Constant-wavelength neutron diffraction study of cubic perovskites BaTaO₂N and BaNbO₂N

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Local structural disorder of perovskite oxynitrides BaTaO₂N and BaNbO₂N is investigated by constant-wavelength neutron powder diffraction measurements at 300 and 6 K. Temperature-dependent diffraction line-broadening analyses together with the Rietveld refinements confirm that both perovskites retain average structures of simple cubic symmetry down to 6 K. While the Ta and Nb atoms in the above oxynitrides have remarkably large displacement parameters, indicative of pronounced octahedral distortions, the rigidity of Ba sublattice seems to suppress the cooperative propagation of long-range octahedral tilting.

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The perovskite-type oxynitrides emerged recently as a promising material class for developing pigments,^{1,2)} photocatalysts,^{3–5)} dielectrics,^{6–8)} colossal magnetoresistance,^{9,10)} etc. The functionalities relevant to above applications stem primarily from the coexistence of nitrogen and oxygen atoms within the anion sublattice. Nitrogen being more polarizable and less electronegative than oxygen, the oxynitride-type compounds generally have narrower band gaps and more covalent metal-anion bonds, compared with the analogous oxides. Such modifications in the electronic structure and the bonding nature have immediate impacts on the range of optical absorption and dielectric behaviors.⁶⁾

Besides the above described electronic effects, the mixed anion composition in oxynitrides presents intriguing structural subjects: anion ordering and local structural disorder. These two phenomena occur contrariwise to each other. That is, a complete O/N ordering in oxynitrides corresponds to an absence of local structural disorder, whereas a statistical O/N distribution means a substantial disruption of the lattice periodicity. Particularly the primitive cubic perovskites BaTaO₂N and BaNbO₂N are regarded to have purely random O/N arrangements in the anion sublattice, and hence to be typical examples in which the local and average structural descriptions largely deviate. In fact, while the conventional diffraction studies using X-ray⁶⁾ and neutron¹¹⁾ radiations invariably indicated an average structure of $Pm\bar{3}m$ symmetry for BaTaO₂N and BaNbO₂N, the zone-axis electron diffraction (ED),¹²⁾ extended X-ray absorption fine structure (EXAFS),¹³⁾ and pair-distribution-function (PDF)¹⁴⁾ analyses for BaTaO₂N revealed evidences supporting short-range structural distortions around Ta atoms. On the one hand, above inconsistency reflects the sensitivity of the latter local probes to short-range structural phenomena, but on the other hand, it raises a question: Would there be no local information retrievable from the bulk diffraction analysis of the above oxynitride perovskites? At this point it can be mentioned that the previous neutron powder diffraction (NPD) study of BaTaO₂N and BaNbO₂N, conducted at 300 and 4 K employing the time-of-flight method, has reported only brief structural parameters leaving a room for

in-depth discussions.¹¹⁾ In this regard, we performed a constant-wavelength NPD study of BaTaO₂N and BaNbO₂N at 300 and 6 K paying careful attention to various diffraction features such as temperature-dependent evolutions of peak widths and occurrence of extra reflections as well as the Rietveld fit parameters. It is shown that among others the atomic displacement parameters (U_{iso}) can serve as useful indicators of the local lattice disorder, especially when an explicit structural transition cannot be defined on the average scale.

Powder samples of BaTaO₂N and BaNbO₂N were prepared by ammonolysis using BaCO₃ (Aldrich, 99.98%), Ta₂O₅ (Aldrich, 99.99%), and Nb₂O₅ (Aldrich, 99.99%). Stoichiometric amounts of powder reagents were thoroughly mixed in ethanol using an agate mortar and pestle for 1.5 h. The reactant mixture was heated at 1273 K for BaTaO₂N and at 1223 K for BaNbO₂N for total of 60 h, with intermittent grindings, in ammonia flow of ≈ 50 sccm. For a reference, KTaO₃ were also prepared by heating a stoichiometric mixture of K₂CO₃ (Alfa-Aesar, 99.0%) and Ta₂O₅ (Aldrich, 99.99%) at 1273 K for 60 h in air.

Constant-wavelength NPD data were collected on high resolution powder diffractometer (HRPD) installed at HANARO facility in Korea Atomic Energy Research Institute (KAERI). The HANARO-HRPD system is equipped with a Ge(331) monochromator and a 32-channel ³He multi-detector system. Powder sample was packed in a vanadium can which was then mounted in a closed cycle helium refrigerator. We used ≈ 7.5 g of BaTaO₂N, ≈ 4.8 g of BaNbO₂N, and ≈ 5.2 g of KTaO₃. The data were collected at 300 and 6 K for BaTaO₂N and BaNbO₂N, and at 300 K for KTaO₃, with a wavelength of 1.8367 Å over the 2θ range 10–155° at a step size 0.05°. The GSAS-EXPGUI software suite^{15,16)} was employed for the structure refinement by Rietveld method and also for constructing Fourier maps.

The pentavalent cations Ta⁺⁵ and Nb⁺⁵ have nearly the same ionic radii,¹⁷⁾ $r = 0.64$ Å (CN = 6), and their coherent neutron-scattering lengths are also very similar,¹⁸⁾ 6.9 fm for Ta and 7.1 fm for Nb. Accordingly BaTaO₂N and BaNbO₂N are isostructural and exhibit very similar NPD patterns at 300 K, which correspond to the typical primitive cubic perovskite structure. Although the geometric consideration based on the perovskite tolerance factor (τ)¹⁹⁾ and the inequity of Ta(Nb)–O/

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Fig. 1. Rietveld refinement of NPD patterns collected at 300 K for (a) BaTaO₂N and (b) BaNbO₂N. The measured (circles), calculated (lines), and difference (lower lines) profiles are shown. Tick marks indicate allowed reflections.

Ta(Nb)–N bonds within BaTaO₂N and BaNbO₂N are incompatible with the $Pm\bar{3}m$ symmetry, neither compound exhibited explicit indications (peak splittings or supercell diffractions) of structural deviation from the simple cubic cell. The Rietveld refinements in space group $Pm\bar{3}m$ with Ba at 1a (0, 0, 0), Ta(Nb) at 1b (1/2, 1/2, 1/2), and O/N at 3c (0, 1/2, 1/2) sites converged with $R_{wp} = 5.2\%$ for BaTaO₂N and $R_{wp} = 5.1\%$ for BaNbO₂N (Fig. 1). The refined a parameters, 4.1129(1) Å for BaTaO₂N and 4.1267(1) Å for BaNbO₂N agree well to the previous reports.^{6,11} From the refinements of atomic site occupancies the compositions of the above oxynitrides were found as BaTa_{1.000(4)}O_{0.667}N_{0.326(2)} and BaNb_{1.008(3)}O_{0.667}N_{0.324(2)}, very close to the ideal stoichiometry. Here it can be mentioned that the atomic occupancy has correlations with the displacement parameter and the scale factor as well. In order to avoid complication, we fixed the scale factor during the simultaneous refinements of atomic occupancies and displacement parameters. We also examined the possibilities of O/N ordering or the pseudo-cubic tetragonal distortion in above oxynitrides by the Rietveld analysis using alternative structure models based on $P4mm$, $P4/mmm$, $P43m$, or $P432$ symmetries, but observed little improvements in the refinement R -factors.

Although the Rietveld refinement revealed no compelling evidence against the $Pm\bar{3}m$ type structure solution for BaTaO₂N and BaNbO₂N, we could recognize that several atoms in those compounds possess unusually large isotropic displacement parameters. Table 1 lists the refined U_{iso} values of all the constituents in BaTaO₂N and BaNbO₂N, together with those of a

Table 1. Isotropic atomic displacement parameters U_{iso} (Å² × 100) for BaTaO₂N, BaNbO₂N, and KTaO₃

Atom	T/K	BaTaO ₂ N ^a	BaNbO ₂ N ^a	KTaO ₃ ^a	BaTaO ₂ N ^b	BaNbO ₂ N ^b
Ba(K)	300	0.56(3)	0.45(2)			
	6	0.24(3)	0.19(3)	0.53(4)	0.54	0.53
Ta(Nb)	300	0.98(2)	0.91(2)			
	6	0.73(2)	0.68(2)	0.25(2)	0.62	0.98
O/N	300	0.91(3)	0.90(2)			
	6	0.67(2)	0.60(2)	0.60(2)	0.70	0.87

^aThis work.

^bFrom Ref. 11. Originally reported in the form of B_{iso} , and converted using the relation $B_{iso} = 8\pi^2 U_{iso}$.

model cubic perovskite KTaO₃. In general the atomic displacement parameter should be negatively correlated with the atomic mass, if the atomic vibrations are induced solely by the thermal factors. Such a trend is well represented in the case of KTaO₃. However in the oxynitride perovskites, the octahedral Ta and Nb atoms were found with markedly large U_{iso} parameters, nearly four times that of Ta atom in KTaO₃. It was also found that the anion components in BaTaO₂N and BaNbO₂N have somewhat larger U_{iso} values than O atom in KTaO₃. In contrast, the dodecahedral Ba atoms in BaTaO₂N and BaNbO₂N showed very similar U_{iso} values to that of K atom in KTaO₃. These findings allow us to depict the local structures of BaTaO₂N and BaNbO₂N as followed. The octahedral units in above oxynitride perovskites are more or less distorted at least dynamically, and possibly they have static disorders in a non-cooperative fashion. It is noteworthy that the Ba atoms in above oxynitrides show U_{iso} values in normal ranges, implying that the Ba sublattices maintain the ideal cubic arrangement despite the substantial distortion of neighboring octahedral network. We postulate that the well-ordered geometry of Ba sublattice plays a crucial role for realizing the cubic symmetry of BaTaO₂N and BaNbO₂N on average.

In order to further study the local atomic motions in oxynitride perovskites, we have constructed observed (F_{obs}) and difference ($\Delta F = F_{obs} - F_{cal}$) Fourier maps for BaNbO₂N, as presented in Fig. 2. The plots for BaTaO₂N, examined in the same manner, were found to contain practically equivalent features to those of BaNbO₂N. The F_{obs} maps shown in Figs. 2(a) and 2(b) visualize the nuclear density distributions, where we can notice that Nb is more widely distributed around its equilibrium position than Ba or O/N. This finding well accords with the large U_{iso} parameter of Nb atom, pointed out ahead. The difference maps given in Figs. 2(c) and 2(d) provide information on the directionality of the atomic displacements. Both Ba and Nb appear to have localized motion preferentially towards the polyhedral edges, along (110) for Nb and (100) for Ba.

Given the non-ideal packing geometry of BaTaO₂N and BaNbO₂N,¹⁹ it is of interest to investigate whether they display any structural evolution upon cooling. The Rietveld refinement of 6 K NPD data showed that both BaTaO₂N and BaNbO₂N maintain the room temperature crystal symmetry. The lattice parameters at 6 K were determined as 4.1049(1) Å for BaTaO₂N and 4.11604(6) Å for BaNbO₂N, corresponding to the linear cell contraction of 7 and 9 ppm/K, respectively. For each oxynitride, the composition refined using 6 K data agreed with the result from 300 K data, within one standard deviation. Again the use of tetragonal models for 6 K data resulted in only trivial improvements of the Rietveld fit, compared with the cubic model. In order to ascertain the absence of symmetry-lowering,

Fig. 2. Fourier nuclear density maps (a, b) F_{obs} and (c, d) ΔF for BaNbO_2N . (a) and (c) correspond to the plane $z = 1/2$ with Nb at the center, whereas (b) and (d) correspond to the plane $z = 0$ with Ba at the center. The contours are shown at intervals of $0.2 \text{ fm } \text{\AA}^{-3}$ for F_{obs} , and $0.02 \text{ fm } \text{\AA}^{-3}$ for ΔF . Dotted lines indicate negative contours.

we have examined the temperature-dependent evolution of diffraction line-widths. We assume that even a subtle departure from the cubic unit cell and the consequent peak splitting will accompany discernible broadening of diffraction lines, especially at higher 2θ angles and at lower temperatures. For the NPD patterns of BaTaO_2N , BaNbO_2N , and Si standard (NIST SRM640d), diffraction peak widths (full-width-at-half-maximum) were determined by the fitting with software XFIT.²⁰⁾ As shown in Fig. 3, the peak widths for BaTaO_2N and BaNbO_2N vary with second-order polynomial dependences on the 2θ value, quite similarly to those for SRM640d. Overall, the peak widths for BaTaO_2N and BaNbO_2N are somewhat larger than those of SRM640d, which is attributable to the size and strain broadening effects²¹⁾ in oxynitride samples. On the other hand, the peak widths for BaTaO_2N and BaNbO_2N do not show any temperature-dependences, as does SRM640d. Such an invariance of peak width can be firm evidence that both BaTaO_2N and BaNbO_2N have the average structure of cubic symmetry in the entire range between ambient and cryogenic temperatures. As well demonstrated by the present examples, we suggest that the temperature-dependence of peak widths can serve as a useful clue for examining the symmetry evolutions in crystals.

In summary, we utilized the constant-wavelength NPD technique to address the structural characteristics of oxynitride perovskites BaTaO_2N and BaNbO_2N . While both compounds contain considerably distorted octahedral network, their average structures remain as the primitive cubic symmetry, which we attribute to the rigidity of Ba sublattice. The anion disorder and the local structural distortion are deemed as inherent structural behaviors of oxynitride compounds, and present potentials for deriving unique material functions. In particular, the marked atomic displacements in BaTaO_2N and BaNbO_2N are promising for applications areas such as thermoelectric²²⁾ and relaxor-ferroelectrics.

Fig. 3. NPD peak widths for (a) Si standard, (b) BaTaO_2N , and (c) BaNbO_2N , measured at 300 K (circles) and 6 K (crosses).

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References

- 1) M. Jansen and H. P. Lertschert, *Nature*, **404**, 980–982 (2000).
- 2) F. Chevre, F. Tessier and R. Marchand, *Eur. J. Inorg. Chem.*, **6**, 1223–1230 (2006).
- 3) M. Higashi, R. Abe, T. Takata and K. Domen, *Chem. Mater.*, **21**, 1543–1549 (2009).
- 4) A. Kasahara, K. Nukumizu, T. Takata, J. N. Kondo, M. Hara, H. Kobayashi and K. Domen, *J. Phys. Chem. B*, **107**, 791–797 (2003).
- 5) K. Maeda and K. Domen, *J. Phys. Chem. C*, **111**, 7851–7861 (2007).
- 6) Y.-I. Kim, P. M. Woodward, K. Baba-Kishi and C.-W. Tai, *Chem. Mater.*, **16**, 1267–1276 (2004).
- 7) Y.-I. Kim, W. Si, P. M. Woodward, K. E. Sutter, S. Park and T. Vogt, *Chem. Mater.*, **19**, 618–623 (2007).
- 8) A. Ziani, C. Le Paven-Thivet, L. Le Gendre, D. Fasquelle, J. C. Carru, F. Tessier and J. Pinel, *Thin Solid Films*, **517**, 544–549 (2008).
- 9) A. B. Jorge, J. Oro-Sole, A. M. Bea, N. Mufti, T. T. M. Palstra, J. A. Rodgers, J. P. Attfield and A. Fuentes, *J. Am. Chem. Soc.*, **130**, 12572–12573 (2008).
- 10) A. Kusmartseva, M. Yang, J. Oro-Sole, A. M. Bea, A. Fuentes and J. P. Attfield, *Appl. Phys. Lett.*, **95**, 022110 (2009).
- 11) F. Pors, R. Marchand, Y. Laurent, P. Bacher and G. Rault,

- Mater. Res. Bull.*, **23**, 1447–1450 (1988).
- 12) R. L. Withers, Y. Liu, P. M. Woodward and Y.-I. Kim, *Appl. Phys. Lett.*, **92**, 102907 (2008).
- 13) B. Ravel, Y.-I. Kim, P. M. Woodward and C. M. Fang, *Phys. Rev. B*, **73**, 184121 (2006).
- 14) K. Page, M. W. Stoltzfus, Y.-I. Kim, T. Proffen, P. M. Woodward, A. K. Cheetham and R. Seshadri, *Chem. Mater.*, **19**, 4037–4042 (2007).
- 15) A. C. Larson and R. B. von Dreele, “Los Alamos National Laboratory Report No. LAUR 86-748”, (1994).
- 16) B. H. Toby, *J. Appl. Cryst.*, **34**, 210–213 (2001).
- 17) R. D. Shannon, *Acta Crystallogr., Sect. A: Cryst. Phys., Diffraction, Theor. Gen. Crystallogr.*, **32**, 751–767 (1976).
- 18) V. F. Sears, *Neutron News*, **3**, 26–37 (1992).
- 19) For a perovskite AMX₃, tolerance factor is defined as $\tau = (r_A + r_X)/\sqrt{2}(r_M + r_X)$ which is unity for the ideal cubic perovskite structure. Using the ionic radii of Ba⁺² (1.61 Å), Ta⁺⁵ (0.64 Å), Nb⁺⁵ (0.64 Å), O⁻² (1.4 Å), and N⁻³ (1.5 Å), $\tau = 1.04$ for both BaTaO₂N and BaNbO₂N.
- 20) R. W. Cheary and A. A. Coelho, “XFIT-Koalariet”, Daresbury Laboratory, Warrington (1996). Available from <http://www.ccp14.ac.uk>.
- 21) R. A. Young, “The Rietveld Method”, Oxford University Press, New York (1993).
- 22) B. C. Sales, B. C. Chakoumakos, D. Mandrus and J. W. Sharp, *J. Solid State Chem.*, **146**, 528–532 (1999).