

Formation Condition and Ferroelectric Properties of Niobate Tetragonal Tungsten Bronze (TTB) Type Ferroelectrics

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Crystal structure of $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ was tried to determine by Rietveld analysis using powder X-ray diffraction data. This compound has tetragonal tungsten bronze (TTB) structure with general formula, $(A1)_2(A2)_4(B1)_2(B2)_8(O1)_8(O2)_8(O3)_4(O4)_2(O5)_4(O6)_4$. However, it was difficult to determine the distribution of Ba and Y in A1 and A2 sites by the analysis only. Combination of Rietveld analysis and site potentials calculation as well as lattice energy calculations helped to determine the distribution. As the result, it was clarified that Ba^{2+} cations occupy A2 (pentagonal tunnel site) and Y^{3+} cations occupy A1 (cubic site). The distribution of cations at each site coincides with the distribution estimated by the difference of ionic radii. This supports the formation condition of TTB which was proposed in our previous report. $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ shows ferroelectric characteristics. In this compound, remanent polarization decreases slightly with the composition X. On the other hand, the result of crystal structure determination reveals that atomic positions along c-axis for A1, A2, B1 and B2 cations are also decreased with the composition X. This would suggest that the dependence of remanent polarization on composition X is derived by the dependence of atomic coordinates on composition X.

Key words: Tetragonal tungsten bronze, Crystal structure, Ferroelectricity, New compound, $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$

I. Introduction

Pb(Zr,Ti)O₃ is regarded as one of the most promising ferroelectric materials due to its high remanent polarization for non-volatile ferroelectric random access memory (FR-AM) application so far. Since lead is a toxic element and it is not desired for ecological aspect, lead-free ferroelectric material such as bismuth-layer-structure-ferroelectrics (BL-SF¹), i.e., Bi₄Ti₃O₁₂²⁾ and SrBi₂Ta₂O₉ (SBT or Y1)³⁾ are considered to use for FRAM. However vapor pressure of bismuth is not so low and it is also not suitable for silicon technology.

Most compounds with tetragonal tungsten bronze (TTB) structure show ferroelectric characteristics. Representative tungsten bronze type compounds are (Sr,Ba)Nb₂O₆ (SBN), (Pb,Ba)Nb₂O₆ (PBN) and Ba₄Na₂Nb₁₀O₃₀ (BNN). However, these materials are not suitable for FRAM. Since SBN has high dielectric constant,⁴⁾ PBN contains toxic and volatile lead and BNN contains volatile sodium. These elements are detrimental for silicon technology. From these points, ferroelectric compounds with low dielectric constant without lead, alkali and any other volatile elements are desired.

TTB type compounds with formula, $Ba_{5-5X}R_{10X/3}Nb_{10}O_{30}$ (R=La, Sm and Y) were once reported by Masuno in 1964.⁵⁾ However, formation of TTB type compounds for other rare earth cations as well as their characteristics have not been reported. Moreover, the possibility for FRAM application has not been investigated. In our previous paper, synthesis

of a series of new TTB type compounds having general formula, $Ba_{3.75}R_{0.833}Nb_{10}O_{30}$ (R=Nd, Eu, Gd, Dy, Ho and Er) has been reported.⁶⁾

The target of this work is to clarify the distribution of cation for each site for $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ and to clarify the relationship between ferroelectric characteristics and crystal structure as a representative of TTB type compound with general formula, $Ba_{5-5X}R_{10X/3}Nb_{10}O_{30}$.

II. Experimental Procedure

The specimens were prepared by a conventional solid state reaction from starting materials of reagent grade BaCO₃, Y₂O₃ and Nb₂O₅. These starting materials were weighted according to the following composition: $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ where X=0.1–0.6. The powders were mixed by ball-milling in ethanol with zirconia balls for 20 h. The resultant slurries were then dried using a rotary evaporator. The powder mixtures were pressed into pellets and calcined at 900°C for 2 h in air. Then the pellets were ground and pressed into pellets. The pellets were put in the platinum crucible and sintered at 1,300°C for 4 h in air.

Powder X-ray diffraction data were collected on a Philips PW-1700 powder diffractometer system operated at 40 kV and 30 mA using graphite-monochromated CuK α X-rays. For identification, lattice parameters calculation and Rietveld analysis intensity data were collected for 2.5 second at 0.01°2 θ intervals over the range between 10 and

140°2 θ . Lattice parameters were calculated using "RLC-3"⁷. Rietveld analysis was carried out using a program "RIFTAN"⁸ was used. Site potential and lattice energy calculations were carried out using a program "MADEL."⁹ Macintosh personal computer was used for these calculations.

Electrical characteristics were measured for the pellets. The pellets were polished and painted platinum paste on both surfaces of the pellet and fired at 800°C for 1h. Ferroelectric properties such as P-E hysteresis curves were measured using RT-66A (Radiant Technology).

III. Results and Discussion

1. Crystal structure determination for $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$

Powder X-ray diffraction spectra can be indexed as tetragonal symmetry with lattice parameters of $a=1.24449$ nm and $c=0.394200$ nm. General formula of TTB type compounds can be expressed as $(A1)_2(A2)_4(B1)_2(B2)_8(O1)_8(O2)_8(O3)_4(O4)_2(O5)_4(O6)_4$.¹⁰ Schematic drawing of TTB type compounds along c-axis is shown in Fig. 1. In the TTB type compounds, it is regarded that the structure is consisted of the network of corner sharing BO_6 octahedra, therefore, the B sites (both B1 and B2 sites) are believed to be fully occupied.¹¹ On the contrary, vacancies are often observed at the A sites. In addition to the distribution of vacancies, the distribution of cations at A1 (pentagonal site having 15-fold coordination) and A2 (cubic site 12-fold coordination) sites are also complicated. For example, in SBN, it was reported that A1 site is consisted of Sr (occupancy, $G=0.822$) while A2 site is consisted of 0.406Ba/0.594Sr ($G=0.847$).¹² Another example is $Pb_{0.596}Ba_{0.404}Nb_{2.037}O_6$.¹³ In this compound, A1 site is occupied by Pb ($G=0.551\%$) and A2 site is occupied by 0.475Pb/0.500Ba ($G=0.975$).

Therefore the crystal structure of $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$ was

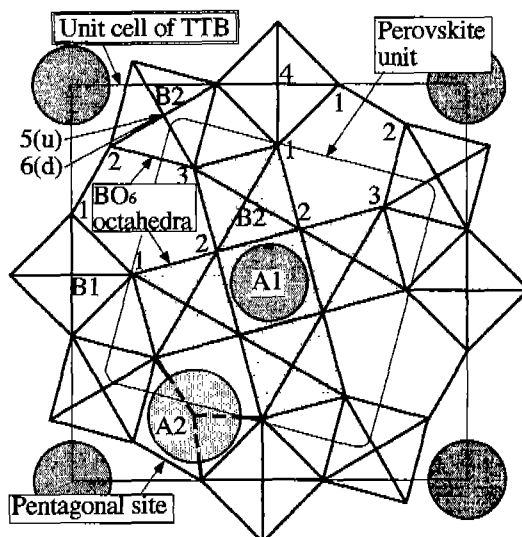


Fig. 1. Schematic drawing of TTB type compounds along c-axis.

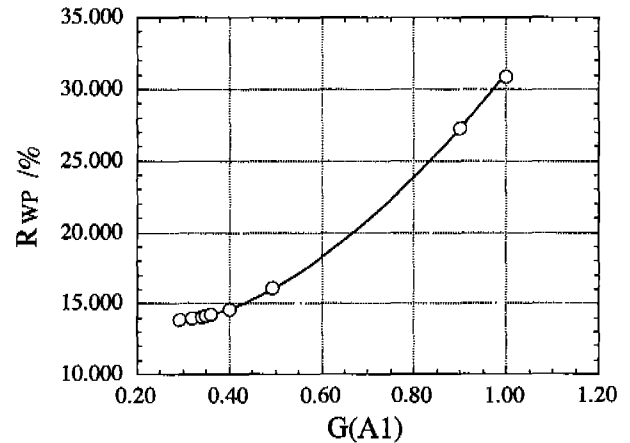


Fig. 2. Change of Rwp and site occupancy G at A1 site on the basis of Model-5.

tried to determine by the following four models and the Rwp-factors were compared.

[Model-1] Y and Ba occupy A1 and A2 site, respectively;

A1 site is occupied by Y ($G=0.830$) and A2 site is occupied by Ba ($G=0.895$)

[Model-2] Both A1 and A2 sites are occupied by imaginary element of 0.1818Y/0.8182Ba with same occupancies ($G=0.7638$)

[Model-3] Supposing partially substitution (10%) of Ba at A1 site;

A1 site is occupied by 0.6896Y/0.3104Ba ($G=0.6042$) and A2 site is occupied by Ba ($G=0.8438$)

[Model-4] Y occupies A2 site;

A1 site is occupied by Ba only ($G=0.7638$) and A2 site is occupied by 0.2726Y/0.7274Ba ($G=0.7638$)

[Model-5] Both A1 and A2 sites are occupied by imaginary element of 0.1818Y/0.8182Ba with same occupancies as Model-2, however, G is different between A1 and A2 sites.

Model-1, 2, 3 and 4 gives final R_{wp} values of 13.32, 22.58, 16.21 and 24.08%, respectively. This result suggests that Model-1 is plausible and Y and Ba occupy A1 and A2 site independently. However, the result of Model-5 also gives same R_{wp} value (=13.32%) was obtained at occupancy G at A1 site is 0.2915 (G at A2 is 1.0000). These results show that it is difficult to determine the distribution of cations and vacancies by powder X-ray diffraction only. Therefore from the Rietveld analysis, two possibilities of distribution on cations can be suggested for $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$, i.e., Model-1 and Model-5 with $G(A1)=0.2915$.

2. Site potential and lattice energy calculations

Determination of the distribution of cations and vacancies in $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$ is very important to consider the formation condition for this compounds. Therefore site potentials and lattice energy calculations were tried for the two probable models, i.e., model-1 and Model-5 with $G(A1)=0.2915$. Table 1 shows the result of the calculations for the

Table 1. Calculation of Site Potentials and Lattice Energy for Model-1 and Model-5

	Model-1		Model-5	
	Species	Potential	Species	Potential
$\phi(A1)/\text{\AA}^{-1}$	Y^{3+}	-2.028	$0.1818Y^{3+}$ $0.8182Ba^{2+}$	-2.4124
$\phi(A2)/\text{\AA}^{-1}$	Ba^{2+}	-0.5406	Ba^{2+}	0.1405
$\phi(B1)/\text{\AA}^{-1}$	Nb^{5+}	-2.8167	Nb^{5+}	-1.9253
$\phi(B2)/\text{\AA}^{-1}$	Nb^{5+}	-1.3889	Nb^{5+}	-0.5939
$\phi(O1)/\text{\AA}^{-1}$	O^{2-}	0.4803	O^{2-}	0.7179
$\phi(O2)/\text{\AA}^{-1}$	O^{2-}	1.3258	O^{2-}	1.4
$\phi(O3)/\text{\AA}^{-1}$	O^{2-}	1.1223	O^{2-}	1.5142
$\phi(O4)/\text{\AA}^{-1}$	O^{2-}	-0.3971	O^{2-}	-0.9284
$\phi(O5)/\text{\AA}^{-1}$	O^{2-}	2.0717	O^{2-}	1.0649
$\phi(O6)/\text{\AA}^{-1}$	O^{2-}	1.4873	O^{2-}	1.1423
Lattice Energy/ kcal/mol		-155,300		-100,700

two models. Table 1 indicates that site potentials of each cation for Model-1 are deeper than those for Model-5. In Model-5, site potentials for cations are occasionally take shallow or positive values which means that such occupation condition is not stable.

As shown in Table 1, lattice energy for Model-1 turned out to be -155,300 kcal/mol while for Model-5, it turned out to be -100,700 kcal/mol. This result also indicates that distribution of cations and vacancies for Model-1 is much more stable than that for Model-5. Therefore, it can be considered that Model-1 is reliable.

In general there is a tendency that cations with large ionic radii occupy large A2 sites (pentagonal tunnel sites) and those with small ionic radii occupy A1 sites (cubic sites). Actually, in SBN, PBN and $Pb_2KTa_5O_{15}$,¹⁴⁾ larger cations occupy the A2 sites. In $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$, ionic radii of Ba^{2+} is larger than that of Y^{3+} . Therefore it is expected that Ba^{2+} would occupy A2 sites. The result of site potential and lattice energy calculations also agrees with this consideration from the point of the size of cations.

In our previous report,⁶⁾ two kinds of tolerance factors for both A1 and A2 sites were proposed to estimate the stability of TTB type compound. In the course of calculation, the distribution of cations at A1 and A2 sites for $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$ were speculated that A2 site was occupied by large Ba^{2+} cations and A1 site was occupied by small Y^{3+} cations. Consequently, the results of the combination of the Rietveld analysis and site potential and lattice energy calculations supports the proposed formation conditions.

In this way, crystal structure of $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$ was determined by the combination of Rietveld analysis and site potentials and lattice energy calculations. Powder X-ray diffraction data for the compounds were shown in Table 2.

3. Ferroelectric characteristics and crystal structure of $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$

For $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$, the direction of polarization is con-

Table 2. Powder X-ray Diffraction Data for $Ba_{3.75}Y_{0.833}Nb_{10}O_{30}$

h	k	l	d	I(obs)	I(calc)	h	k	l	d	I(obs)	I(calc)
2	2	0	4.40023	981	502	6	4	0	1.72591	28	28
0	0	1	3.94222	21728	20677	3	2	2	1.71169	7278	7526
3	1	0	3.93568	9433	8969	7	2	0	1.70955	1820	1878
1	1	1	3.59774	597	467	6	3	1	1.67869	11966	12151
3	2	0	3.45182	35636	32312	4	0	2	1.6651	1169	1200
2	0	1	3.3302	15991	14304	4	1	2	1.6504	31871	31944
2	1	1	3.21703	92732	88373	3	3	2	1.63607	8373	8194
4	0	0	3.11143	4545	4349	7	3	0	1.6342	1050	1022
4	1	0	3.01853	100000	98276	4	2	2	1.60851	8705	8067
2	2	1	2.93619	22003	22201	7	1	1	1.60718	15506	14374
3	3	0	2.93348	27636	27653	5	5	1	1.60718	5508	5105
3	1	1	2.78525	83200	83604	6	5	0	1.59351	838	790
4	2	0	2.78295	21038	21136	6	4	1	1.58103	658	713
3	2	1	2.59698	23570	24001	7	2	1	1.56843	5682	6078
4	3	0	2.48914	32	30	8	0	0	1.55571	2976	3056
4	0	1	2.44236	9517	9073	4	3	2	1.54528	8	9
5	1	0	2.44081	556	529	7	4	0	1.5437	4258	4400
4	1	1	2.39665	1195	1139	8	1	0	1.5437	1598	1651
3	3	1	2.35341	3367	3277	5	1	2	1.5335	114	121
5	2	0	2.31111	6512	6426	7	3	1	1.50963	660	701
4	2	1	2.27352	244	237	8	2	0	1.50927	6148	6530
4	4	0	2.20011	1223	1041	5	2	2	1.49973	1773	1854
5	3	0	2.13442	14941	15106	6	5	1	1.47738	2456	2287
4	3	1	2.10471	760	757	4	4	2	1.46809	555	496
5	1	1	2.07524	1023	1040	6	6	0	1.46674	3940	3542
6	0	0	2.07429	3873	3910	8	3	0	1.45666	5026	4558
6	1	0	2.04606	589	538	5	3	2	1.44808	6509	5953
5	2	1	1.99376	4588	4408	8	0	1	1.44711	16	15
0	0	2	1.97111	31329	30458	7	5	0	1.44679	1846	1699
6	2	0	1.96784	7929	7713	7	4	1	1.43743	2471	2279
5	4	0	1.94369	339	334	8	1	1	1.43743	1235	1139
1	1	2	1.92345	322	277	6	0	2	1.42887	1762	1650
4	4	1	1.92117	261	210	6	1	2	1.41954	289	262
2	0	2	1.87909	785	720	8	2	1	1.4095	221	201
5	3	1	1.87697	3892	3599	6	2	2	1.39263	3792	3652
2	1	2	1.85804	749	724	8	4	0	1.39147	696	670
6	3	0	1.8553	13280	12891	5	4	2	1.38399	171	163
6	0	1	1.83568	11131	10593	6	6	1	1.37468	543	543
6	1	1	1.81603	384	384	9	1	0	1.3744	614	615
2	2	2	1.79887	410	403	8	3	1	1.36637	4209	4198
3	1	2	1.76243	1574	1573	7	5	1	1.35821	1986	2048
6	2	1	1.76067	25203	25242	6	3	2	1.35098	6034	6357
7	1	0	1.76009	13158	13180	7	6	0	1.34993	73	78
5	5	0	1.76009	10407	10424	9	2	0	1.34993	15	16
5	4	1	1.74332	21777	21808						

sidered to lie along c-axis¹⁰⁾ by the application of axial ratio calculation reported by Giess.¹⁶⁾ Guo *et al.*¹³⁾ have reported that macroscopic ferroelectric polarization of TTB type compound can be calculated qualitatively on the basis of the atomic coordinate if the polarization direction is along the c-

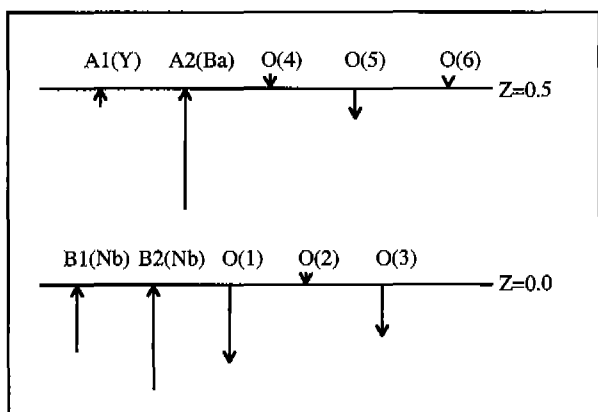


Fig. 3. Magnitude and sense of atomic displacements (in atomic coordinates) along the c-axis. Macroscopic polarization is indicated by the large arrow.

axis. Fig. 3 shows magnitude and sense of atomic displacements (in atomic coordinates) along the c-axis. Macroscopic polarization is indicated by the large arrow. For oxygen, the atomic coordinates along the c-axis were almost constant with the increase of X. The positions of cations were considered in the following discussion.

In $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ system, single phase TTB was obtained for $X=0.2, 0.25$ and 0.3 . For $X=0.4$, a small amount of $YNbO_4$ was detected. Fig. 4 shows change of atomic coordinates along c-axis with composition X. In this figure, change of remanent polarization with composition X is also plotted. This figure indicates that atomic coordinates along c-axis for A1, A2, B1 and B2 decreases with the increase of X. Fig. 4 also shows that remanent polarization has tendency to decrease slightly with composition X. Therefore it would be mentioned that the dependence of remanent polarization on composition X is derived by the dependence of atomic coordinates on composition X.

IV. Conclusions

In this work, the crystal structure and distribution of cations and vacancies for $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ were determined by the combination of Rietveld analysis using powder X-ray diffraction and site potentials and lattice energy calculations. As the result it was clarified that this compound has the tetragonal tungsten bronze (TTB) structure with a general formula, $(A1)_2(A2)_4(B1)_2(B2)_8(O1)_8(O2)_8(O3)_4(O4)_2(O5)_4(O6)_4$ and Ba^{2+} cations occupy A2 (pentagonal tunnel site) and Y^{3+} cations occupy A1 (cubic site). The distribution of cations at each site coincides with the distribution estimated by the difference of ionic radii. This supports the formation condition of TTB which was proposed in our previous report. $Ba_{5-5X}Y_{10X/3}Nb_{10}O_{30}$ shows ferroelectric characteristics.

In this compound, remanent polarization decreases slightly with the composition X. On the other hand, the result of crystal structure determination reveals that atomic posi-

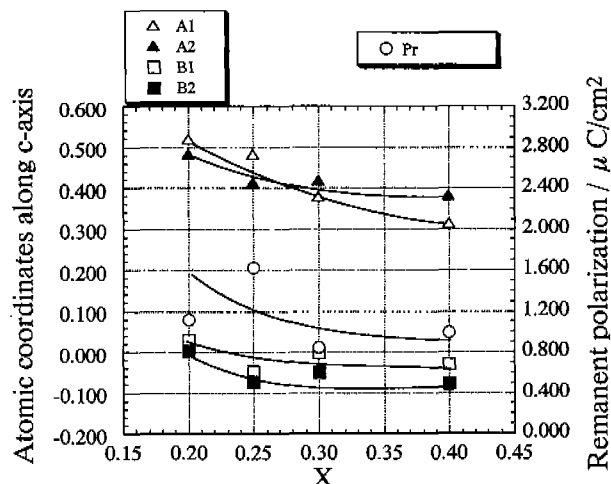


Fig. 4. Change of atomic coordinates along c-axis and remanent polarization with composition X.

tions along c-axis for A1, A2, B1 and B2 cations are also decreased with the composition X. This would suggest that the dependence of remanent polarization on composition X is derived by the dependence of atomic coordinates on composition X.

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