Journal of the European Ceramic Society 22 (2002) 87–91

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Strontium/titanium cosubstituted $Ba_4Sm_2Ti_4Ta_6O_{30}$ dielectric ceramics

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Received 23 August 2000; received in revised form 16 January 2001; accepted 3 February 2001

Abstract

Modification of the dielectric properties of $Ba_4Sm_2Ti_4Ta_6O_{30}$ ceramics by Sr substitution for Ba on the A-sites and Ti substitution for Ta on the B-sites was investigated. With increasing Ti concentration, the temperature coefficient of the dielectric constant was significantly improved together with decreased dielectric loss and slightly decreased dielectric constant. The minimum temperature coefficient of -470ppm/°C was obtained in the composition of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}(x=3.0)$ with $\varepsilon = 111$, $Qf = 200$ GHz.

Keywords: $Ba_4Sm_2Ti_4Ta_6O_{30}$; Dielectric properties; Tungsten–bronze structure

1. Introduction

Recently, high-performance dielectric ceramics as the key materials for resonators and temperature-compensated capacitors are of great interest and technological importance due to the rapid progress in microwave telecommunications and satellite broadcasting.[1–4] High-ε dielectric ceramics ($\varepsilon > 110$) attract more and more attention for size miniaturization of related devices and some work has been carried out to search for promising candidates for new materials.[5,6]

In a previous work,[7] dielectric ceramics in the BaO–Sm_2O_3–TiO_2–Ta_2O_5 quaternary system were proposed and investigated, for the five typical compositions $BaSm_5Ti_7Ta_3O_{30}$, $Ba_2Sm_4Ti_6Ta_4O_{30}$, $Ba_3Sm_3Ti_5Ta_5O_{30}$, $Ba_4Sm_2Ti_4Ta_6O_{30}$ and $Ba_5SmTi_3Ta_7O_{30}$. Ceramics based on the latter three compositions, which tend to form the tungsten-bronze phase, have a high dielectric constant in the range from 114 to 175 and a low dielectric loss in the order of 10^{-3}. But their relatively large negative temperature coefficient of dielectric constant must be suppressed into an acceptable level if the microwave and high frequency applications are considered. With substituting Ba by Sr in $Ba_3Sm_3Ti_5Ta_5O_{30}$ ceramics, Xu et al.[8] markedly improved the temperature coefficient of dielectric constant from -1500 to -800 ppm/°C, where the dielectric constant was 110, and dielectric loss was 2.0×10^{-3}.

Up to now, modifications of this quaternary system are all focused on substitution for Ba on A sites, and it is difficult to realize synergic modification by this mean. Mizuta et al.[9] reported that partial substitution of Al^{3+} ions for Ti^{4+} ions on B-sites of tungsten bronze-type $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solutions decreased the negative τ_f value. They also pointed out that the positive τ_f value of the $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$(R = Nd and La) solid solution can be adjusted to zero. Wu et al.[10] demonstrated that Zr substitution for Ti in the BaO–Nd_2O_3–TiO_2 system improved the τ_ε value. So, the question is whether the temperature coefficient can be suppressed by some suitable substitution for Ti^{4+} or Ta^{5+} on the B-sites in the BaO–Sm_2O_3–TiO_2–Ta_2O_5 tungsten bronze system.

Among the ceramics in BaO–Sm_2O_3–TiO_2–Ta_2O_5 system, $Ba_4Sm_2Ti_4Ta_6O_{30}$ dielectric ceramic has special importance because of its high dielectric constant and relatively low dielectric loss ($\varepsilon_r = 160$, $\tan\delta = 0.0035$). In the present work, modification of dielectric properties of $Ba_4Sm_2Ti_4Ta_6O_{30}$ ceramics by Sr substitution for Ba on the A-sites and Ti substitution for Ta on the

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0955-2219/01/$ - see front matter
PII: S0955-2219(01)00233-3

B-sites was investigated for developing high-ε dielectric ceramics with small temperature coefficient.

2. Experimental

The objective ceramics with compositions $Ba_4Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ($x=1.0$, 1.5, 2.0, 2.5 and 3.0, respectively) were prepared by conventional ceramics processing. High purity $BaCO_3$ (>99.95%), $SrCO_3$ (>99.95%), Sm_2O_3 (>99.5%), TiO_2 (>99.8%) and Ta_2O_5 (>99.99%) powders were used as raw materials. Mixtures of the powders were ground by attrition in a polyethylene jar with zirconia balls in ethanol for 24 h, then dried and calcined in a high-purity alumina crucible at 1300°C for 3 h in air. Calcination was followed by a second attrition grinding to reach a homogeneous granulometric distribution. Added with organic binders (5 wt.% polyvinyl alcohol), the granules of the compositions were palletized into cylindrical compacts of 12 mm in diameter and 2–5mm in thickness at a pressure of about 98 MPa. The disks were sintered at 1330 to 1380°C for 3 h in air to yield dense ceramics. The samples were cooled at a rate of 2°C/min from the sintering temperature to 1100°C, and then cooled in the furnace.

Bulk density was measured by the dimensional method for the polished samples. Phase composition and microstructure were characterized by X-ray diffraction (XRD) analysis using a graphite diffracted beam monochromator (Rigaku D/max-3B, CuK_α, $\lambda = 1.5406$ Å).

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 the dielectric constant was evaluated at 10 KHz from room temperature to 85°C by another LCR meter (WK4210) equipped with a themostat. Silver paste was used for the electrodes. Microwave dielectric properties were measured by Hakki and Coleman's dielectric resonator method.[11]

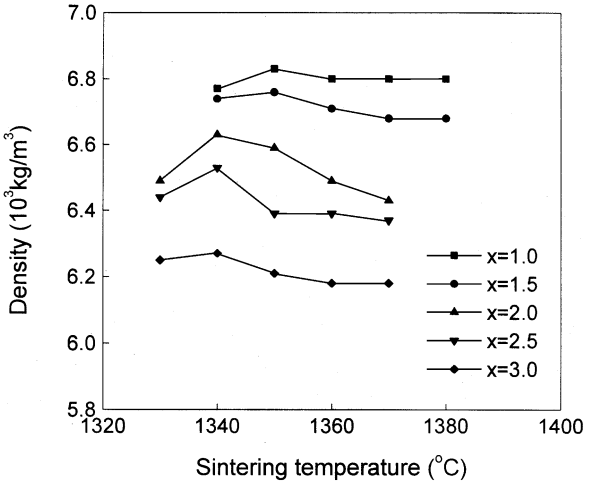

Fig. 1. Densities of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics with various compositions as functions of sintering temperature.

Table 1
Theoretical, bulk and relative density of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics

x	Densification temperature (°C)	Theoretical density (kg/m^3)	Bulk density (kg/m^3)	Relative density
1.0	1350	6700	6352	94.8%
1.5	1350	6310	6287	99.6%
2.0	1340	5915	6166	–
2.5	1340	5517	6073	–
3.0	1340	5121	5831	–

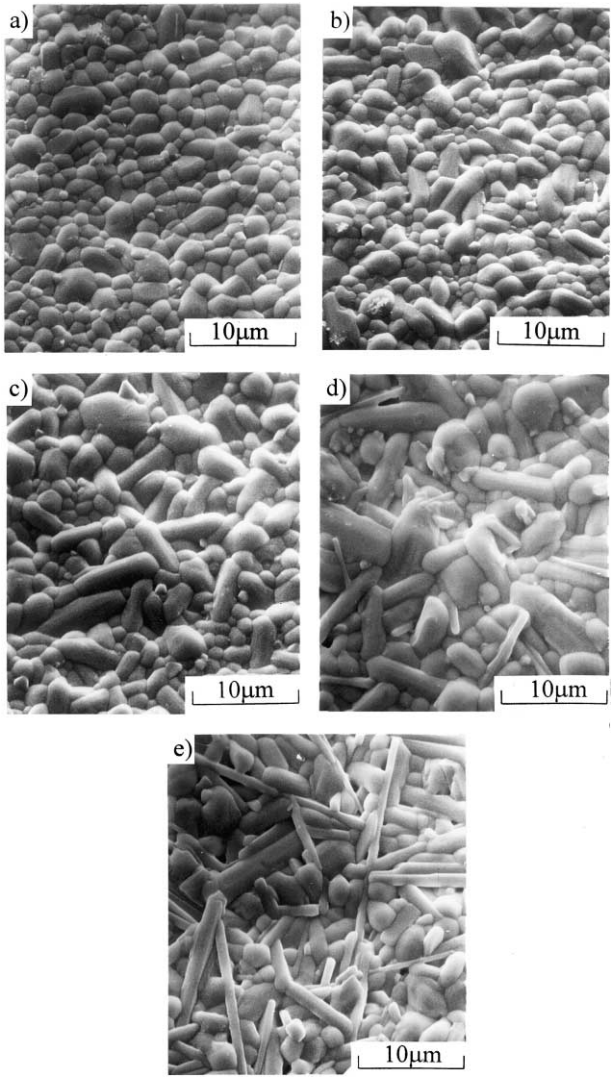

Fig. 2. SEM micrographs of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics: (a) $x=1.0$, sintered at 1350°C; (b) $x=1.5$, sintered at 1350°C; (c) $x=2.0$, sintered at 1340°C; (d) $x=2.5$, sintered at 1350°C; (e) $x=3.0$, sintered at 1340°C.

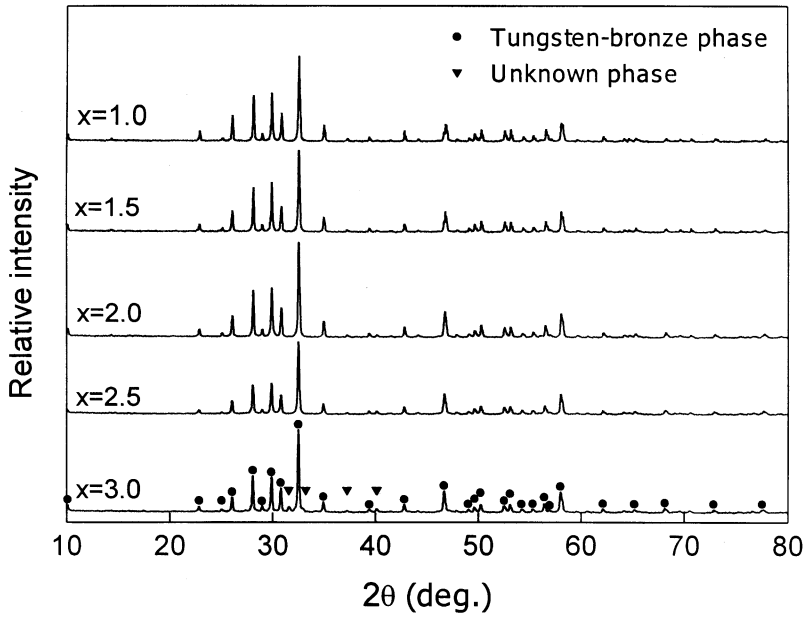

Fig. 3. XRD patterns of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics sintered at the densification temperature in air for 3 h.

3. Results and discussion

The bulk density of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$($x$ = 1.0, 1.5, 2.0, 2.5 and 3.0) dielectric ceramics is shown as a function of sintering temperature in Fig. 1. The present ceramics can be well sintered in the temperature range from 1340 to 1350°C, and both the theoretical and bulk density decrease with increasing substitution of Ti for Ta (see Table 1). For the compositions with $x \geqslant 2.0$, the bulk density tends to be greater than the predicted theoretical density. This is the evidence that some secondary phase appears at these situations. With increasing Ti concentration, the optimal sintering temperatures of the present ceramics slightly decrease from 1350 to 1340°C. This tendency is also confirmed by the microstructures of the present ceramics (Fig. 2). The single phase ceramics with $x < 2.0$ need the higher densification temperature and form the fine isometric grain morphology, while the reduced densification temperature is required for the ceramics with $x \geqslant 2.0$ where the columnar structures are observed as the result of the formation of some liquid phase during the sintering.

The $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ dielectric ceramics with $x = 1.0$ and 1.5 were identified as a single phase tungsten bronze-type solid solutions in agreement with JCPDS file No. 48-0966 [Fig. 3(a) and (b)]. With gradual substitution of Ti for Ta, some infinitesimal peaks of a secondary phase emerge in the XRD patterns of the compositions of $x = 2.0$, 2.5 and 3.0, which is shown in Fig. 3(c)–(e). Fig. 4 gives the unit cell volume of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics obtained by least-squares refinement of X-ray diffraction data as a function of composition x. The unit cell volume increases with increasing x.

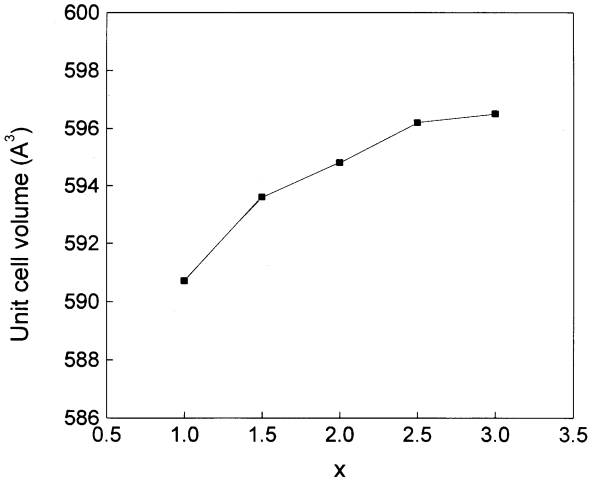

Fig. 4. The unit cell volume of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics as a function of x.

The dielectric properties as functions of composition and frequency are listed in Table 1, for the present ceramics sintered at the optimal sintering temperatures of each composition. High dielectric constants and low dielectric loss are indicated for all these dense ceramics. The considerable decrease in the dielectric constant of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics compared with that of $Ba_4Sm_2Ti_4Ta_6O_{30}$ ceramics is due to the substitution of Sr for Ba on A-sites. Moreover, the dielectric constant slightly decreases with increasing content

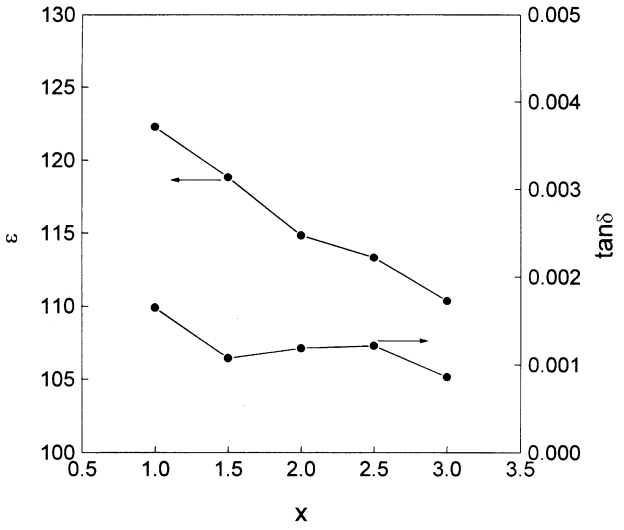

Fig. 5. Dielectric constant and dielectric loss of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics as functions of x.

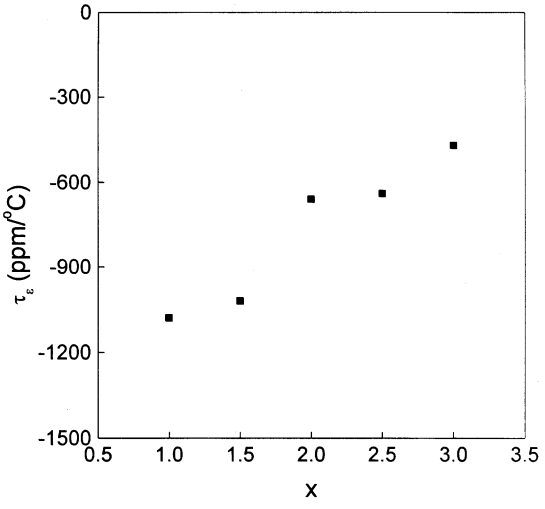

Fig. 6. Temperature coefficient of dielectric constant of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics as a function of x.

of Ti, as shown in Fig. 5. This decrease can be followed using the Clausius–Mosotti equation:

$$\varepsilon_r = \frac{3V_m + 8\pi\alpha_D}{3V_m - 4\pi\alpha_D} = 1 + \frac{12\pi(\alpha_D/V_m)}{3 - 4\pi(\alpha_D/V_m)}$$

where V_m is the molar volume and α_D is the net dielectric polarizability. Thus the decrease is ascribed to two factors: one is the decrease in the net dielectric polarizability α_D with increasing substitution of Ti for Ta (the ionic polarizability of Ti and Ta is 2.93 and 4.73, respectively)[12] and the slight expansion of the unit cell volume.

The present modified ceramics by Sr/Ti co-substitution have the significantly decreased dielectric loss compared with that of the end-member $Ba_4Sm_2Ti_4Ta_6O_{30}$ (0.0035 at 1 MHz), and the very low dielectric loss even

Table 2
Dielectric properties of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics sintered at the densification temperature in air for 3 h

Composition	100 KHz		500 KHz		1 MHz		5 MHz	
	ε	tanδ	ε	tanδ	ε	tanδ	ε	tanδ
$Ba_4Sm_2Ti_4Ta_6O_{30}$	161.8	0.0035	161.3	0.0035	160.8	0.0035		
$x=1.0$	122.4	0.00135	122.3	10^{-6}	122.3	0.00165	122.8	10^{-6}
$x=1.5$	118.9	0.00062	118.8	10^{-6}	118.8	0.00108	119.3	10^{-6}
$x=2.0$	114.9	0.00064	114.8	10^{-6}	114.9	0.00119	115.3	10^{-6}
$x=2.5$	113.4	0.00068	113.3	10^{-6}	113.3	0.00123	113.8	10^{-6}
$x=3.0$	110.4	0.00078	110.3	10^{-6}	110.4	0.00086	110.8	10^{-6}

Table 3
Microwave dielectric properties of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics

Composition	Sintering temperature (°C)	f_0 (GHz)	ε	tanδ	Qf (GHz)
$x=2.0$	1340°C×3 h	3.63	114	0.024	151
$x=2.5$	1340°C×3 h	4.16	114	0.029	143
$x=3.0$	1340°C×3 h	3.32	111	0.017	200

less than 10^{-6} is indicated at the frequencies of 500 KHz and 5 MHz (see Table 2). Because the effective ionic radius of Sr^{2+} (1.44 Å) is smaller than that of Ba^{2+} (1.61 Å),[13] the inner strain of the present ceramics is reduced by Sr substitution for Ba, which leads to the decrease of the dielectric loss. The octahedra titling due to Ti substitution for Ta also contribute to the decrease of dielectric loss.

The temperature coefficient of dielectric constant of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$ ceramics is shown as a function of x in Fig. 6. Compared with that of the end-member of $Ba_4Sm_2Ti_4Ta_6O_{30}$($\tau_\varepsilon = -2200$ ppm/°C), the τ_ε value is suppressed by Sr substitution for Ba and Ti substitution for Ta. The τ_ε value decreases with increasing Ti concentration, and the minimum temperature coefficient of −470 ppm/°C is obtained in the composition of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}$($x=3.0$). It may be caused by the variation of the temperature-dependence of the macroscopic polarizability by Ti substitution for Ta. The detailed reason remains to be investigated further.

The microwave dielectric properties were evaluated by Hakki and Coleman's dielectric resonator method. As shown in Table 3, dielectric loss at microwave frequency is still too large due to the frequency dispersion of the present ceramics, which have weak relaxor ferroelectricity.

4. Conclusions

The temperature coefficient of the dielectric constant is suppressed significantly by substitution of Sr for Ba and Ti for Ta simultaneously in $Ba_4Sm_2Ti_4Ta_6O_{30}$

ceramics, while the dielectric constant remains above 110. The minimum temperature coefficient of dielectric constant (−470 ppm/°C) is obtained in the composition of $Ba_2Sr_2Sm_2Ti_{4+x}Ta_{6-x}O_{30-x/2}(x=3.0)$. Substitution of Sr for Ba also markedly reduced the dielectric loss. At the frequency of 500 KHz and 5 MHz, the dielectric loss of the present ceramics is even less than 10^{-6}. But at microwave frequency, the dielectric loss at microwave frequency is still too large due to the frequency dispersion of the present ceramics.

The present ceramics have great application potential for high-frequency capacitors and temperature-compensate capacitors. Considering microwave application, whether the frequency dispersion can be restrained to reduce the dielectric loss at microwave frequency is the key issue.

Acknowledgements

This work was financially supported by Chinese National High-Tech Project under grant number 863-715-006-0072 and Special Program for Outstanding Young Scientists of Zhejiang Province under grant number RC98028.

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