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Some Tungsten–Bronze Compounds in the $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ System

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Some dielectric oxides have been synthesized and characterized in the $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ system. Through X-ray powder diffraction analysis, $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ are identified as tetragonal tungsten–bronze compounds, and their lattice constants are $a = b = 12.4007(7)$ Å, $c = 3.9030(3)$ Å and $a = b = 12.4826(6)$ Å, $c = 3.9295(5)$ Å, respectively. The possible space group is *P4bm*. The polycrystalline samples of these compounds exhibit high dielectric constant (137 ~ 160) and low dielectric loss, tan $\delta < 7\times10^{-4}$ at 1 MHz.

1. INTRODUCTION

Dielectric ceramics in the system $BaO–Nd_2O_3–TiO_2$ have received much attention because of their important application as microwave dielectric resonators and filters (1–3), and the most important compositions fall in the solid solution of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ with the so-called new tungsten–bronze structure (4). With appropriate modification, a high dielectric constant (80–94), high Qf value (>5,000 GHz), and small temperature coefficient of resonant frequency (-15 ppm/°C $< \tau_f <$ 15 ppm/°C) can be obtained in these ceramics (5, 6).

Searching for new dielectric ceramics with higher dielectric constant ($\varepsilon > 100$), the authors recently investigated the $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ system, and the previous work suggested the presence of some new compounds with $A_6B_{10}O_{30}$ normal tungsten–bronze structure. Although the compounds with $A_6B_{10}O_{30}$ tungsten–bronze structure generally show ferroelectric nature and high dielectric loss (7, 8), the present ceramics have high dielectric constant and very low dielectric loss (9, 10). Therefore these ceramics have great potential in microwave application if the temperature coefficient can be suppressed to an acceptable level, and the understanding of their crystal structures is a key point for such property modification.

In the present paper, we report the structure characterization of $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ compounds together with the room-temperature dielectric properties.

2. EXPERIMENTAL

The compounds $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ were synthesized through solid state reaction from the high-purity powders of $BaCO_3$ (>99.95%), Nd_2O_3 (>99.99%), TiO_2 (>99.99%), and Ta_2O_5(>99.99%). The starting powders were carefully mixed by ball-milling with zirconia media in ethanol for 24 h then were heated at 1260°C (for the former) or 1300°C (for the latter) in air for 3 h. These heated powders were pressed into disc compacts at 98 MPa after grinding and then were sintered at 1310°C (for the former) and 1450°C (for the later) in air for 3 h to yield dense polycrystalline samples. The basic reaction for the synthesis could be represented by

$$4BaCO_3 + Nd_2O_3 + 4TiO_2 + 3Ta_2O_5 \rightarrow Ba_4Nd_2Ti_4Ta_6O_{30} + 4CO_2\ (g)$$

or

$$10BaCO_3 + Nd_2O_3 + 6TiO_2 + 7Ta_2O_5 \rightarrow 2Ba_5NdTi_3Ta_7O_{30} + 10CO_2\ (g).$$

Finally, the sintered polycrystalline samples were ground to prepare the powders for X-ray diffraction analysis.

X-ray diffraction measurements were conducted with a graphite diffracted beam monochromator (Rigaku D/max-3B, Cu$K\alpha$, $\lambda = 1.5406$ Å) using the following settings: step scan, 10–100° range, 0.02° step size, and 10 s collection time. An initial set of lattice parameters was obtained by least-squares refinement of the angular positions of the reflections obtained in the 2θ range 10–100°. Rietveld refinements were then carried out in an isotropic approximation of the thermal parameters, using the program DBW9006.

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TABLE 1
Crystallographic Parameters for $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$

	$Ba_4Nd_2Ti_4Ta_6O_{30}$	$Ba_5NdTi_3Ta_7O_{30}$
Space group	*P4bm*	*P4bm*
a (Å)	12.4007(7)	12.4826(6)
b (Å)	12.4007(7)	12.4826(6)
c (Å)	3.9030(3)	3.9295(5)
α (deg.)	90	90
β (deg.)	90	90
γ (deg.)	90	90
Cell volume (Å^3)	599.73(1)	611.69(2)
Formula weight	2622.09	2721.11
Cell content	$Z = 1$	$Z = 1$
2θ-range, time/step	10°–100°, 10 s	10°–100°, 10 s
X-ray radiation	Cu$K\alpha$1 ($\lambda = 1.5406$ Å)	Cu$K\alpha$1 ($\lambda = 1.5406$ (Å)
Reliability factors	$R_B = 0.045$, $R_P = 0.061$, $R_{WP} = 0.079$	$R_B = 0.036$, $R_P = 0.062$, $R_{WP} = 0.082$

The dielectric characterization was performed for the polycrystalline samples with an LCR meter (HP4284A) at 1 MHz.

3. RESULTS AND DISCUSSION

Through the initial least-squares refinement, the patterns of $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ were indexed to the tetragonal unit cells with $a = b = 12.4007$, $c = 3.9030$ and $a = b = 12.4826$, $c = 3.9295$, similar to those for $Ba_4La_2Ti_4Nb_6O_{30}$ (11) and $Ba_5LaTi_3Nb_7O_{30}$ (12), respectively. Because the only $h01$: $h = 2n + 1$ and $h00$: $h = 2n + 1$ systematic extinctions were unambiguously detected, we were allowed to propose as the possible space group *P4bm*. Based on the initial crystal structure model for $Ba_6Ti_2Nb_8O_{30}$ (13), the Rietveld refinement was carried out in an isotropic approximation of the thermal parameters. The refinement converged with $R_B = 0.045$, $R_P = 0.061$, $R_{WP} = 0.079$ for $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $R_B = 0.036$, $R_P = 0.062$, $R_{WP} = 0.082$ for $Ba_5NdTi_3Ta_7O_{30}$. The results for the refinement are listed in Table 1, and the atomic positions and thermal parameters are given in Tables 2 and 3. Figures 1 and 2 show the comparison of the experimental plot with that obtained by refinement, along with the calculated residuals. The selected bond lengths and angles are listed in Tables 4 and 5. In $Ba_4Nd_2Ti_4Ta_6O_{30}$, the (Ba, Nd)–O bonds range from 2.628(20) to 2.843(12) Å, and the (Ti, Ta)–O bonds range from 1.816(22) to 2.059(18) Å. Similarly, the (Ba, Nd)–O bonds range from 2.672(20) to 2.870(20) Å and the (Ti, Ta)–O bonds range from 1.834(23) to 2.151(18) Å, in $Ba_5NdTi_3Ta_7O_{30}$.

TABLE 2
Positional and Thermal Parameters for $Ba_4Nd_2Ti_4Ta_6O_{30}$

Atom	Position	x	y	z	Occupancy	B (Å^2)
Ba(1)	2a	0.0000	0.0000	0.0000	0.6667	1.00(4)
Nd(1)	2a	0.0000	0.0000	0.0000	0.3333	1.00(4)
Ba(2)	4g	0.1663(3)	0.3237(3)	0.0000	0.6667	1.55(3)
Nd(2)	4g	0.1663(3)	0.3237(3)	0.0000	0.3333	1.55(3)
Ti(1)	4h	0.2134(4)	0.0739(4)	0.5000	0.4000	0.65(3)
Ta(1)	4h	0.2134(4)	0.0739(4)	0.5000	0.6000	0.65(3)
Ti(2)	4h	0.4254(4)	0.2848(4)	0.5000	0.4000	0.32(10)
Ta(2)	4h	0.4254(4)	0.2848(5)	0.5000	0.6000	0.32(10)
Ti(3)	2d	0.5000	0.0000	0.5000	0.4000	0.97(2)
Ta(3)	2d	0.5000	0.0000	0.5000	0.6000	0.97(2)
O(1)	4h	0.2863(21)	0.2186(21)	0.5000	1.0	1.32(30)
O(2)	4h	0.1549(18)	0.4907(19)	0.5000	1.0	1.41(39)
O(3)	4g	0.4059(15)	0.3086(19)	0.0000	1.0	1.25(45)
O(4)	2c	0.0000	0.5000	0.0000	1.0	2.36(55)
O(5)	4h	0.0635(21)	0.1280(20)	0.5000	1.0	1.45(35)
O(6)	4g	0.2059(17)	0.0530(14)	0.0000	1.0	0.76(35)
O(7)	4h	0.0040(19)	0.3421(19)	0.5000	1.0	0.96(42)
O(8)	4h	0.3613(17)	0.4360(17)	0.5000	1.0	2.76(36)

TABLE 3
Positional and Thermal Parameters for $Ba_5NdTi_3Ta_7O_{30}$

Atom	Position	x	y	z	Occupancy	B (Å^2)
Ba(1)	2a	0.0000	0.0000	0.0000	0.8333	1.20(6)
Nd(1)	2a	0.0000	0.0000	0.0000	0.1667	1.20(6)
Ba(2)	4g	0.1760(1)	0.3325(1)	0.0000	0.8333	1.86(5)
Nd(2)	4g	0.1760(1)	0.3325(1)	0.0000	0.1667	1.86(5)
Ti(1)	4h	0.2134(7)	0.0736(6)	0.5000	0.3000	0.98(4)
Ta(1)	4h	0.2120(6)	0.0750(6)	0.5000	0.7000	0.98(4)
Ti(2)	4h	0.4240(4)	0.2842(7)	0.5000	0.3000	0.51(7)
Ta(2)	4h	0.4240(4)	0.2842(7)	0.5000	0.7000	0.51(7)
Ti(3)	2d	0.5000	0.0000	0.5000	0.3000	1.19(3)
Ta(3)	2d	0.5000	0.0000	0.5000	0.7000	1.19(3)
O(1)	4h	0.2798(22)	0.2217(20)	0.5000	1.0	1.15(18)
O(2)	4h	0.1536(26)	0.4895(14)	0.5000	1.0	1.32(50)
O(3)	4g	0.4253(15)	0.2929(17)	0.0000	1.0	1.40(36)
O(4)	2c	0.0000	0.5000	0.0000	1.0	1.58(28)
O(5)	4h	0.0753(17)	0.1332(16)	0.5000	1.0	1.17(37)
O(6)	4g	0.2063(21)	0.0735(18)	0.0000	1.0	1.41(36)
O(7)	4h	0.0083(22)	0.3362(15)	0.5000	1.0	1.21(43)
O(8)	4h	0.3684(22)	0.4387(15)	0.5000	1.0	1.17(37)

The proposed structures determined for $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ are isostructures with $Ba_4La_2Ti_4Nb_6O_{30}$ and $Ba_5LaTi_3Nb_7O_{30}$, respectively, which belong to the filled tungsten–bronze structure with a general formula of $A_6B_{10}O_{30}$ (7, 13). In the present tungsten–bronze compounds, ten oxygen-octahedra containing Ta and Ti ions share corner atoms, and larger ions of Nd and Ba fill six cages, four 15-coordinated and two 12-coordinated sites.

Table 6 gives the dielectric properties of $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ polycrystalline samples. The high dielectric constant (137 ~ 160) and low dielectric loss, $\tan\delta < 7 \times 10^{-4}$ at 1 MHz are indicated in the well-sintered

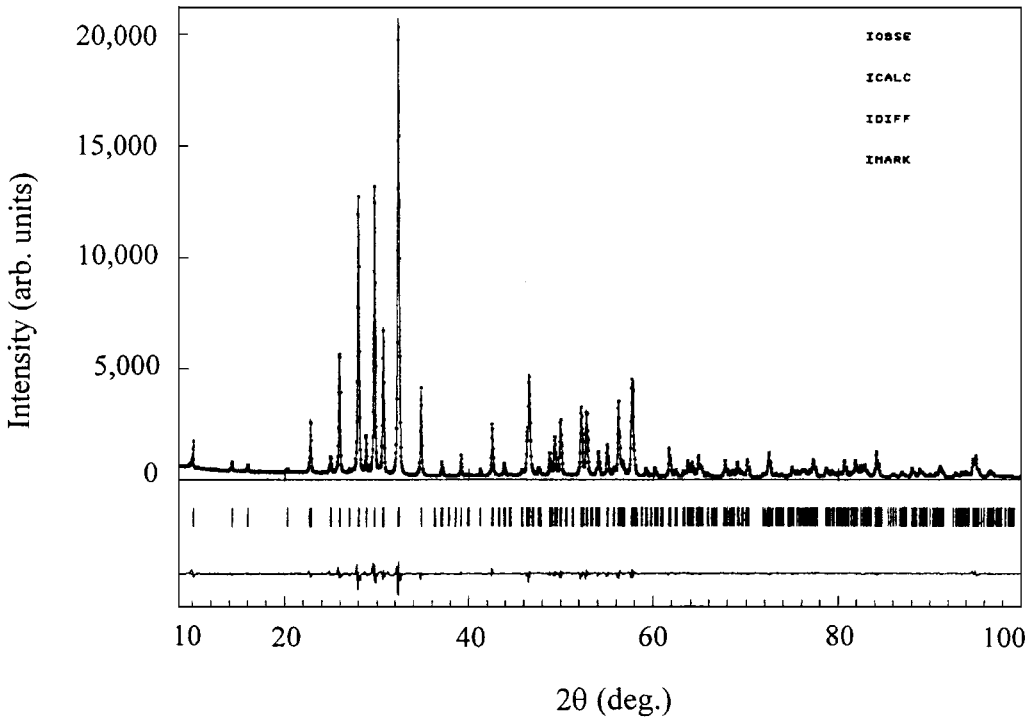

FIG. 1. Observed and calculated X-ray diffraction patterns (Cu$K\alpha$ radiation, $\lambda = 1.5406$ Å) for $Ba_4Nd_2Ti_4Ta_6O_{30}$ with their difference shown below.

polycrystalline samples of the present tungsten–bronze compounds. Compared with the previous work (9), the dielectric loss for $Ba_5NdTi_3Ta_7O_{30}$ has been decreased significantly by increasing the powder synthesis temperature to 1300°C, and this might be concerned with the increased crystallinity.

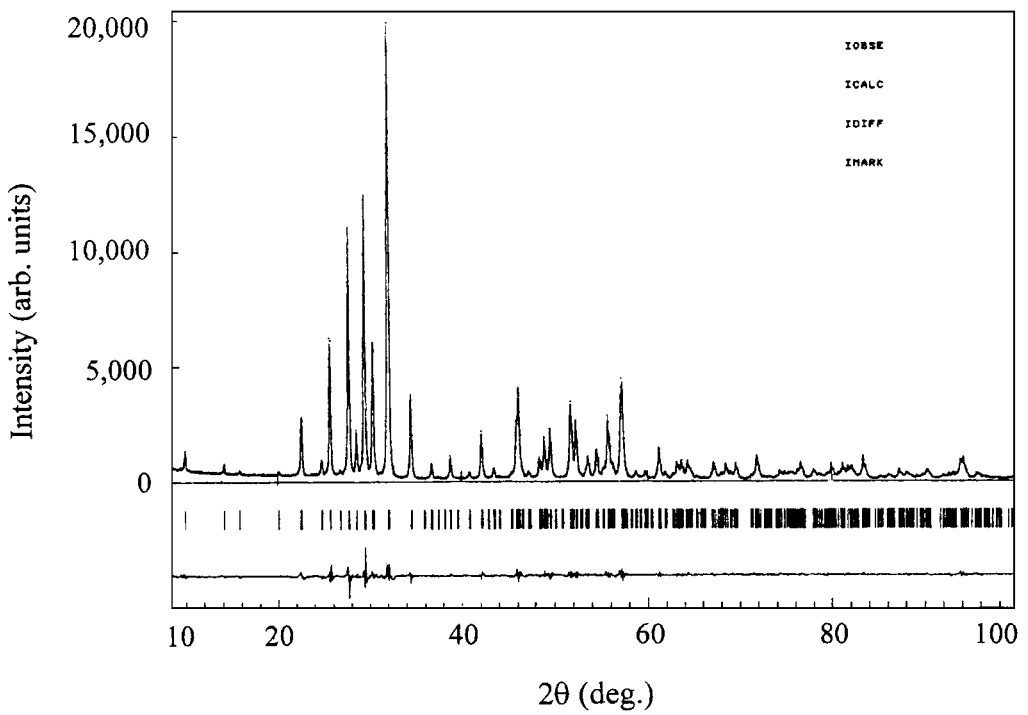

FIG. 2. Observed and calculated X-ray diffraction patterns (Cu$K\alpha$ radiation, $\lambda = 1.5406$ Å) for $Ba_5NdTi_3Ta_7O_{30}$ with their difference shown below.

TABLE 4
Selected Bond Distances and Angles for $Ba_4Nd_2Ti_4Ta_6O_{30}$

Bond distances (Å)		Bond angles (deg.)	
Ba(1)–O(3)	2.652(22)	O(3)–Ba(1)–O(5)	113.79
Ba(1)–O(5)	2.631(13)	O(3)–Ba(1)–O(6)	78.31
Ba(1)–O(6)	2.628(20)	O(3)–Ba(1)–O(8)	122.58
Ba(1)–O(8)	2.726(13)	O(6)–Ba(1)–O(8)	122.98
Ba(2)–O(1)	2.777(12)	O(1)–Ba(2)–O(2)	149.70
Ba(2)–O(2)	2.819(18)	O(1)–Ba(2)–O(7)	86.10
Ba(2)–O(7)	2.843(12)	O(2)–Ba(2)–O(7)	55.25
Ti(1)–O(1)	2.017(27)	O(1)–Ti(1)–O(2)	98.15
Ti(1)–O(2)	1.967(25)	O(1)–Ti(1)–O(5)	90.80
Ti(1)–O(5)	1.957(2)	O(1)–Ti(1)–O(6)	91.09
Ti(1)–O(6)	1.969(2)	O(1)–Ti(1)–O(8)	172.91
Ti(1)–O(8)	1.921(18)	O(5)–Ti(1)–O(6)	87.64
Ti(2)–O(1)	1.902(26)	O(1)–Ti(2)–O(3)	91.69
Ti(2)–O(3)	1.988(4)	O(1)–Ti(2)–O(5)	174.80
Ti(2)–O(5)	2.042(23)	O(1)–Ti(2)–O(7)	101.56
Ti(2)–O(7)	1.816(22)	O(1)–Ti(2)–O(8)	93.64
Ti(2)–O(8)	2.059(18)	O(5)–Ti(2)–O(8)	81.16
Ti(3)–O(2)	1.899(24)	O(2)–Ti(3)–O(4)	90.00
Ti(3)–O(4)	1.951(1)	O(2)–Ti(3)–O(7)	96.81
Ti(3)–O(7)	1.982(22)	O(4)–Ti(3)–O(7)	90.00

4. CONCLUSIONS

$Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ have been synthesized and identified as tetragonal tungsten–bronze compounds, and their lattice constants are $a = b = 12.4007$ Å, $c = 3.9030$ Å and $a = b = 12.4826$ Å, $c = 3.9295$ Å, respectively. These compounds all belong to the possible space group *P*4*bm*. The polycrystalline samples of these compounds exhibit high dielectric constant and low dielectric loss, and this suggests the potential for microwave application of the present materials. Active work on materials development in the present system is in progress by the authors' group.

TABLE 5
Selected Bond Distances and Angles for $Ba_5NdTi_3Ta_7O_{30}$

Bond distances (Å)		Bond angles (deg.)	
Ba(1)–O(3)	2.747(21)	O(3)–Ba(1)–O(5)	113.79
Ba(1)–O(5)	2.739(14)	O(3)–Ba(1)–O(6)	89.77
Ba(1)–O(6)	2.732(25)	O(3)–Ba(1)–O(8)	118.54
Ba(1)–O(8)	2.672(18)	O(6)–Ba(1)–O(8)	118.87
Ba(2)–O(1)	2.730(18)	O(1)–Ba(2)–O(2)	155.58
Ba(2)–O(2)	2.788(13)	O(1)–Ba(2)–O(7)	82.05
Ba(2)–O(7)	2.870(20)	O(2)–Ba(2)–O(7)	55.50
Ti(1)–O(1)	2.025(27)	O(1)–Ti(1)–O(2)	85.15
Ti(1)–O(2)	1.964(23)	O(1)–Ti(1)–O(5)	97.24
Ti(1)–O(5)	1.877(22)	O(1)–Ti(1)–O(6)	97.85
Ti(1)–O(6)	1.966(1)	O(1)–Ti(1)–O(8)	178.95
Ti(1)–O(8)	1.969(23)	O(5)–Ti(1)–O(6)	89.92
Ti(2)–O(1)	1.961(28)	O(1)–Ti(2)–O(3)	87.20
Ti(2)–O(3)	1.967(1)	O(1)–Ti(2)–O(5)	172.75
Ti(2)–O(5)	2.151(22)	O(1)–Ti(2)–O(7)	96.58
Ti(2)–O(7)	1.834(23)	O(1)–Ti(2)–O(8)	92.12
Ti(2)–O(8)	2.049(21)	O(5)–Ti(2)–O(8)	80.62
Ti(3)–O(2)	1.921(32)	O(2)–Ti(3)–O(4)	90.00
Ti(3)–O(4)	1.964(1)	O(2)–Ti(3)–O(7)	94.90
Ti(3)–O(7)	2.047(18)	O(4)–Ti(3)–O(7)	90.00

TABLE 6
Room Temperature Dielectric Characteristics of $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$ Polycrystalline Samples (at 1 MHz)

Composition	Sintering conditions	Dielectric constant	tan δ
$Ba_4Nd_2Ti_4Ta_6O_{30}$	1310°C × 3 h, in air	137	0.0007
$Ba_5NdTi_3Ta_7O_{30}$	1450°C × 3 h, in air	160	0.000018

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