Structural and Ferroelectric Properties of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$ Solid Solutions

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タングステンブロンズ型 $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$ 固溶体の結晶構造と強誘電特性

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Solid solutions of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$ were synthesized and examined with regard to their ferroelectric properties. No abnormal changes of lattice parameters were found over the investigated range of solid solution. Hysteresis curve measurement indicated that the polarization property could be improved by employing different rare earth cations. The coercive field (E_c) decreased as the composition approached $\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$. The remanent polarization (P_r) of the solid solution was higher than those of end members, and maximum values were observed at $X=0.4-0.6$. Variation of Curie temperature and cell distortion showed the same tendency as that of E_c . Atomic displacement calculated from refined structural parameters agreed with the abnormal change of P_r . The contribution of larger macroscopic polarization for $X=0.4-0.6$ region could be apparently attributed to the larger displacement of Nb^{5+} ions.

[Received July 1, 1999; Accepted September 14, 1999]

Key-words : Ferroelectric, Tungsten bronze, Rietveld method

1. Introduction

Ferroelectric materials include titanates, zirconates, and niobates with oxygen-octahedral structure types. For example, perovskite type compounds BaTiO_3 , PbTiO_3 , $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$, and their solid solutions are well known on pyroelectric and dielectric application, whereas many niobates such as $(\text{Ba}, \text{Sr})\text{Nb}_2\text{O}_6^{(1)}$ and $(\text{Pb}, \text{Ba})\text{Nb}_2\text{O}_6^{(2)}$ having a tetragonal or orthorhombic tungsten bronze structure are also very attractive because of their potential for many electrooptic or pyroelectric application. In the tungsten bronze group, the study about $\text{BaO}-\text{Ln}_2\text{O}_3-\text{Nb}_2\text{O}_5$ pseudo ternary system was seldom noticed except for one report from Masuno.⁽³⁾ In our previous paper,⁽⁴⁾ the compounds $\text{Ba}_{3.75}\text{Ln}_{0.83}\text{Nb}_{10}\text{O}_{30}$ ($\text{Ln}=\text{La}-\text{Er}, \text{Y}$) with tetragonal tungsten bronze (TTB) structure were proposed to be a new candidate for thin film material applied on non-volatile memory devices. Compounds in this system do not contain any volatile or toxic elements like Pb or Bi which are used in $\text{Pb}(\text{ZrTi})\text{O}_3$ and $\text{SrBi}_2\text{Ta}_2\text{O}_9$. Merit of alkali free reduces the compositional deviation and increases the processing stability. These compounds were synthesized by conventional solid state reaction and measured for dielectric and ferroelectric properties. C-axial polarization was preferred for processing, and it also was provided with suitable electrical properties of lower dielectric constant and higher Curie temperature than $(\text{Ba}, \text{Sr})\text{Nb}_2\text{O}_6$.⁽⁵⁾ Anyway, the ferroelectric properties are still not satisfying because the lower coercive field and remanent polarization for compositions containing larger rare earth ions (e.g., Sm, Eu). Inversely, the compositions containing smaller rare earth ions (e.g., Ho and Y) have the higher coercive field and remanent polarization. It seems to be interesting to understand the variation of structure and properties on the compounds containing the larger and smaller rare earth ions (e.g., Sm and Y) together. In this study, solid solution ceramics of $\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$ were synthesized. Structural and ferroelectric properties were reported.

2. Experimental

The substitutional formula for these compounds could be considered as $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$. Substitution amount was from $X=0.0$ to $X=1.0$. Ceramics were prepared by conventional solid state reaction using reagent grade BaCO_3 , Y_2O_3 and Nb_2O_5 . The raw materials were mixed in ethanol for 12 h with Y_2O_3 stabilized ZrO_2 balls in a plastic mill, dried and calcined at 1050°C for 2 h. The reground calcined powder were pressed into pellets with 10 mm in diameter and 3 mm in thickness at a pressure of 98 MPa. The specimens were sintered in air at $1250-1300^\circ\text{C}$ for 4 h. Specimens with relative density higher than 90% were prepared for following measurements.

Lattice constant determination was proceeded with X-ray powder diffractometer (PW1700, Philips, Holland) using $\text{Cu K}\alpha$ radiation and measuring Bragg angles between $2\theta=10^\circ$ and 140° . Specimens were painted with platinum electrode and heated at 800°C for 1 h to enhance the adhesion. $P-E$ curves were measured by ferroelectric test system (RT66A, Radiant Technologies Inc., U.S.A.). Dielectric properties were measured by impedance analyzer (HP4192A, Hewlett Packard, U.S.A.). Structural parameters were determined by the Rietveld analysis program, RIETAN.⁽⁶⁾

3. Results and discussion

3.1 Ferroelectric properties and cell distortion

The X-ray diffraction patterns of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$ solid solution are very similar to each other. All the peaks of each compound can be well indexed. The whole range of solid solution ($X=0.0-1.0$) can, therefore, be confirmed to be single phase of tetragonal tungsten bronze structure. The lattice parameters a and c show continuous changes with X value as shown in Fig. 1.

Figure 2 shows values of E_c and P_r measured at room temperature for $X=0.0-1.0$. The value of E_c decreases as the composition approaches $\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$. The value

Fig. 1. Lattice parameters a and c as a function of Sm content of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$.

Fig. 2. Dependence of P_r and E_c on Sm content of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$.

of P_r increased to maximum between $X=0.4-0.6$ and thereafter decreased gradually. The sequence of changes in the character of the hysteresis curve was generally illustrated with three shapes plotted above Fig. 2. The curve is "slanted" in cases having high Y content. In case having high Sm content, the P - E curve is "slim." In the region of solid solution the P - E curves become "square," which is optimum for memory application. Results of hysteresis curves measurement indicate that the ferroelectric property could be improved by the employment of different rare earth cations to form solid solution.

Figure 3(a) shows the tetragonal tungsten bronze structure which consists of a frame work of oxygen octahedra sharing corners in such a way that there are three types of interstitial sites A, B and C. The general formula is $(\text{A}1)_2(\text{A}2)_4(\text{C})_4(\text{B}1)_2(\text{B}2)_8\text{O}_{30}$ where the sites A1, A2, B1, B2 and C can be filled by different valency cations or be partially empty. In tungsten bronze system, the quantity of axial ratio ($\sqrt{10}c/a$) has been used to evaluate the distortion of BO_6 octahedra within the perovskite subunit shown in Fig. 3(b).²⁾ Some attempts to relate Curie temperature with axial ratio for ferroelectric materials having tungsten bronze structure have been successfully reported by Giess et al.⁷⁾ and Pouchard et al.⁸⁾ They showed that Curie temperature varies linearly with axial ratio.

T_c is defined as the dielectric peak temperature in this work. Figure 4 shows the change of axial ratio and T_c from

Fig. 3. (a) Projection of TTB structure along $[001]$, (b) Perovskite subunit in TTB structure.

Fig. 4. Relationship between axial ratio $\sqrt{10}c/a$, T_c and Sm content of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$.

$X=0.0-1.0$. Both of axial ratio and T_c show the same decreasing tendency and linear-like relationship with X value. These results agree with our previous report discussing about the new tungsten-bronze compounds $\text{Ba}_{3.75}\text{Ln}_{0.83}\text{Nb}_{10}\text{O}_{30}$ ($\text{Ln}=\text{La}-\text{Er}, \text{Y}$).⁴⁾ The linear change would indicate the similar substitution behavior of rare-earth ions for a sequence of solid solution. In other words, Y and Sm ions are at the same site in the lattice. The decrease of axial ratio can also be interpreted as that the switching of polarization direction becomes more easily, i.e., coercive field (E_c) is considered to decrease at the same time. It agrees with the change of E_c shown in Fig. 2.

3.2 Structural parameters refinement and polarization calculation

Macroscopic and microscopic properties of displacive ferroelectrics usually can be determined from the small displacements of ions from their symmetry positions (paraelectric $\leftrightarrow$ ferroelectric). Ferroelectrics such as BaTiO_3 ⁹⁾ or $(\text{BaSr})\text{Nb}_2\text{O}_6$,¹⁰⁾ calculated spontaneous polarization can be well predicted on the basis of observed ionic displacements and the assignment of the usual charge to the various ions. In this study structural parameters were refined by the Rietveld analysis program, RIETAN, based on the space group $P4bm$ (Vol. I, 100). The intensity of the strongest three peaks (311), (410), and (211) was calculated to distinguish the ions species and occupancy of A site for $(\text{SrBa})\text{Nb}_2\text{O}_6$.¹¹⁾ In this work, five different occupied conditions I-V were assumed for A site occupied by ions Y, Sm, or Ba ion. Assumption of composition $X=0.5$ is listed in Table 1 as an example. Comparing with the calculated value of $I_{(311)}/I_{(410)}$ on the different assumptions, the experimental value (1.15) shows the occupied condition of A site might be close to condition I (1.08). The identical

Table 1. Measured and Calculated Values of $I_{(311)}/I_{(410)}$ for $X=0.5$ Composition

	Atoms in A1site	Amount of atoms	ratio of (Ba:Sm:Y)			G	Atoms in A2 site	Amount of atoms	ratio of (Ba:Sm:Y)			G	$I_{(311)}/I_{(410)}$
I	Sm+Y	0.83	0.00	0.50	0.50	0.42	Ba	3.75	1.00	0.00	0.00	0.94	1.08
II	Sm+Y	0.58	0.00	0.29	0.71	0.29	Ba+Sm	4.00	0.94	0.06	0.00	1.00	0.94
III	Sm+Y	0.58	0.00	0.71	0.29	0.29	Ba+Y	4.00	0.94	0.00	0.06	1.00	0.98
IV	Ba+Sm+Y	2.00	0.58	0.21	0.21	1.00	Ba	2.58	1.00	0.00	0.00	0.65	1.97
V	Ba+Sm+Y	1.53	0.82	0.09	0.09	0.76	Ba+Sm+Y	3.06	0.82	0.09	0.09	0.76	1.63
X=0.5													1.15

result was obtained from similar calculation for other compositions. Finally the atomic species and occupancy of compositions $X=0.0-1.0$ were fixed under the condition I. In other words, the A1 site ($G(\text{Occupancy})=0.42$) is occupied by Y or/and Sm ions and A2 site ($G=0.94$) is occupied by Ba ions, respectively.

The atomic coordinates were refined with fixed occupancy obtained above in order to minimize correlation effects. The atomic coordinates of $\text{Ba}_{0.27}\text{Sr}_{0.75}\text{Nb}_2\text{O}_{5.78}$ ¹²⁾ were used as starting parameters in this work. The final reliability factors R_{wp} for $X=0.0-1.0$ are about 11–13 (%). The reliability factors for $X=0.0, 0.5$, and 1.0 are listed in Table 2 and the refined coordinates of Ba, Y/Sm, Nb, and O atoms for $X=0.5$ are listed in Table 3. Result of pattern fitting by Rietveld method for $X=0.5$ composition was plotted in Fig. 5, and the indices of main peaks were also marked.

The change of cation coordinates for compositions $X=0.0-1.0$ are shown in Fig 6. The position of Ba atom almost does not change along with the increase of X value, relatively, the position of Y/Sm atom decreases gradually to below $Z=0.5$. The position of Nb atom increases to maximum between $X=0.4-0.6$ and thereafter decreased gradually. The variation of position for Nb atoms might depend on the Y/Sm atom in the structure. The coexistence of Y and Sm leads to the larger displacement of Nb ions from $Z=0$. It is probably due to significant local structural distortion from the cation substitution or compositional difference caused by solid solution method.

The direction of cation displacement could be related directly to the orientation of the macroscopic polarization as illustrated in Fig 7. Assuming a point-charge model, the ap-

Fig. 5. Result of pattern fitting by Rietveld method for $X=0.5$ composition.

Fig. 6. Change of cation coordinates on Sm content of $(1-X)\text{Ba}_{3.75}\text{Y}_{0.83}\text{Nb}_{10}\text{O}_{30}-X\text{Ba}_{3.75}\text{Sm}_{0.83}\text{Nb}_{10}\text{O}_{30}$.

Table 2. Reliability Factors (%) for $X=0.0, 0.5$ and 1.0 Compositions

	R_{wp}	R_p	R_t	R_f	S
X=0	12.39	9.40	2.79	1.65	2.35
X=0.5	11.16	8.25	2.85	1.73	2.13
X=1.0	11.82	8.86	3.50	2.15	2.21

Table 3. Refined Structural Parameters for $X=0.5$ Composition

	neq	* G	n	x	y	z	B
Sm & Y	2	0.4165	0.8333	0	0	0.4972(14)	0.19
Ba	4	0.9375	3.7500	0.1733(10)	0.6724(12)	0.5100(18)	0.86
Nb(1)	2	1	2	0	0.5	0.0399(22)	0.17
Nb(2)	8	1	8	0.0716(8)	0.2092(8)	0.0503(12)	0.06
O(1)	8	1	8	0.3439(14)	0.0007(5)	-0.0036(12)	1.57
O(2)	8	1	8	0.1381(10)	0.0698(9)	-0.0201(13)	1.95
O(3)	4	1	4	0.2800(14)	0.7800(22)	0.0220(23)	1.68
O(4)	4	0.5	2	-0.0155(12)	0.4845(18)	0.6019(15)	2.05
O(5)	8	0.5	4	0.3022(13)	0.4268(24)	0.5735(29)	4.07
O(6)	8	0.5	4	0.2482(13)	0.4160(20)	0.6878(24)	2.55

Fig. 7. Absolute atomic displacements of metal atoms from mean oxygen atoms layers and the macroscopic polarization sense indicated by the large arrow.

proach of theoretical spontaneous polarization was proceeded using the expression:

$$P_s = \frac{e}{V} \sum Z_i \Delta i$$

Where the summation is over the lattice volume V containing i ions with charge Z_i , and Δi is the atomic displacement vector along the polarization axis, the total polarization taking into account each ions can be calculated. Calculated and measured values were plotted in Fig. 8 for solid solution from $X=0.0$ to $X=1.0$. The calculated spontaneous polarization (P_{cal}) and both of saturation polarization (P_s) and remanent polarization (P_r) all show the same tendency related to X value, i.e., increasing to the maximum value and thereafter decreased gradually. The calculated values are about 4–6 times as large as saturation polarization referred to different ceramic solid solution. They might be reasonably considered to be the “expectant value” from single crystal or c -axis oriented thin film.

From the change of atomic displacement and both of ion number and valence in a unit cell, the contribution of larger macroscopic polarization for $X=0.4$ – 0.6 region can be apparently attributed to the larger Nb^{5+} ions displacement. This result agrees with other lead-free tungsten bronze compounds such as $(SrBa)Nb_2O_6$ ¹²⁾ reported by Jamieson et al., on the other hand, Pb and Ba ions play more important

roles on macroscopic polarization in $(Pb, Ba)Nb_2O_6$ compound reported by Guo et al.¹³⁾

4. Conclusion

Solid solution ceramics of $(1-X)Ba_{3.75}Y_{0.83}Nb_{10}O_{30} - XBa_{3.75}Sm_{0.83}Nb_{10}O_{30}$ were synthesized and examined for ferroelectric properties. The hysteresis curve measurements indicated that the polarization property could be improved by solid solution method. The coercive field and Curie temperature decrease as the composition approached $Ba_{3.75}Sm_{0.83}Nb_{10}O_{30}$. It could be explained from the change of cell distortion expressed with axial ratio ($\sqrt{10} c/a$). Calculated value of spontaneous polarization obtained from refined structural parameters agrees with observed values for this sequence of ceramic solid solution. Both of them show the same tendency that increase to maximum and thereafter decreased gradually. Results of calculation indicate that the contribution of larger macroscopic polarization for $X=0.4$ – 0.6 region can be apparently attributed to the larger displacement of Nb^{5+} ions.

Acknowledgment The authors wish to thank Dr. Takaaki Tsurumi for providing us with polarization measuring equipment.

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Fig. 8. Dependence of P_{cal} , P_s and P_r on Sm content of $(1-X)Ba_{3.75}Y_{0.83}Nb_{10}O_{30} - XBa_{3.75}Sm_{0.83}Nb_{10}O_{30}$.