.M. and S.K. conceived and planned the study. The samples were synthesized by A.H. The theoretical calculations were carried out by K.S. and H.M. TEM observation was performed by Y.M. The Raman spectroscopy measurements were carried out by K.K. A.H. and M.T. The original draft was written by Y.M. with contributions from all authors. S.K. revised and edited the manuscript and supervised the work. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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REFERENCES

1. Kageyama, H.; Hayashi, K.; Maeda, K.; Attfield, J.P.; Hiroi, Z.; Rondinelli, J.M.; Poeppelmeier, K. R. Expanding frontiers in materials chemistry and physics with multiple anions. *Nat. Commun.* **2018**, 9, 1-15.
2. Xie, R. J.; Hirosaki, N. Silicon-based oxynitride and nitride phosphors for white LEDs—A review. *Sci. Technol. Adv. Mater.* **2007**, 8, 588-600.

3. Harada, J.K.; Charles, N.; Poeppelmeier, K. R.; Rondinelli, J.M. Heteroanionic Materials by Design: Progress Toward Targeted Properties. *Adv. Mater.* **2019**, 31, 1805295/1-26.
4. Maeda, K.; Takeiri, F.; Kobayashi, G.; Matsuishi, S.; Ogino, H.; Ida, S.; Mori, T.; Uchimoto, Y.; Tanabe, S.; Hasegawa, T.; Imanaka, N.; Kageyama, H. Recent progress on mixed-anion materials for energy applications. *Bull. Chem. Soc. Jpn.* **2022**, 95, 26-37.
5. Maeda, K.; Domen, K. New Non-Oxide Photocatalysts Designed for Overall Water Splitting under Visible Light. *J. Phys. Chem. C* **2007**, 111, 7851-7861.
6. Jansen, M.; Letschert, H. P. Inorganic yellow-red pigments without toxic metals. *Nature* **2000**, 404, 980-982.
7. Tessier, F.; Marchand, R. Ternary and higher order rare-earth nitride materials: synthesis and characterization of ionic-covalent oxynitride powders. *J. Solid. State. Chem.* **2003**, 171, 143-151.
8. Kim, Y. I.; Woodward, P. M.; Baba-Kishi, K. Z.; Tai, C. W. Characterization of the Structural, Optical, and Dielectric Properties of Oxynitride Perovskites AMO_2N ($\text{A} = \text{Ba}, \text{Sr}, \text{Ca}$; $\text{M} = \text{Ta}, \text{Nb}$). *Chem. Mater.* **2004**, 16, 1267-1276.
9. Kikkawa, S.; Sun, S. K.; Masubuchi, Y.; Nagamine, Y.; Shibahara, T. Ferroelectric Response Induced in *cis*-Type Anion Ordered SrTaO_2N Oxynitride Perovskite. *Chem. Mater.* **2016**, 28, 1312-1317.
10. Hosono, A.; Masubuchi, Y.; Higuchi, M.; Kikkawa, S. Ferroelectric BaTaO_2N perovskite - Towards structure-property relationship study on high-quality crystals and ceramics prepared with the aid of liquid phase. *Solid State Sci.* **2023**, 144, 107310/1-10.

11. Ebbinghaus, S. G.; Abicht, H. P.; Dronskowski, R.; Muller, T.; Reller, A.; Weidenkaff, A. Perovskite-related oxynitrides – Recent developments in synthesis, characterization and investigations of physical properties. *Prog. Solid State Chem.* **2009**, 37, 173-205.
12. Jorge, A. B.; Oro-Sole, J.; Bea, A. M.; Mufti, N.; Palstra, T. T. M.; Rodgers, J. A.; Attfield, J. P.; Fuertes, A. Large Coupled Magnetoresponses in EuNbO_2N . *J. Am. Chem. Soc.* **2008**, 130, 12572-12573.
13. Kato, H.; Ueda, K.; Kobayashi, K.; Kakihana, M. Photocatalytic water oxidation under visible light by valence band controlled oxynitride solid solutions $\text{LaTaON}_2\text{-SrTiO}_3$. *J. Mater. Chem. A* **2015**, 3, 11824-11829.
14. Aguiar, R.; Logvinovich, D.; Weidenkaff, A.; Rachel, A.; Reller, A.; Ebbinghaus, S. G. The vast colour spectrum of ternary metal oxynitride pigments. *Dyes Pigm.* **2008**, 76, 70-75.
15. Yang, M.; Oro-Sole, J.; Rodgers, J. A.; Jorge, A. B.; Fuertes, A.; Attfield, J. P. Anion order in perovskite oxynitrides. *Nat. Chem.* **2011**, 3, 47-52.
16. Zhang, Y. R.; Motohashi, T.; Masubuchi, Y.; Kikkawa, S. Local anionic ordering and anisotropic displacement in dielectric perovskite SrTaO_2N . *J. Ceram. Soc. Jpn.* **2011**, 119, 581-586.
17. Hinuma, Y.; Moriwake, H.; Zhang, Y. R.; Motohashi, T.; Kikkawa, S.; Tanaka, I. First-Principles Study on Relaxor-Type Ferroelectric Behavior without Chemical Inhomogeneity in BaTaO_2N and SrTaO_2N . *Chem. Mater.* **2012**, 24, 4343-4349.

18. Tatsumi, K.; Hoffmann, R. Bent Cis d^0 MoO_2^{2+} vs. Linear Trans D^0f^0 UO_2^{2+} : A Significant Role for Nonvalence 6p Orbitals in Uranyl. *Inorg. Chem.* **1980**, 19, 2656-2658.
19. Marchand, R.; Pors, F.; Laurent, Y. Preparation and characterization of new oxynitrides with a perovskite structure. *Rev. Int. Hautes. Temp. Refract.* **1986**, 23, 11-15.
20. Pors, F.; Bacher, P.; Marchand, R.; Laurent, Y.; Roult, G. Neutron diffraction structural study of the SrTaO_2N oxynitride perovskite and of the $\text{Ba}_{1-x}\text{Sr}_x\text{TaO}_2\text{N}$ solid solution. *Rev. Int. Hautes. Temp. Refract.* **1987-1988**, 24, 239-246.
21. Pors, F.; Marchand, R.; Laurent, Y.; Bacher, P.; Roult, G. Structural study of BaTaO_2N and BaNbO_2N oxynitrided perovskites. *Mater. Res. Bull.* **1988**, 23, 1447-1450.
22. Gunther, E.; Hagenmayer, R.; Jansen, M. Structural Investigations on the Oxidenitrides SrTaO_2N , CaTaO_2N and LaTaON_2 by Neutron and X-ray Powder Diffraction. *Z. Anorg. Allg. Chem.* **2000**, 626, 1519-1525.
23. Masubuchi, Y.; Sun, S. K.; Kikkawa, S. Processing of dielectric oxynitride perovskites for powder, ceramics, compacts, and thin films. *Dalton Trans.* **2015**, 44, 10570-10581.
24. Castets, A.; Fina, I.; Guarin, J. R.; Oro-Sole, J.; Frontera, C.; Ritter, C.; Fontcuberta, J.; Fuertes, A. High-Temperature Synthesis and Dielectric Properties of LaTaON_2 . *Inorg. Chem.* **2021**, 60, 16484-16491.
25. Hosono, A.; Masubuchi, Y.; Nagamine, Y.; Shibahara, T.; Kikkawa, S. Piezoresponse and microstructure of BaTaO_2N . *J. Eur. Ceram. Soc.* **2018**, 38, 3478-3482.

26. Hosono, A.; Masubuchi, Y.; Yasui, S.; Takesada, M.; Endo, T.; Higuchi, M.; Itoh, M.; Kikkawa, S. Ferroelectric BaTaO₂N Crystals Grown in a BaCN₂ Flux. *Inorg. Chem.* **2019**, *58*, 16752-16760.
27. Porter, S. H.; Huang, Z.; Woodward, P. M. Study of Anion Order/Disorder in RTaN₂O (R = La, Ce, Pr) Perovskite Nitride Oxides. *Crystal Growth Des.* **2014**, *14*, 117-125.
28. Wolff, H.; Dronslowski, R. First-Principles and Molecular-Dynamics Study of Structure and Bonding in Perovskite-Type Oxynitrides ABO₂N (A=Ca, Sr, Ba; B=Ta, Nb). *J. Comput. Chem.* **2008**, *29*, 2260-2267.
29. Kikkawa, S.; Masubuchi, Y. Solving the puzzle of the dielectric nature of tantalum oxynitride perovskites, *Z. Naturforsch. B* **2021**, *76*, 543-545.
30. Page, K.; Stoltzfus, M. W.; Kim, Y. I.; Proffen, T.; Woodward, P. M.; Cheetham, A. K.; Seshadri, R. Local Atomic Ordering in BaTaO₂N Studied by Neutron Pair Distribution Function Analysis and Density Functional Theory. *Chem. Mater.* **2007**, *19*, 4037-4042.
31. Wang, X.; Jiang, B.; Zhang, Y.; Kim, Y. I.; Page, K. Influence of Cation Size on the Local Atomic Structure and Electronic Properties of Ta Perovskite Oxynitrides. *Inorg. Chem.* **2021**, *60*, 14190-14201.
32. Ravel, B.; Kim, Y. I.; Woodward, P. M.; Fang, C. M. Role of local disorder in the dielectric response of BaTaO₂N. *Phys. Rev. B* **2006**, *73*, 184121/1-7.
33. Shibata, N.; Findlay, S. D.; Kohno, Y.; Sawada, H.; Kondo, Y.; Ikuhara, Y. Differential phase-contrast microscopy at atomic resolution, *Nat. Phys.* **2012**, *8*, 611-615.

34. Campanini, M.; Erni, R.; Yang, C. H.; Ramesh, R.; Rossell, M. D. Periodic Giant Polarization Gradients in Doped BiFeO₃ thin film, *Nano Lett.* **2018**, 18, 717-724.
35. Huang, Q.; Chen, Z.; Cabral, M. J.; Wang, F.; Zhang, S.; Li, F.; Li, Y.; Ringer, S. P.; Luo, H.; Mai, Y. W.; Liao, X. Direct observation of nanoscale dynamics of ferroelectric degradation. *Nat. Commun.* **2021**, 12, 2095/1-7.
36. Veselinovic, L.; Mitric, M.; Li, M.; Vukomanovic, M.; Hadzic, B.; Markovic, S.; Uskokovic, D. The effect of Sn for Ti substitution on the average and local crystal structure of BaTi_{1-x}Sn_xO₃ ($0 < x < 0.20$). *J. Appl. Cryst.* **2014**, 47, 999-1007.
37. Buscaglia, V.; Tripathi, S.; Petkov, V.; Dapiaggi, M.; Deluca, M.; Gajovic, A.; Ren, Y. Average and local atomic-scale structure in BaZr_xTi_{1-x}O₃ ($x = 0.10, 0.20, 0.40$) ceramics by high-energy x-ray diffraction and Raman spectroscopy. *J. Phys. Condens. Matter.* **2014**, 26, 065901/1-13.
38. Mahana, S.; Rakshit, B.; Basu, R.; Dhara, S.; Joseph, B.; Manju, U.; Mahanti, S. D.; Topwal, D. Local inversion symmetry breaking and spin-phonon coupling in the perovskite GdCrO₃. *Phys. Rev. B* **2017**, 96, 104106/1-9.
39. Dervishi, E.; Ji, Z.; Htoon, H.; Sykora, M.; Doorn, S. K. Raman spectroscopy of bottom-up synthesized graphene quantum dots: size and structure dependence. *Nanoscale* **2019**, 11, 16571-16581.
40. Shoji, T.; Sugo, D.; Nagasawa, F.; Murakoshi, K.; Kitamura, N.; Tsuboi, Y. Highly sensitive detection of organic molecules on the basis of a poly(N-isopropylacrylamide) microassembly formed by plasmonic optical trapping. *Anal. Chem.* **2017**, 89, 532-537.

41. Cialla-May, D.; Krafft, C.; Rosch, P.; Deckert-Gaudig, T.; Frosch, T.; Jahn, I. J.; Pahlow, S.; Stiebing, C.; Meyer-Zedler, T.; Bocklitz, T.; Schie, I.; Deckert, V.; Popp, J. Raman spectroscopy and imaging in bioanalytics. *Anal. Chem.* **2022**, 94, 86-119.
42. Helal, M. A.; Aftabuzzaman, M.; Tsukada, S.; Kojima, S. Role of polar nanoregions with weak random fields in Pb-based perovskite ferroelectrics. *Sci. Rep.* **2017**, 7, 44448/1-11.
43. Hildebrandt, R.; Sturm, C.; Wieneke, M.; Dadgar, A.; Grundmann, M. Raman tensor determination of transparent uniaxial crystals and their thin films—a-plane GaN as exemplary case. *Appl. Phys. Lett.* **2021**, 119, 121109/1-5.
43. Kranert, C.; Sturm, C.; Schmidt-Grund, R.; Grundmann, M. Raman Tensor Formalism for Optically Anisotropic Crystals. *Phys. Rev. Lett.* **2016**, 116, 127401/1-5.
45. Deluca, M.; Higashino, M.; Pezzotti, G. Raman tensor elements for tetragonal BaTiO₃ and their use for in-plane domain texture assessments. *Appl. Phys. Lett.* **2007**, 91, 091906/1-3.
46. Gray, D. J. Jr; Merz, T. A.; Hikita, Y.; Hwang, H. Y.; Mabuchi, H. Orientation-resolved domain mapping in tetragonal SrTiO₃ using polarized Raman spectroscopy. *Phys. Rev. B* **2016**, 94, 214107/1-8.
47. Ishigaki, T.; Hoshikawa, A.; Yonemura, M.; Morishima, T.; Kamiyama, T.; Oishi, R.; Aizawa, K.; Sakuma, T.; Tomota, Y.; Arai, M.; Hayashi, M.; Ebata, K.; Takano, Y.; Komatsuzaki, K.; Asano, H.; Takano, Y.; Kasao, T. IBARAKI materials design diffractometer (iMATERIA) – versatile neutron diffractometer at J-PARC. *Nucl. Instr. Methods Phys. Res. A* **2009**, 600, 189-191.

48. Oishi-Tomiyasu, R.; Yonemura, M.; Morishima, T.; Hoshikawa, A.; Torii, S.; Ishigaki T.; Kamiyama, T. Application of matrix decomposition algorithms for singular matrices to the Pawley method in Z-Rietveld. *J. Appl. Crystallogr.* **2012**, 45, 299–308.
49. Momma, K.; Izumi, F. VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *J. Appl. Crystallogr.* **2011**, 44, 1272–1276.
50. Fujii, Y.; Noju, M.; Shimizu, T.; Taniguchi, H.; Itoh, M.; Nishio, I. Raman Tensor Analysis of Crystalline Lead Titanate by Quantitative Polarized Spectroscopy. *Ferroelectrics* **2014**, 462, 8-13.
51. Gray, D. J.; Merz, T. A.; Hikita, Y.; Hwang, H. Y.; Mabuchi, H. Orientation-resolved domain mapping in tetragonal SrTiO₃ using polarized Raman spectroscopy. *Phys. Rev. B* **2016**, 94, 214107/1-8.
52. Kresse, G.; Furthmüller, J. Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set. *Comput. Mater. Sci.* **1996**, 6, 15–50.
53. Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, 54, 11169–11186.
54. Perdew, J. P.; Ruzsinszky, A.; Csonka, G. I.; Vydrov, O. A.; Scuseria, G. E.; Constantin, L. A.; Zhou, X.; Burke, K. Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces. *Phys. Rev. Lett.* **2008**, 100, 136406/1-4.

55. Capillas, C.; Aroyo, M. I.; Perez-Mato, J. M. Methods for Pseudosymmetry Evaluation: A Comparison between the Atomic Displacements and Electron Density Approaches. *Z. Kristallogr. Cryst. Mater.* **2005**, 220, 691–699.
56. Capillas, C.; Tasci, E. S.; De La Flor, G.; Orobengoa, D.; Perez-Mato, J. M.; Aroyo, M. I. A New Computer Tool at the Bilbao Crystallographic Server to Detect and Characterize Pseudosymmetry. *Z. Kristallog.* **2011**, 226, 186–196.
57. Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A Climbing Image Nudged Elastic Band Method for Finding Saddle Points and Minimum Energy Paths. *J. Chem. Phys.* **2000**, 113, 9901–9904.
58. King-Smith, R. D.; Vanderbilt, D. Theory of Polarization of Crystalline Solids. *Phys. Rev. B* **1993**, 47, 1651–1654.
59. Borisevich, A. Y.; Ovchinnikov, O. S.; Chang, H. J.; Oxley, M. P.; Yu, P.; Seidel, J.; Eliseev, E. A.; Morozovska, A. N.; Ramesh, R.; Pennycook, S. J.; Kalinin, S. V. Mapping octahedral tilts and polarization across a domain wall in BiFeO₃ from Z-contrast scanning transmission electron microscopy. *ACS Nano* **2010**, 4, 6071–6079.
60. Findlay, S. D.; Shibata, N.; Sawada, H.; Okunishi, E.; Kondo, Y.; Ikuhara, Y. Dynamics of annular bright field imaging in scanning transmission electron microscopy. *Ultramicroscopy* **2010**, 110, 903–923.
61. Son, Y. G.; Jeong, I. K. High-Pressure Raman Spectroscopy of Perovskite Oxynitride SrTaO₂N. *J. Korean Phys. Soc.* **2016**, 69, 822–825.

62. Moriwake, H.; Konishi, A.; Ogawa, T.; Fisher, C. A. J.; Kuwabara, A.; Shitara, K.; Fu, D. Polarization fluctuations in the perovskite-structured ferroelectric AgNbO_3 . *Phys Rev B* **2018**, 97, 224104/1-6.
63. Carreaud, J.; Bogicevic, C.; Dkhil, B.; Kiat, J. M. Dielectric evidences of core-shell-like effects in nanosized relaxor $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$. *Appl. Phys. Lett.* **2008**, 92, 242902/1-3.
64. Hosono, A. Study on Microcrystals and Ceramics of Ferroelectric BaTaO_2N Oxynitride Perovskite. Hokkaido University, **2020**, 1-200. doi.org/10.14943/doctoral.k14024, <http://hdl.handle.net/2115/78317>.

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