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High permittivity and low loss dielectric ceramics in the $BaO–La_2O_3–TiO_2–Ta_2O_5$ system

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Abstract

Dielectric ceramics were synthesized and characterized in the $BaO–La_2O_3–TiO_2–Ta_2O_5$ quaternary system for the three typical compositions: $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$, which formed the filled tungsten-bronze structures. The present ceramics indicated high dielectric constant ε (127.7–148.1) and low dielectric loss tanδ (in the order of 10^{-4}–10^{-3} at 1 MHz). Meanwhile, the temperature coefficient of dielectric constant τ_ε varied from −728 to −1347 ppm/°C with increasing Ba and Ta and decreasing La and Ti concentration in the temperature range of 20–85 °C. The present ceramics are promising candidates for high-ε and low loss dielectric ceramics, and the suppression of τ_ε should be the primary issue in the future work.

Keywords: $(Ba,La)_6$ $(Ti,Ta)_{10}$ O_{30}; $BaO–La_2O_3–TiO_2–Ta_2O_5$; Dielectric properties; Tungsten-bronze structure

1. Introduction

Because of the important applications in microelectronics and microwave communication systems, dielectric ceramics especially temperature stable high-ε dielectric ceramics with low dielectric loss have attracted more and more scientific and commercial interests.[1–8] In most of these applications, a high dielectric constant (ε) and a low dielectric loss (tanδ) are generally required together with a small temperature coefficient of dielectric constant (τ_ε).

In the previous work,[7,8] dielectric ceramics in the $BaO–Ln_2O_3–TiO_2–Ta_2O_5$ (Ln = Nd and Sm) quaternary systems were proposed and investigated, for the typical compositions $Ba_3Ln_3Ti_5Ta_5O_{30}$, $Ba_4Ln_2Ti_4Ta_6O_{30}$ and $Ba_5LnTi_3Ta_7O_{30}$ with filled type tungsten-bronze structure. In the Nd-containing system,[7] a dielectric constant of 103–159, a low dielectric loss in the order of 10^{-4} at 1 MHz are indicated. While in the case of Ln = Sm,[8] the tungsten bronze ceramics have a high dielectric constant in the range from 134 to 175, a low dielectric loss in the order of 10^{-3}. The mutual problem for the above systems is the relatively large negative temperature coefficient of dielectric constant.

In the present work, a similar system $BaO–La_2O_3–TiO_2–Ta_2O_5$ is discussed. Ceramics with compositions of $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ are prepared and characterized, and the structures and dielectric properties are compared with those in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ and $BaO–Sm_2O_3–TiO_2–Ta_2O_5$ systems.

2. Experimental procedures

Ceramics with compositions $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ were synthesized by powder processing from reagent-grade $BaCO_3$ (>99.95%), La_2O_3 (>99.99%), TiO_2 (>99.8%) and Ta_2O_5 (>99.99%) raw powders. Mixtures of the raw powders were ground by attrition in a polyethylene jar with zirconia balls in ethanol for 24 h, then calcined in a high-purity alumina crucible at 1260 °C for 3 h in air. Calcination was followed by a second attrition grinding to reach a homogeneous granulometric distribution. Added with organic binders (8 wt.% polyvinyl alcohol), the granules of the reground powders were pressed into cylindrical compacts of 12 mm in diameter and 2–5 mm

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in thickness, under the pressure of about 98 MPa. The disks were sintered at 1375–1425 °C for 3 h in air. The ceramics were cooled at a rate of 2 °C /min from sintering temperature to 1100 °C, and then cooled with furnace.

The microstructures of sintered samples were characterized by X-ray diffraction (XRD) analysis using a graphite diffracted beam monochromator (Rigaku D/max-3B, CuK_{α}, $\lambda = 1.5406$ Å) and scanning electron microscopy (SEM, HITACH S-570) observation on the polished and thermal-etched surfaces.

Silver paste was used as electrodes, it was blushed on each side of the ceramic disc and fired at 500 °C in air for 30 min. The dielectric characteristics at room temperature were determined from capacitance measurements by an LCR meter (HP4285A) at 100 kHz, 500 kHz, 1 MHz, and 5 MHz, respectively. The temperature dependence of dielectric constant was evaluated at 1 MHz from room temperature to 85 °C, by another LCR meter (HP4284A) equipped with a thermostat. Microwave dielectric properties were measured by Hakki and Coleman's dielectric resonator method.[9]

3. Results and discussion

The three typical compositions $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ take the tetragonal tungsten bronze structure(hereafter abbr. TTB). All peaks in the XRD patterns for the ceramics based on these three compositions (Fig. 1) can be assigned to the tungsten bronze phase (JCPDS cards No.38-1331, 39-0255 and 39-1445). The crystal parameters are listed in Table 1, and we can find that the unit cell volume of the present tungsten bronze compounds increases with increasing Ba and Ta and decreasing La and Ti concentration. Moreover, even $Ba_3La_3Ti_5Ta_5O_{30}$ has the stable tungsten bronze structure, unlike in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ and $BaO–Sm_2O_3–TiO_2–Ta_2O_5$ systems. The discrepancy between present and the previous systems originates from tolerance factor and average electronegativity differences. The tolerance factor for TTB structure has been discussed by Wakiya et al.[10] According to the general formula, there are two kinds of A sites for TTB structure, one is A_1 site with 12-fold coordination which is identical to that in perovskite structure, the other is A_2 site with 15-fold coordination. Therefore two kinds of tolerance factor for A sites can be given by the following equations:[10]

$$t_{A1} = \frac{r_{A1} + r_O}{\sqrt{2}(r_B + r_O)} \tag{1}$$

$$t_{A2} = \frac{(r_{A2} + r_O)}{\sqrt{23 - 12\sqrt{3}}(r_B + r_O)} \tag{2}$$

where r_A, r_B and r_O are the ionic radii of the A and B site ions and the O^{-2} ion, respectively. In order to better understand the relationship between tolerance factor and the stability of TTB structure, combination of the two kinds of tolerance factor can be denoted as

Table 1
Lattice parameter of dielectric ceramics in the $BaO–La_2O_3–TiO_2–Ta_2O_5$ system

Composition	a or b (Å)	c (Å)	V (Å^3)
$Ba_3La_3Ti_5Ta_5O_{30}$	12.3660	3.8979	596.056
$Ba_4La_2Ti_4Ta_6O_{30}$	12.4353	3.9186	605.949
$Ba_5LaTi_3Ta_7O_{30}$	12.4884	3.9369	613.996

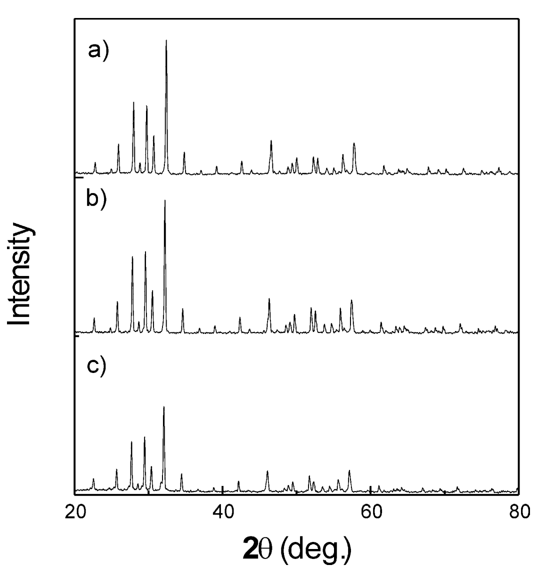

Fig. 1. XRD patterns of (a) $Ba_3La_3Ti_5Ta_5O_{30}$, (b) $Ba_4La_2Ti_4Ta_6O_{30}$ and (c) $Ba_5\ LaTi_3Ta_7O_{30}$.

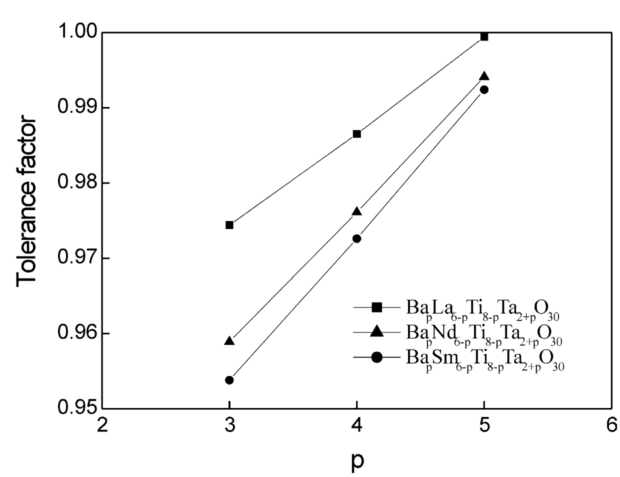

Fig. 2. Tolerance factor (t) of tungsten bronze compounds $Ba_pLn_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$ (Ln = La, Nd, Sm) as function of composition p.

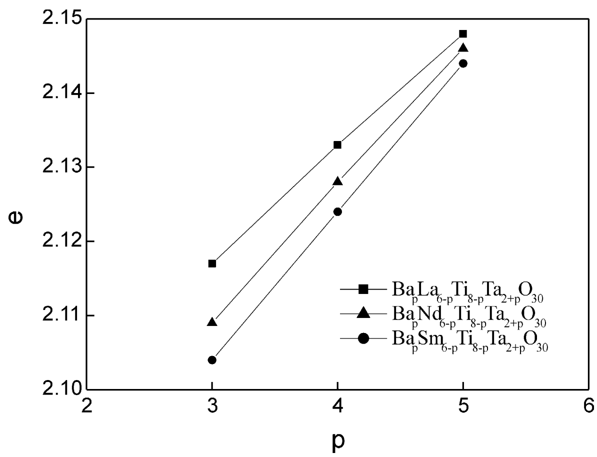

Fig. 3. Average electronegativity difference (e) of tungsten bronze compounds $Ba_pLn_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$ (Ln = La, Nd, Sm) as function of composition p.

Table 2
Room-temperature dielectric properties of tungsten bronze ceramics in $BaO–La_2O_3–TiO_2–Ta_2O_5$ system compared with those in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$[7] and $BaO–Sm_2O_3–TiO_2–Ta_2O_5$[8] systems (at 1 MHz)

Composition	Sintering temperature (°C)	ϵ	Tanδ	τ_ϵ (ppm/°C)
$Ba_3La_3Ti_5Ta_5O_{30}$	1425	127.7	0.0021	−728
$Ba_4La_2Ti_4Ta_6O_{30}$	1400	128.0	0.0003	−1080
$Ba_5LaTi_3Ta_7O_{30}$	1425	148.1	0.0008	−1347
$Ba_3Nd_3Ti_5Ta_5O_{30}$	1400	103.1	0.0088	−1300[a]
$Ba_4Nd_2Ti_4Ta_6O_{30}$	1310	136.9	0.0007	−1500[a]
$Ba_5NdTi_3Ta_7O_{30}$	1450	159.2	0.0029	−1750[a]
$Ba_3Sm_3Ti_5Ta_5O_{30}$	1500	134.4	0.0046	−1500[a]
$Ba_4Sm_2Ti_4Ta_6O_{30}$	1450	159.6	0.0035	−2000[a]
$Ba_5SmTi_3Ta_7O_{30}$	1550	174.6	0.0019	−2500[a]

[a] At 10 kHz.

$$t = \frac{t_{A1} + 2t_{A2}}{3} \quad (3)$$

On the other hand, the electronegativity difference is another important parameter to evaluate the stability of crystal structure written as

$$e = (\chi_{A–O} + \chi_{B–O})/2 \quad (4)$$

where $\chi_{A–O}$, $\chi_{B–O}$ are the electronegativity difference of the A and B site cations with O^{-2} ion, respectively. By using the general formula for the present tungsten bronze compounds of $Ba_pLn_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$, the average electronegativity difference e can be written as

$$e = \left[p\chi_{Ba–O} + (6-p)\chi_{Ln–O} + (8-p)\chi_{Ti–O} + (2+p)\chi_{Ta–O}\right]/16 \quad (5)$$

As shown in Figs. 2 and 3, $Ba_pLa_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$ have larger tolerance factor and average electronegativity differences than $Ba_pNd_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$ and $Ba_pSm_{6-p}Ti_{8-p}Ta_{2+p}O_{30}$, but those for $Ba_3La_3Ti_5Ta_5O_{30}$ are almost the same as for $Ba_4Nd_2Ti_4Ta_6O_{30}$ and $Ba_4Sm_2Ti_4Ta_6O_{30}$. Therefore, $Ba_3La_3Ti_5Ta_5O_{30}$ takes the stable tungsten bronze structure without secondary phase, while some secondary phase is observed in $Ba_3Nd_3Ti_5Ta_5O_{30}$ and $Ba_3Sm_3Ti_5Ta_5O_{30}$.

The dense ceramics based on $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ can be obtained by sintering at temperatures ranging from 1375 to 1425 °C, and the optimum densification temperature is 1425, 1400 and 1425 °C, respectively. Fig. 4 gives the SEM micrographs of the polished and thermal-etched surfaces of the dense ceramics. No obvious pores and abnormal grains are observed in these pictures, which confirm good densification and a homogenous microstructure.

Table 2 shows the room-temperature dielectric characteristics of the present ceramics together with those for similar compositions in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ and $BaO–Sm_2O_3–TiO_2–Ta_2O_5$ systems. The present ceramics have a high dielectric constant of 127.7–148.1, and the highest and lowest dielectric constant are indicated in $Ba_5LaTi_3Ta_7O_{30}$ and $Ba_3La_3Ti_5Ta_5O_{30}$, respectively, similar to that shown in $BaO–Nd_2O_3–TiO_2–Ta_2O_5$ and $BaO–Sm_2O_3–TiO_2–Ta_2O_5$ systems. The compositions $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ indicate a very low dielectric loss: 0.0003 and 0.0008 at 1 MHz, respectively, while $Ba_3La_3Ti_5Ta_5O_{30}$ has a dielectric loss of 0.0021 at 1 MHz. The smallest temperature coefficient of dielectric constant (−728 ppm/°C) is obtained in $Ba_3La_3Ti_5Ta_5O_{30}$, and those for $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$ are −1080 and

Table 3
Room temperature dielectric properties of ceramics in the $BaO–La_2O_3–TiO_2–Ta_2O_5$ system as function of frequency

Composition	Sintering temperature (°C)	100 kHz		500 kHz		1 MHz		5 MHz	
		ε	Tanδ	ε	Tanδ	ε	Tanδ	ε	Tanδ
$Ba_3La_3Ti_5Ta_5O_{30}$	1425	127.8	0.0001	127.6	0.0017	127.7	0.0021	128.0	0.0048
$Ba_4La_2Ti_4Ta_6O_{30}$	1400	127.8	0.0001	127.8	0.0001	128.0	0.0003	128.6	0.0014
$Ba_5LaTi_3Ta_7O_{30}$	1425	148.2	0.0020	148.0	0.0009	148.1	0.0008	148.7	0.0011

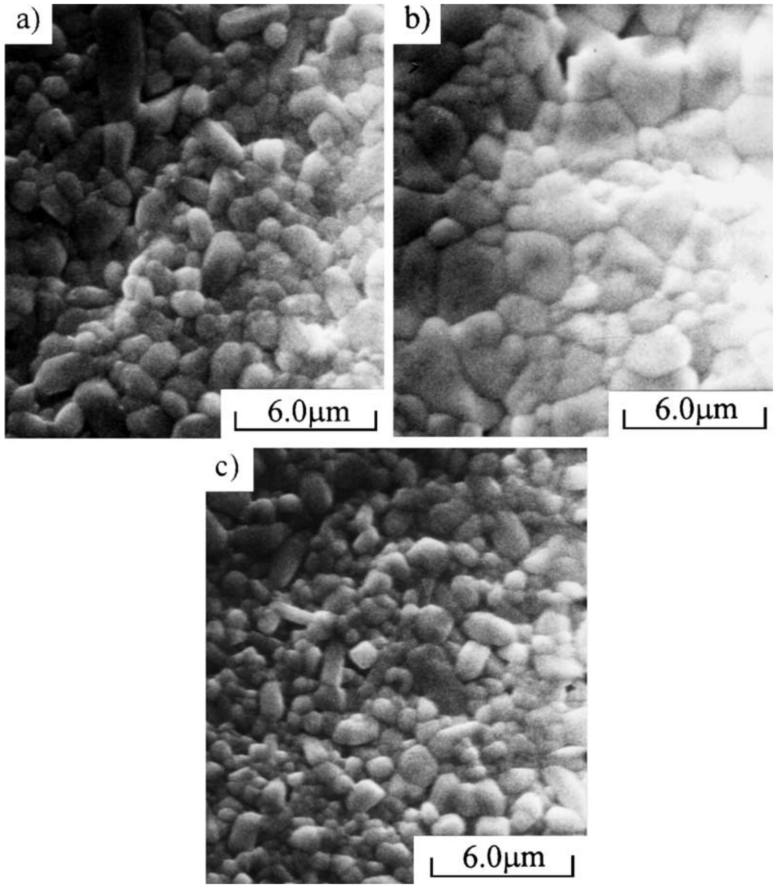

Fig. 4. SEM micrographs of polished and thermal-etched surfaces of (a) $Ba_3La_3Ti_5Ta_5O_{30}$, (b) $Ba_4La_2Ti_4Ta_6O_{30}$ and (c) Ba_5 $LaTi_3Ta_7O_{30}$ ceramics.

Table 4
Microwave dielectric properties of ceramics in the BaO–La_2O_3–TiO_2–Ta_2O_5 system

Composition	Sintering temperature (°C)	f_0 (GHz)	ε	Tanδ	$Q{\cdot}f$ (GHz)
$Ba_3La_3Ti_5Ta_5O_{30}$	1425	3.1	126.6	0.027	115
$Ba_4La_2Ti_4Ta_6O_{30}$	1425	3.47	131.8	0.0064	542
$Ba_5LaTi_3Ta_7O_{30}$	1425	3.27	146.3	0.0057	574

−1347 ppm/°C, respectively. Compared with the BaO–Nd_2O_3–TiO_2–Ta_2O_5 and BaO–Sm_2O_3–TiO_2–Ta_2O_5 systems, tungsten bronze ceramics in BaO–La_2O_3–TiO_2–Ta_2O_5 system generally have a slightly smaller dielectric constant, a lower dielectric loss and an obviously smaller temperature coefficient of dielectric constant.

The temperature dependency of dielectric constant at 1 MHz is shown in Fig. 5. There is no significant peak observed in these figures, and the dielectric constant generally decreases with increasing temperature. Table 3 gives the variation of room-temperature dielectric characteristics of the present ceramics. Though the dielectric loss varies with frequency, the dielectric constant is almost frequency independent. This suggests the paraelectric nature of the present ceramics at and above room-temperature.

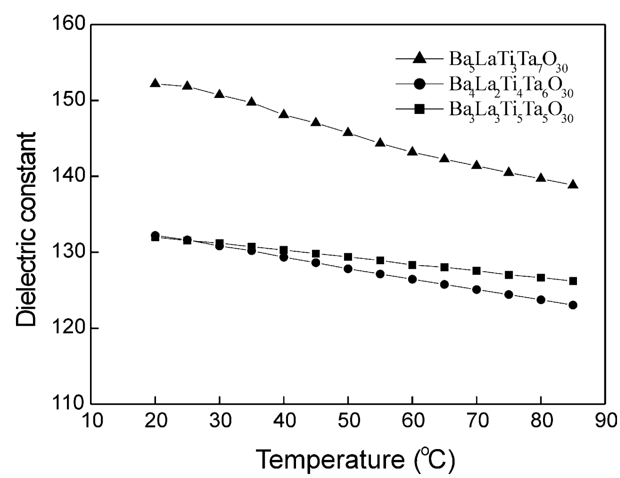

Fig. 5. Variation of dielectric constant with temperature at 1 MHz: $Ba_3La_3Ti_5Ta_5O_{30}$ sintered at 1425 °C; $Ba_4La_2Ti_4Ta_6O_{30}$ sintered at 1400 °C; $Ba_5LaTi_3Ta_7O_{30}$ sintered at 1425 °C.

The microwave dielectric properties are listed in Table 4. The dielectric constant at microwave frequencies shows a slight difference compared with that at 1 MHz, and the $Q{\cdot}f$ value ranges from 115 to 574 GHz. The relatively lower $Q{\cdot}f$ is due to the frequency relaxation, and it is the key issue to improve $Q{\cdot}f$ and to reduce the temperature coefficient of dielectric constant when the microwave application is considered.

4. Conclusion

The high-ε dielectric ceramics were prepared and characterized in $BaO–La_2O_3–TiO_2–Ta_2O_5$ system. The tungsten bronze single-phase structure was observed in all three typical compositions $Ba_3La_3Ti_5Ta_5O_{30}$, $Ba_4La_2Ti_4Ta_6O_{30}$ and $Ba_5LaTi_3Ta_7O_{30}$, and the present ceramics indicated high dielectric constant ε (127.7–148.1) and low dielectric loss tanδ (in the order of 10^{-4}–10^{-3} at 1 MHz). Meanwhile, the temperature coefficient of dielectric constant τ_ε varied from −728 to −1347 ppm/°C with increasing Ba and Ta content and decreasing La and Ti content in the temperature range of 20–85 °C.

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