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Dielectric Characteristics of Ceramics in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ System

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Abstract

Dielectric ceramics in the $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ system were prepared and characterized. The ceramics with tungsten–bronze structure based on the compositions $Ba_2NdTi_2Ta_3O_{15}$ and $Ba_5NdTi_3Ta_7O_{30}$ had a high dielectric constant (>100) with a lower frequency-dependency when complete densification was achieved; a low dielectric loss was obtained in the former. © 1998 Elsevier Science Limited. All rights reserved

Keywords: dielectric properties, tungsten bronze, microstructure-final, tantalates

1 Introduction

Tungsten–bronze compounds belong to an important family of dielectric materials which display interesting ferroelectric, pyroelectric. piezoelectric, and nonlinear optic behaviours.[1,2] In previous investigations, the ferroelectric nature of tungsten-bronze compounds has been especieally emphasized, and less attention has been focused on those compounds with paraelectric nature which occur in the tungsten–bronze family.

In recent work on composite dielectric ceramics in the $Ba(Mg_{1/3}Ta_{2/3})O_3–BaO.Nd_2O_3.5TiO_2$ system conducted with a view to finding, new candidates for microwave dielectric applications, the presence of some new compounds in the $BaO–Nd_2O_3$.–$Ta_2O_5–TiO_2$ system (hereafter referred to as BNTT) was suggested;[3,4] the compounds were considered to belong to the tungsten-bronze family. Because such composite ceramics have low dielectric loss, it is interesting to determine the dielectric characteristics more fully. In this paper, ceramics based on the compositions $Ba_2NdTi_2Ta_3O_{15}$, $Ba_3Nd_3Ti_5Ta_5O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$, which have the tungsten–bronze structure $(A',A'')_6(B'B'')_{10}O_{30}$ were prepared, and their microstructures and dielectric properties were evaluated.

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2 Experiments

High-purity powders of $BaCO_3$ (>99·95%), Nd_2O_3 (>99·99%), TiO_2 (>99·99%), and Ta_2O_5 (>99·99%) were adopted as the starting materials, and ceramic powders with the compositions mentioned above were synthesized by calcination of the mixed powders at 1260°C in air for 3 h, followed by ball-milling with zirconia media in ethanol for 24 h. Disc compacts with dimensions 12 mm in diameter and 2 to 4 mm in height were formed by pressing at 98 MPa, and those were then sintered at 1310 to 1450°C in air for 3 h to yield dense ceramics.

X-ray diffraction (XRD) analysis using Ni-filtered Cu_α radiation and scanning electron microscopy (SEM) were carried out for phase composition and microstructure characterization. The dielectric properties at room temperature were determined by an LCR meter (HP4284A) at 1, 10, 100, 500 KHz and 1 MHz, respectively, and the temperature dependence of the dielectric constant was evaluated at 10 kHz by another LCR meter (WK4210) equipped with a thermostat.

3 Results and Discussion

Dense ceramics with the three different compositions could be easilly fabricated, but different densification temperatures were needed for the various compositions. Densification of $Ba_2NdTi_2Ta_3O_{15}$ ceramics can he performed at 1310°C, while temperatures above 1400°C are needed for the densification of $Ba_5NdTi_3Ta_7O_{30}$ and $Ba_3Nd_3Ti_5Ta_5O_{30}$ ceramics (see Fig. 1). Figure 2 gives SEM micrographs of ceramics sintered at different temperatures.

Fine columnar structures appear in ceramics sintered at 1340°C for all compositions, and abnormally grown, plate-like grains in $Ba_3Nd_3Ta_5Ta_5O_{30}$ ceramics sintered at 1430°C. XRD analysis showed that three compositions all have the $(A',A'')_6(B',B'')_{10}O_{30}$ tungsten–bronze structure, and that single phase structures are obtained in $Ba_2NdTi_2Ta_3O_{15}$ and $Ba_5NdTi_3Ta_7O_{30}$, while a secondary phase is found in the $Ba_3Nd_3Ti_5Ta_5O_{30}$ materials. The details of the crystal structural analysis will be reported.[5]

Table 1 gives the room-temperature dielectric characteristics of BNTT ceramics with various

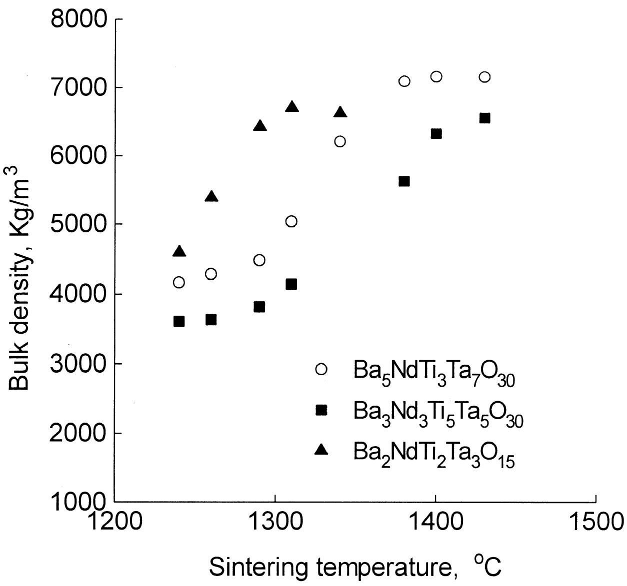

Fig. 1. Density of BNTT ceramics with various compositions as function of sintering temperature.

Table 1. Dielectric characteristics of ceramics in BaO–Nd_2O_3.–Ta_2O_5–TiO_2 system

Composition	*Sintering condition*	*Frequency*	ε	*tan*δ
$Ba_2NdTi_2Ta_3O_{15}$	1310°C×3 h, in air	1 kHz	138·8	0·0038
		10 kHz	137·3	0·0047
		100 kHz	136·9	0·0026
		500 kHz	136·9	0·0012
		1 MHz	136·9	0·0007
$Ba_3Nd_3Ti_5Ta_5O_{30}$	1400°C×3 h, in air	1 kHz	117·7	0·3392
		10 kHz	109·1	0·0641
		100 kHz	104·7	0·0215
		500 kHz	103·5	0·0110
		1 MHz	103·1	0·0088
$Ba_5NdTi_3Ta_7O_{15}$	1400°C×3 h, in air	1 kHz	166·5	0·2242
		10 kHz	163·4	0·0274
		100 kHz	162·6	0·0046
		500 kHz	162·4	0·0016
		1 MHz	162·4	0·0013
	1450°C×3 h, in air	1 kHz	171·66	0·2800
		10 kHz	161·14	0·0432
		100 kHz	159·74	0·0085
		500 kHz	159·33	0·0039
		1 MHz	159·22	0·0029

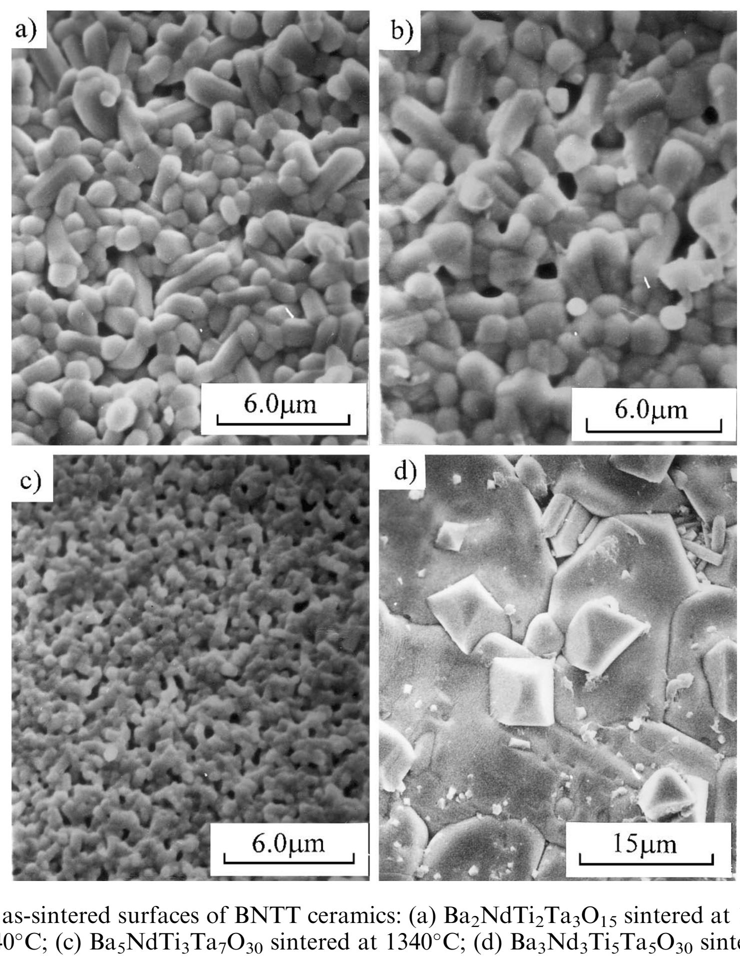

Fig. 2. SEM micrographs of as-sintered surfaces of BNTT ceramics: (a) $Ba_2NdTi_2Ta_3O_{15}$ sintered at 1340°C; (b) $Ba_3Nd_3Ti_5Ta_5O_{30}$ sintered at 1340°C; (c) $Ba_5NdTi_3Ta_7O_{30}$ sintered at 1340°C; (d) $Ba_3Nd_3Ti_5Ta_5O_{30}$ sintered at 1430°C.

compositions. $Ba_2NdTi_2Ta_3O_{15}$ has high dielectric constant with low frequency-dependence and low dielectric loss, $Ba_5NdTi_3Ta_7O_{30}$ has a higher dielectric constant and slightly higher frequency-dependence and dielectric loss. The strongest frequency-dependence of dielectric constant and a much higher dielectric loss are found in $Ba_3Nd_3Ti_5Ta_5O_{30}$ ceramics, perhaps due to the complex phase constitution and inhomogeneity.

The temperature-dependence of the dielectric constant is shown in Figs 3–6 for BNTT ceramics with various compositions. $Ba_2NdTi_2Ta_3O_{15}$ and $Ba_5NdTi_3Ta_7O_{30}$ have negative temperature coefficients above room temperature, while broadened dielectric constant peaks with significant frequency dependence, suggesting relaxor ferroelectric behavior, are observed for $Ba_5NdTi_3Ta_7O_{30}$ and $Ba_3Nd_3Ti_5Ta_5O_{30}$ ceramics sintered at lower temperatures where full densification is not achieved. Even for the dense ceramics, the negative temperature coefficient of dielectric constant is greater than 1000 ppm°C^{-1}; hence, controlling temperature coefficient becomes an important issue for such ceramics when microwave applications are considered. Moreover, because the large leakage current increases rapidly with increasing temperature, the capacitance data become unstable; the temperature dependence of the dielectric constant could not therefore be measured for $Ba_3Nd_3Ti_5Ta_5O_{30}$ ceramics sintered at higher temperatures.

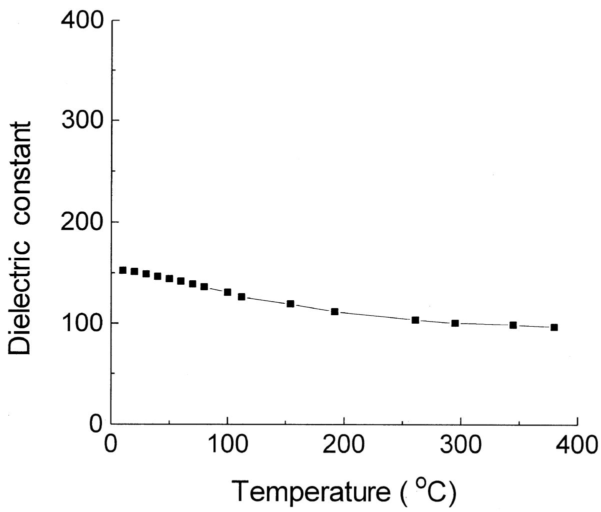

Fig. 3. Temperature dependence of dielectric constant (at 10 kHz) of $Ba_2NdTi_2Ta_3O_{15}$ ceramics sintered at 1340°C in air for 3 h.

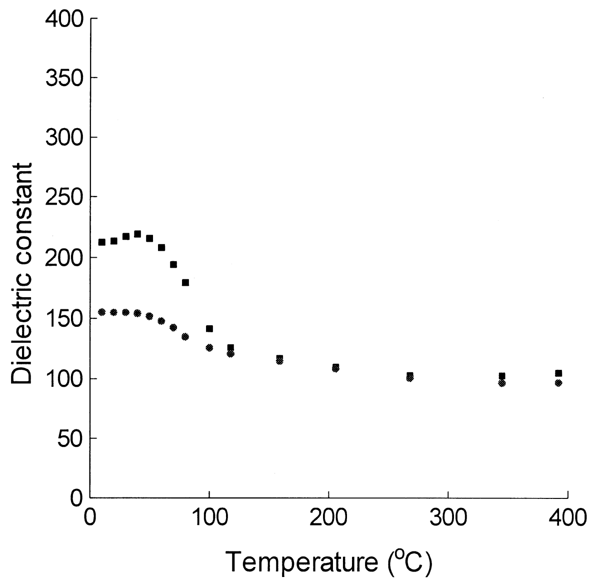

Fig. 5. Temperature dependence of dielectric constant of $Ba_5NdTi_3Ta_7O_{30}$ ceramics sintered at 1340°C in air for 3 h: (■) at 1 kHz and (●) at 10 kHz.

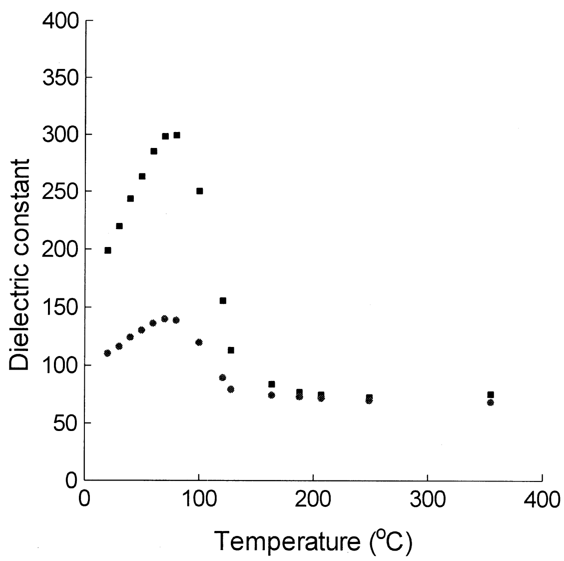

Fig. 4. Temperature dependence of dielectric constant of $Ba_3Nd_3Ti_5Ta_5O_{30}$ ceramics sintered at 1340°C in air for 3 h: (■) at 1 kHz and (●) at 10 kHz.

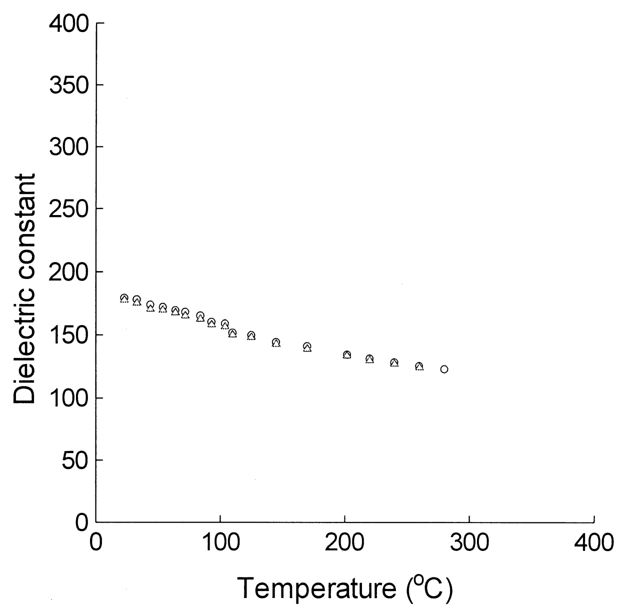

Fig. 6. Temperature dependence of dielectric constant of $Ba_5NdTi_3Ta_7O_{30}$ ceramics sintered at 1400°C in air for 3 h: (○) at 10 kHz and (△) at 100 kHz.

This appears to be concerned with the inhomogeneity, and the details remain to be investigated.

4 Conclusion

In the $BaO–Nd_2O_3–Ta_2O_5–TiO_2$ system, ceramics based on tungsten–bronze compounds with the compositions $Ba_2NdTi_2Ta_3O_{15}$ and $Ba_5NdTi_3Ta_7O_{30}$ have high dielectric constant (> 100) and a lower frequency-dependence when full densification is achieved. Low dielectric loss (0·0007 at 1 MHz) was obtained in dense $Ba_2NdTi_2Ta_3O_{15}$ ceramics together with a high dielectric constant of 137, while the dielectric loss is of the order of 10^{-3} for ceramics based on $Ba_3Nd_3Ti_5Ta_5O_{30}$ and $Ba_5NdTi_3Ta_7O_{30}$.

Acknowledgement

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