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Modified $Ba_3Sm_3Ti_5Ta_5O_{30}$ dielectric ceramics

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Abstract

Dielectric ceramics of $Ba_3Sm_3Ti_5Ta_6O_{30}$ were modified by introducing the nonstoichiometric composition $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ and the sintering characteristics, microstructures and dielectric properties of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics were investigated as a function of the composition. $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dense ceramics, sintered at 1400–l430°C, have complex phase constitutions, containing the tungsten–bronze major phase and the pyrochiore secondary phase. With increasing x, the temperature coefficient of dielectric constant (τ_ε) was pronouncedly improved from −l050 to −610 ppm/°C without considerable increase of dielectric loss, but the dielectric constant (ε) decreased considerably.

Keywords: $Ba_3SmTi_5Ta_5O_{30}$; Dielectric properties; Tungsten–bronze structure

1. Introduction

The rapid progress in microwave telecommunication and satellite broadcasting has been strongly driving the investigation of high-performance microwave dielectric ceramics.[1–7] The desirable properties of microwave dielectric ceramics are high dielectric constant (ε), low dielectric loss (tanδ) and small temperature coefficient of the resonant frequency. Recently, high dielectric constant ceramics ($\varepsilon > 100$) have attracted more and more intensive attentions for size miniaturization of resonators and temperature-compensated capacitors, and some work has been carried out to search promising candidates for the new materials.[8,9]

In the previous work,[10] dielectric ceramics in BaO–Sm_2O_3–TiO_2–Ta_2O_5 quaternary system were proposed and investigated, for the five typical compositions $BaSm_5Ti_7Ta_3O_{30}$, $Ba_2Sm_4Ti_6Ta_4O_{30}$, $Ba_3Sm_3Ti_5Ta_5O_{30}$, $Ba_4Sm_2Ti_4Ta_6O_{10}$ and $Ba_5SmTi_3Ta_7O_{30}$. Ceramics based on the latter three compositions, which tend to form 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}. However, their relatively large negative temperature coefficient of the dielectric constant must be suppressed into an acceptable level if the microwave applications are considered.

In the present work, we focus our attention on modification of $Ba_3Sm_3Ti_5Ta_5O_{30}$ which has a high dielectric constant of 114, low dielectric loss in the order of 10^{-3} and the smallest τ_ε ($\tau_\varepsilon = -1500$ ppm/°C) in the three compositions. The modification is conducted by introducing nonstoichiometric composition $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$. Sintering characteristics. microstructures and dielectric properties of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics are investigated together with the relationship between the dielectric properties and the microstructures.

2. Experimental procedures

Ceramics with nonstoichiometric compositions $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ($x = 0.25$, 0.5, 0.67, 0.75, respectively) were synthesized by powder processing from reagent-grade $BaCO_3$ (>99.95%), Sm_2O_3 (>99.5%), 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 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

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(5 wt.% polyvinyl alcohol), the granules of the reground powders were pelletized into cylindrical compacts of 12 mm in diameter and 2–5 mm in thickness, under the pressure of about 98 MPa. The disks were sintered at 1350–1450°C for 3 h in air to yield dense ceramics. The ceramics were cooled at a rate of 2°C/min from sintering temperature to 1100°C, and then cooled with furnace.

Bulk density was measured by dimensional method for the sintered samples. The microstructures 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.

The dielectric characteristics at room temperature were determined from capacitance measurements by an LCR meter (HP4284A) at 1, 10, 100 and 500 KHz and 1 MHz, respectively. The temperature dependence of 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]

3. Results and discussion

Fig. 1 shows XRD patterns of the present ceramics with different composition sintered at 1430°C. For all the compositions of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics, the tungsten–bronze phase is the major phase and a pyrochlore phase coexists as a secondary phase, and this is similar to that of $Ba_3Sm_3Ti_5Ta_5O_{30}$ ceramics.[10] The tungsten–bronze phase mentioned here is similar to that of $Ba_3La_3Ti_5Nd_5O_{30}$ (JCPDS file No. 39-1331) and the XRD peaks of this phase is in good agreement with JCPDS files No. 39-1331. Moreover, the relative peak intensity corresponding to the pyrochlore phase gradually increases with increasing x. This is suggested that increasing x leads to increased precipitation of the pyrochlore phase. Table 1 lists the phase constitution of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dense ceramics, which indicates that the content of pyrochlore secondary phase generally increases with increasing x though there is anomalous point at $x = 0.5$.

Bulk density is shown as a function of sintering temperature in Fig. 2. For all the four compositions mentioned above, the dense ceramics can be created with ease, although the optimal sintering temperatures slightly increase with increasing x. Fig. 3 shows the SEM photographs of the polished and thermal etched surfaces of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics sintered at 1430°C. It is observed that all the present ceramics are well sintered at 1430°C. Compared with that of the stoichiometric composition of $Ba_3Sm_3Ti_5Ta_5O_{30}$, the microstructures of the present ceramics reflect a more complex grain morphology, which is in agreement to the complex phase constitution which is observed from XRD analysis.

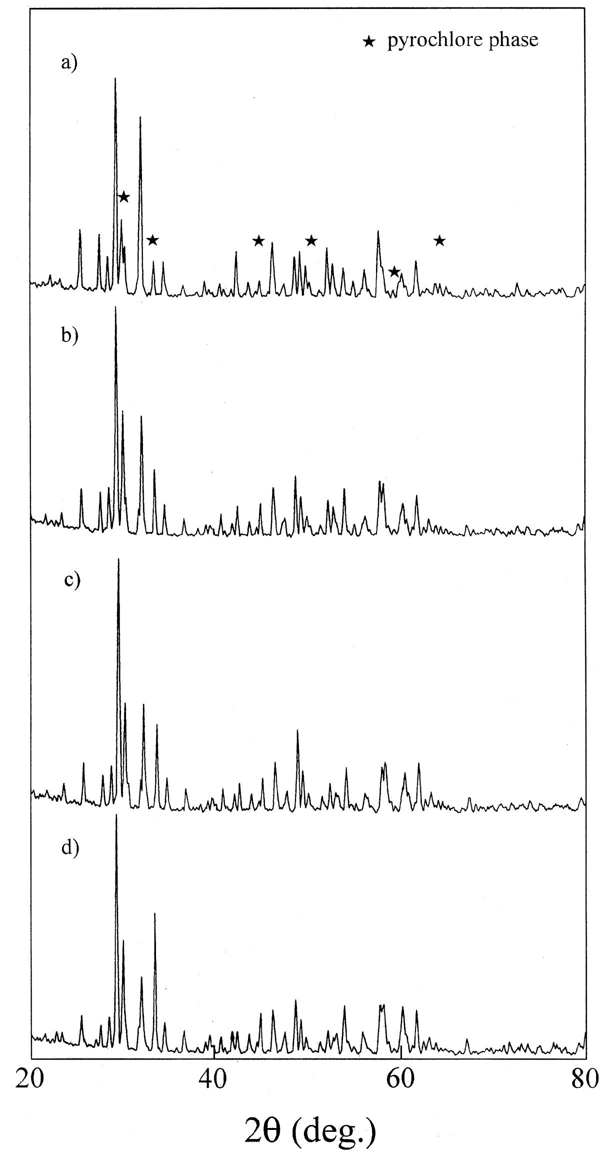

Fig. 1. XRD patterns of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dielectric ceramics sintered at 1430°C in air for 3 h: (a) $x = 0.25$; (b) $x = 0.50$; (c) $x = 0.67$; (d) $x = 0.75$.

Table 1
Phase constitution of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dense ceramics

x	Tungsten–bronze major-phase (%)	Secondary phase (%)
0.25	72.5	27.5
0.50	64.1	35.9
0.67	69.4	30.6
0.75	67.1	32.9

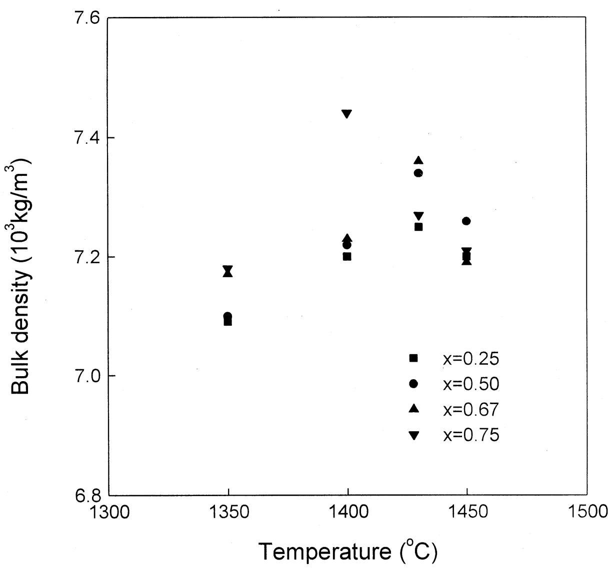

Fig. 2. Densities of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dielectric ceramics, sintered at the densification temperature in air for 3 h.

The variation of temperature coefficient of dielectric constant of the present ceramics is shown in Fig. 4 as a function of composition x, and the relationship between the temperature coefficient and x is almost linear. With increasing x from 0.25 to 0.75, the absolute value of the τ_ε notably decreased from 1050 to 610 ppm/°C while the τ_ε of $Ba_3Sm_3Ti_5Ta_5O_{30}$ is −1500 ppm/°C.[10]

The effect of composition on the dielectric constant and dielectric loss is summarized in Table 2, for the present ceramics sintered at their optimal sintering temperature where the nearly full densification is achieved. Compared with the stoichiometric composition, Ba_{3-3x}–$Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics have an obviously decreased dielectric constant and the low dielectric loss remaining in the order of 10^{-3}. As shown in Fig. 5, the dielectric constant decreased obviously with increasing x. The variation of dielectric loss is more complex and further research is necessary in order to elucidate the relationship between dielectric loss and composition.

Compared with the situation in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solution system,[12] there is a similar variation tendency of dielectric constant and temperature coefficient

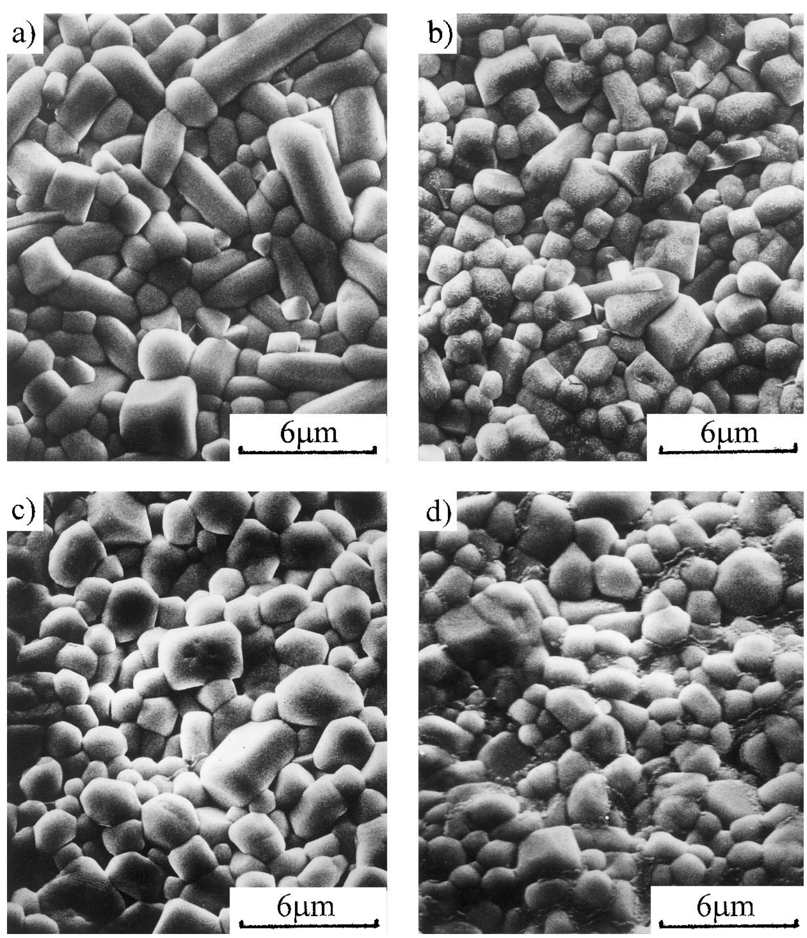

Fig. 3. SEM micrographs of polished and thermal etched surfaces of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ dielectric ceramics sintered at 1430°C in air for 3 h: (a) $x=0.25$; (b) $x=0.50$, (c) $x=0.67$; (d) $x=0.75$.

Table 2
Room-temperature dielectric properties of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$, dense ceramics

	$x=0.25$		$x=0.50$		$x=0.67$		$x=0.75$	
	ε	$\tan\delta$	ε	$\tan\delta$	ε	$\tan\delta$	ε	$\tan\delta$
1 KHz	95.0	0.0055	75.9	0.0017	60.9	0.0016	53.7	0.0009
10 KHz	94.2	0.0036	75.8	0.0011	60.7	0.0015	53.6	0.0008
100 KHz	93.6	0.0030	75.7	0.0017	60.6	0.0024	53.6	0.0012
500 KHz	93.5	0.0027	75.6	0.0019	60.4	0.0027	53.5	0.0012
1 MHz	93.4	0.0028	75.5	0.0021	60.4	0.0030	53.5	0.0014

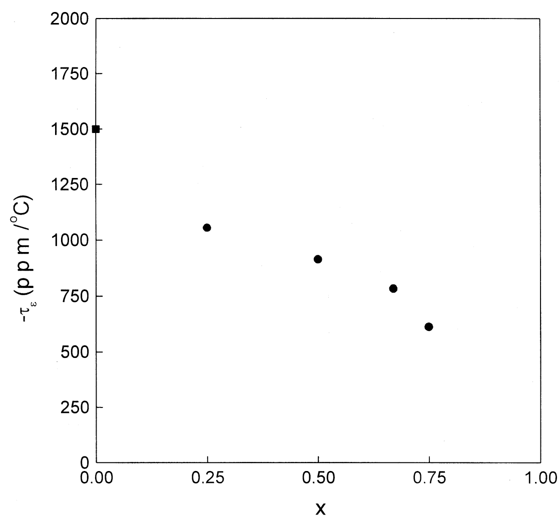

Fig. 4. Temperature coefficient of dielectric constant of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics as a function of x.

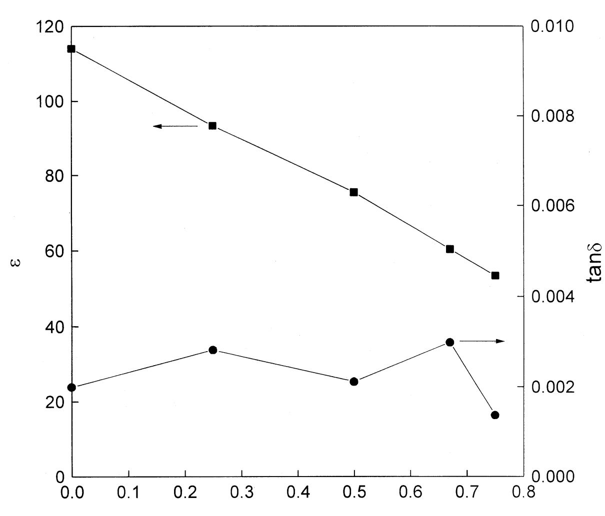

Fig. 5. Dielectric characteristics of $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$ ceramics as a function of x.

of the present ceramics with Sm substitution for Ba. That is, the increase in number of vacancies to maintain charge neutrality and the smaller ionic radii of Sm lead to the shrinkage of the oxygen octahedra and the suppression of B-site ions' movement, and subsequently result in the decrease of dielectric constant and the improvement of temperature coefficient in the present ceramics. However. the effect of secondary phase on the reduction of temperature coefficient should also be emphasized in the present system.

4. Conclusion

Modification of $Ba_3Sm_3Ti_5Ta_5O_{30}$ dielectric ceramics has been investigated by adjusting the composition into $Ba_{3-3x}Sm_{3+2x}Ti_5Ta_5O_{30}$. The present ceramics have good sinterability and complex phase constitution, containing the tungsten–bronze phase as the major phase and the pyrochlore phase as the secondary phase. Increasing x leads to significant improvement of the temperature coefficient from −1050 to −610 ppm/°C while the τ_ε of $Ba_3Sm_3Ti_5Ta_5O_{30}$ ceramics is −1500 ppm/°C. On the other hand, the obviously decreased dielectric constant with increasing x becomes a new problem for the present ceramics.

Acknowledgements

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