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Structure and Microwave Dielectric Characteristics of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ Ceramics as a Function of Sintering Time

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ABSTRACT

Effects of sintering time upon the structures and microwave dielectric characteristics of co-substituted $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics (x=2/3) were investigated. Prolonged sintering had significant effects upon the Qf value and temperature coefficient, and a high Qf value (10,600 GHz) was obtained in the present ceramics combined with high-ε (80) and near-zero temperature coefficient.

Key words : Dielectric properties, $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$, Microstructure, XRD

1. Introduction

The tungsten-bronze-like $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$ (Ln=rare earth metal) solid solutions[1-3] have excellent microwave dielectric properties for dielectric resonator applications used in the microwave telecommunication such as mobile phone systems and satellite broadcasting.[4-6] The tungsten-bronze-like structure is composed of corner-sharing perovskite-like (TiO_6) octahedra. In the framework of linked octahedra, two pentagonal sites (A2) are occupied by Ba; five rhombic sites (A1) are occupied by Ln and Ba, with some vacancies; and the trigonal sites (C) are empty.[7,8] Ohsato *et al.*[7] have proposed the structural formula $[Ln_{8+2x}Ba_{2-3x}]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ ($0 \le x \le 2/3$). The best microwave dielectric properties were obtained for the composition x=2/3 in these solid solution series where Ln and Ba ions occupy A1-sites and A2-sites, respectively. Achieving a near-zero temperature coefficient of resonant frequency (τ_f) in the present ceramics is an important issue. A good combination of high Qf and near-zero τ_f can be attained by the formation of a solid solution of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$, and some successful work has been carried out.[5,9,10] Furthermore, co-substitution of Nd and Sn for Sm and Ti could further improve Qf values in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramics (x=2/3).[11]

In the present work, $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics (x=2/3) are sintered up to 12 h, and the dielectric constant, Qf value, and temperature coefficient of resonant frequency τ_f are investigated as a function of sintering time. Microstructures are characterized by X-ray diffraction and scanning electron microscope for the sintered samples. The variation of microwave dielectric properties with sintering conditions is correlated with the microstructures.

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2. Experimental Procedures

$Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ (x=2/3) ceramics with y=0.1, 0.3, 0.5 and 0.8 were prepared by a solid state reaction process using reagent-grade $BaCO_3$ (99.93%), Nd_2O_3 (99%), Sm_2O_3 (99.5%), TiO_2 (99.5%) and SnO_2 (99.5%) powders. The weighed powders were mixed by ball milling with zirconia media, in ethanol, for 24 h, then heated at 1200°C in air for 3 h after drying. The calcined powders, with 6 wt% of PVA added, were pressed into disks 12 mm in diameter and 26 mm in height and then sintered at 1360°C in air for 3 h, 6 h, and 12 h. After the samples had been cooled from sintering temperature to 1100°C, at a rate of 2°C/min, the ceramics were cooled inside the furnace.

The crystalline phases of sintered specimens were examined by X-Ray Diffraction(XRD) analysis, using CuKα radiation, and the crystal parameters were calculated by least-squares refinement of the XRD data between 20° and 60°. The microstructures were characterized by Scanning Electron Microscopy(SEM) on the polished and thermal-etched surfaces. The dielectric constant ε and quality factor Q (the inverse of dielectric loss, tan δ) in microwave range were evaluated at 45 GHz, using the resonator method of Hakki and Coleman.[12] Because Q factor generally varies inversely with the frequency, f, in the microwave region, the product of Qf was used to evaluate the dielectric loss instead of Q. The temperature coefficient of the dielectric constant, τ_ε was evaluated at 1 MHz, using an LCR meter (Model HP4284A, Hewlett-Packard Co., Palo Alto, CA) equipped with a thermostat. The τ_f value was calculated from the equation,

$$\tau_f = -(\tau_\varepsilon/2) - \alpha \quad (1)$$

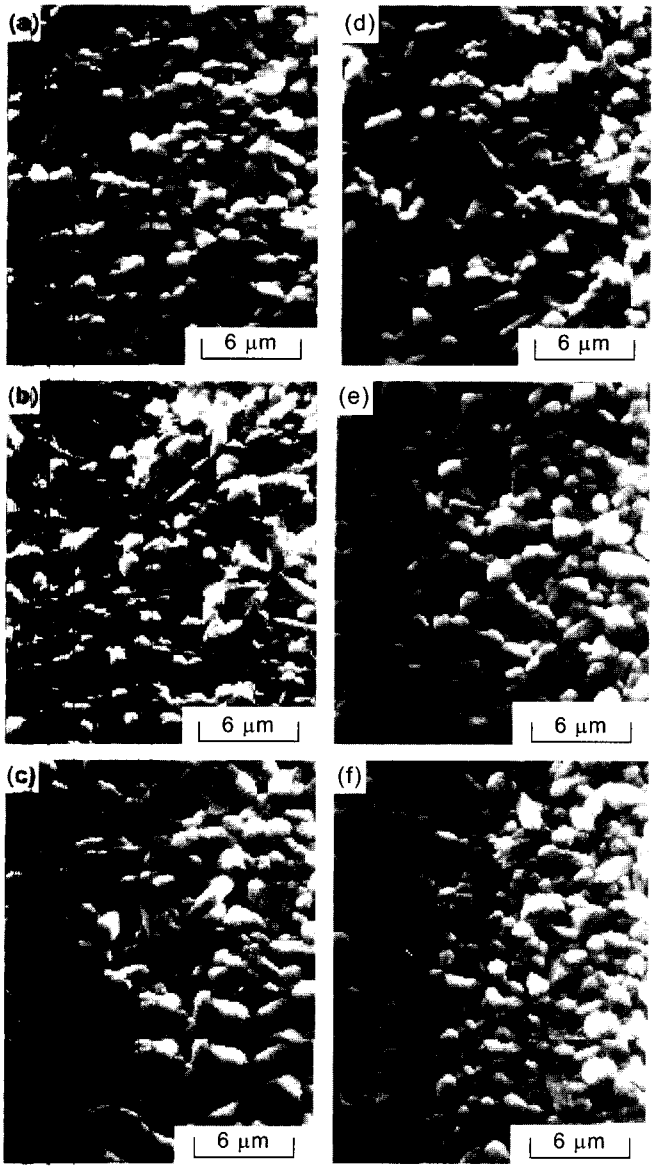

Fig. 1. SEM micrographs of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics sintered at 1360°C for (a) 3 h (y=0.3), (b) 6 h (y=0.3), (c) 12 h (y=0.3), (d) 3 h (y=0.8), (e) 6 h (y=0.8), and (f) 12 h (y=0.8).

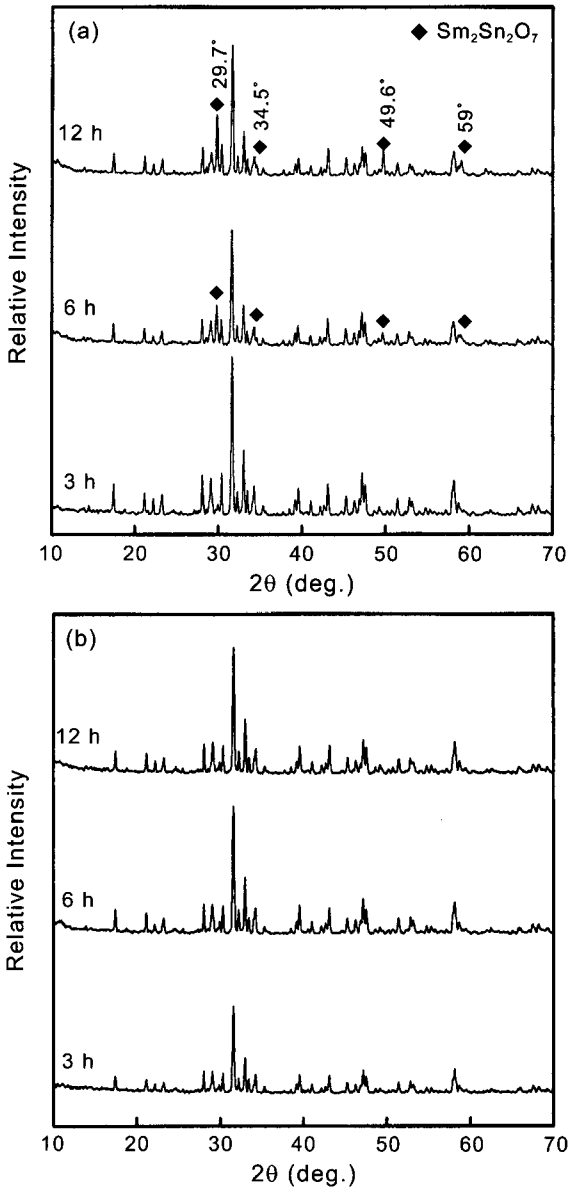

Fig. 2. XRD patterns of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics sintered at 1360°C for 3 h, 6 h, and 12 h. (a) y=0.3, and (b) y=0.8.

where α is the linear thermal expansion coefficient (~10 ppm/°C).[13]

3. Results and Discussion

Fig. 1 shows typical SEM micrographs of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ (y=0.3 and y=0.8) ceramics. Densification of the present ceramics is performed well at the temperature of 1360°C for 3 h, 6 h, and 12 h, and homogeneous microstructures with small grains are observed in the dense ceramics. The present ceramics exhibit a typical columnar grain morphology, which varies little with sintering time for y=0.8, but the aspect ratio varies with sintering time for y=0.3.

As shown in Fig. 2, $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics take the $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$-based tungsten bronze-like structure (JCPDS Card No. 43-235), and no secondary phases are observed in the full range of sintering time (3 h to12 h) for samples with y=0.8. For the composition y=0.3, though no secondary phases are identified for ceramics sintered for 3 h, the variation of the relative intensity of the peaks around 2θ=29.7° and 49.6° and the splitting of the peaks around 2θ=34.5° and 59° indicate the precipitation of $Sm_2Sn_2O_7$ (JCPDS Card No. 13-181) for ceramics sintered for 6 h and 12 h.

The influence of sintering time upon the microwave dielectric properties of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics was shown in Table 1 and also in Figs. 3 and 4.

Table 1. Microwave Dielectric Properties of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{1-z}Sn_z)_{18}O_{54}$ Ceramics

y	z	Sintering time (h)	f_0 (GHz)	e	tanδ	Qf (GHz)	τ_f (ppm/°C)
0	0	3	4.16	81	0.00045	9,240	−11
	0.05	3	4.13	76	0.00066	6,260	+2
	0.1	3	4.42	68	0.0011	4,020	+20
0.1	0.05	3	4.20	76	0.00062	7,130	+6
		6	4.04	76	0.00056	7,214	−2
		12	3.89	76	0.00055	7,072	−3
0.3	0.05	3	4.16	77	0.00053	7,850	+9
		6	4.03	77	0.0005	8,060	+7
		12	4.01	77	0.00049	8,184	+1
0.5	0.05	3	4.04	80	0.00041	9,850	+10
		6	3.83	80	0.00038	10,080	+9
		12	4.02	80	0.0004	10,050	+5
0.8	0.05	3	4.10	80	0.00041	10,000	+19
		6	3.95	80	0.00038	10,400	+12
		12	3.92	80	0.00037	10,600	+11

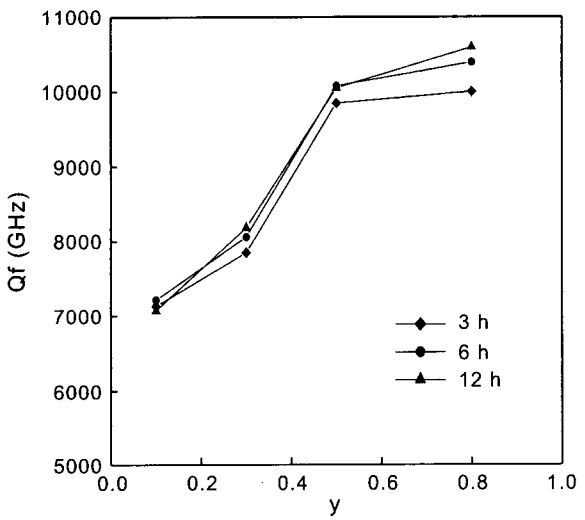

Fig. 3. Qf value of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics as a function of Nd content, y, for various sintering time.

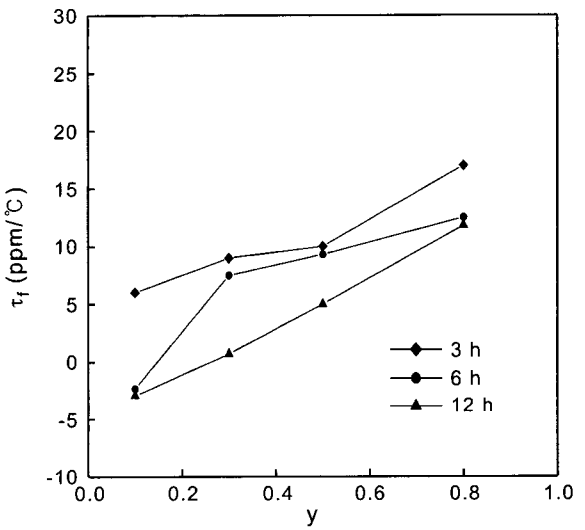

Fig. 4. Temperature coefficient of resonant frequency of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics as a function of Nd content, y, for various sintering time.

Although the dielectric constant is not almost sensitive to the sintering time, Qf factor and temperature coefficient vary significantly with sintering time. Generally the Qf factor increases with extending sintering time, and this tendency becomes more pronounced with increasing y. Prolonged sintering generally increases crystallizability and ordering degree of cations, and subsequently increasing the Qf value. However, for the Sm-rich compositions, the secondary phase prevents such variation tendency.

It should be noted that the temperature coefficient is significantly affected by sintering time in the present ceramics. Increasing sintering time leads to a less negative temperature coefficient τ_ε and subsequently a smaller positive or more negative temperature coefficient τ_f. The phenomenon is very important because we can further improve the temperature coefficient of resonant frequency τ_f to near zero in Nd-rich compositions (y=0.8), which have higher dielectric constant and Qf factors (>10,000 GHz).

The interesting variation tendency of temperature coefficients τ_ε and τ_f vs. sintering time might be primarily concerned with the variation of crystallizability and long-range ordering degree of A-site cations. According to Clausius-Mosotti equation,

$$\frac{\varepsilon-1}{\varepsilon+2}=\frac{\alpha_m}{3V\varepsilon_0} \tag{2}$$

the temperature coefficient of dielectric constant is obtained by differentiation of equation (2) where α_m is the polarizability of a macroscopic small sphere of volume V.[14]

$$\tau_\varepsilon=\frac{1}{\varepsilon}\left(\frac{\partial\varepsilon}{\partial T}\right)_P=\frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(A+B+C) \tag{3}$$

where $A=-\frac{1}{3V}\left(\frac{\partial V}{\partial T}\right)_P=-\alpha$, $B=\frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial V}\right)_T\left(\frac{\partial V}{\partial T}\right)_P$,

$$C=\frac{1}{3\alpha_m}\left(\frac{\partial \alpha_m}{\partial T}\right)_V.$$

This separation of the temperature coefficient into three components was as follows:

(A) The decrease in the number of polarizable intrinsic ions and electrons per unit volume as the temperature increases-a direct consequence of volume expansion.

(B) The increase in the polarizability of a constant number of polarizable intrinsic ions and electrons with the increase in the available volume as the temperature increases.

(C) The dependence on temperature of the polarizability of the intrinsic ions and electrons, the volume remaining constant.

The capacitance C of a parallel-sided capacitor is given by

$$C=\frac{\varepsilon\varepsilon_0 a}{d} \quad (4)$$

where ε_0 is the permittivity of free space, a is the area, and d the separation of the plates. Then the temperature coefficient of capacitance can be obtained as

$$\tau_c=\frac{1}{c}\left(\frac{\partial c}{\partial T}\right)_P=\frac{1}{\varepsilon}\left(\frac{\partial \varepsilon}{\partial T}\right)_P+\alpha \quad (5)$$

α is the linear expansion coefficient and from equation (3), $A=-\alpha$. Therefore, for most insulators,

$$\tau_c=\frac{(\varepsilon-1)(\varepsilon+2)}{\varepsilon}(-\alpha+B+C)+\alpha \quad (6)$$

For the present ceramics ($\varepsilon\geq 1\geq 0$, $\tan\delta\leq 0.1\%$), $\tau_c=\varepsilon(B+C)-\alpha\varepsilon\approx G-\alpha\varepsilon$, where G is a constant. Then,

$$\tau_f=\tau_c-\alpha=G-\alpha(\varepsilon+1) \quad (7)$$

$$\tau_f=-\tau_c/2-\alpha=-[G-\alpha(\varepsilon-1)]/2 \quad (8)$$

In the present situation, the dielectric constant is independent of sintering time, so the variation of temperature coefficient is primarily due to the variation of α. The linear expansion coefficient α is affected by densification, crystallizability and long-range ordering degree. With prolonging sintering time, the increased crystallizability and ordering degree will lead to the decreased α, and subsequently the less negative τ_c. Therefore, the temperature coefficient of resonant frequency τ_f shifts to smaller positive or more negative side.

Through controlling sintering time and microstructures, the excellent microwave dielectric characteristics of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics are obtained for y=0.8 after prolonged sintering: ε=80, Qf=10,600 GHz, τ_f= +11 ppm/°C.

4. Conclusions

The microstructures of the solid solution of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ (x=2/3) were examined by X-ray diffraction and SEM analysis, which collectively provided a better understanding of the property-structure relationship of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}(Ti_{0.95}Sn_{0.05})_{18}O_{54}$ ceramics. Sintering time had significant effects upon the microstructures and microwave dielectric properties in the present ceramics, and the prolonged sintering was generally desired. Moreover, the variation of temperature coefficient of resonant frequency with sintering time could be clarified using Clausius-Mosotti equation. Such phenomenon was important to develop microwave dielectric ceramics with higher dielectric constant combined with high Qf value and near-zero temperature coefficient in the present system.

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