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Effects of sintering conditions on microstructures and microwave dielectric properties of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics ($x=2/3$)

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Abstract

Effects of composition and sintering conditions upon the microstructures and the microwave dielectric characteristics of $Ba_{6-3x}(Sm_{1-btly}Nd_y)_{8+2x}Ti_{18}O_{54}$ solid solution ($x=2/3$) were investigated. The dielectric constant increased and the temperature coefficient of resonant frequency τ_f could be adjusted from negative to positive with increasing Nd content in the solid solution, while the high Qf factor (>9000 GHz) was obtained. It should be emphasized that the temperature coefficient of resonant frequency was significantly affected by sintering time and the zero-temperature coefficient composition shifted to Nd-rich side with increasing sintering time. The excellent microwave dielectric properties were achieved in the ceramics with $y=0.8$ sintered at 1340 °C for 12 h: $\varepsilon=85$, $Qf=9{,}460$ GHz, and calculated $\tau_f=+0.8$ ppm/°C.

Keywords: $Ba_4(Sm, Nd)_{9.3}Ti_{18}O_{54}$; Dielectric properties; Microwave dielectrics; Microstructure-final; Sintering

1. Introduction

Recently, dielectric ceramics in the $BaO–Ln_2O_3–TiO_2$ system (Ln = Nd, Sm) have received much scientific and commercial attention because of the significant applications as microwave resonators and filters in microwave communication[1–8] where high dielectric constant ε, high Qf factor and near-zero temperature coefficient of resonant frequency τ_f are generally required. The microwave dielectric ceramics with good properties in the BaO-Ln_2O_3-TiO_2 system have the general formula $Ba_{6-3x}Ln_{8+2x}Ti_{18}O_{54}$, and the compositions with $x=0.5$, 2/3 and 0.75 have been well investigated.[1,4,5] The previous work has revealed that the best microwave dielectric properties are obtained for the composition of $x=2/3$.[5] The good combination of high Qf factor and near-zero temperature coefficient of resonant frequency τ_f can be achieved by the formation of 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 for the composition of $x=2/3$.[11,12] Compared to the $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ ceramics modified by Bi-substation or $Bi_4Ti_3O_{12}$ addition,[2,7] the $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ solid solutions have higher Qf factor and smaller τ_f,[9,10] but until now there is no report dealing with the effects of sintering conditions upon the microwave properties of the present solid solution.

In the present work, $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ solid solutions with $x=2/3$ are investigated for better combination of high dielectric constant, high Qf value and zero temperature coefficient of resonant frequency τ_f, and the influence of sintering conditions upon microstructures, therefore upon microwave dielectric characteristics is emphasized.

2. Experiments

$Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) ceramics with y = 0.0, 0.1, 0.3, 0.5, 0.6 and 0.8 were prepared by a routine solid state reaction process where the reagent grade $BaCO_3$ (99.95%), Nd_2O_3 (99%), Sm_2O_3 (99.5%) and TiO_2 (99.8%) powders were adopted as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in ethanol for 24 h, and then were calcined at 1200 °C in air for 3h after drying. The calcined powders added with 8 wt.% of PVA were pressed into the discs with dimensions of 12mm in diameter and 2 to 6 mm in height, and then sintered at 1320

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to 1360 °C in air for 3 to 12 h. After cooled from sintering temperature to 1000 °C at a rate of 2 °C min^{-1}, the ceramics were cooled with the furnace.

The bulk density of the sintered ceramics was evaluated by measuring the dimensions and weight. The crystalline phases of the sintered samples were identified by the X-ray powder diffraction pattern, using CuK_α radiation and the microstructures were characterized by scanning electron microscopy (SEM) on the polished and thermal-etched surfaces. The microwave dielectric properties were evaluated at 4–5 GHz by Hakki and Coleman's resonator method,[11] and the temperature coefficient of resonant frequency was calculated from the equation

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

where, α is the linear expansion coefficient (~10 ppm/°C),[12] τ_ε is the temperature coefficient of dielectric constant evaluated at 1 MHz by an LCR meter (HP4284A) equipped with a thermostat.

3. Results and discussion

Densification of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics is performed well at the temperatures of 1340–1360 °C for 3 h, and the fine homogeneous microstructures are observed in the dense ceramics (Fig. 1). All the compositions tend to form fine columnar grains, and less porosity is observed. With prolonging sintering time, the grain size increases together with the aspect ratio (Fig. 2).

Fig. 3 gives the XRD patterns of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics with various compositions sintered at 1340 °C for 3 h. The formation of solid solution of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ is confirmed

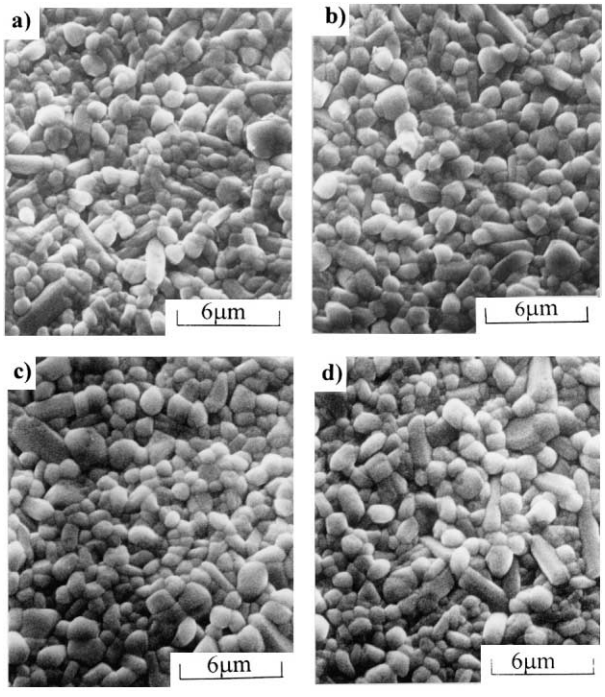

Fig. 1. SEM micrographs of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics sintered at 1340 °C in air for 3 h: (a) $y=0.1$, (b) $y=0.3$, (c) $y=0.6$, (d) $y=0.8$.

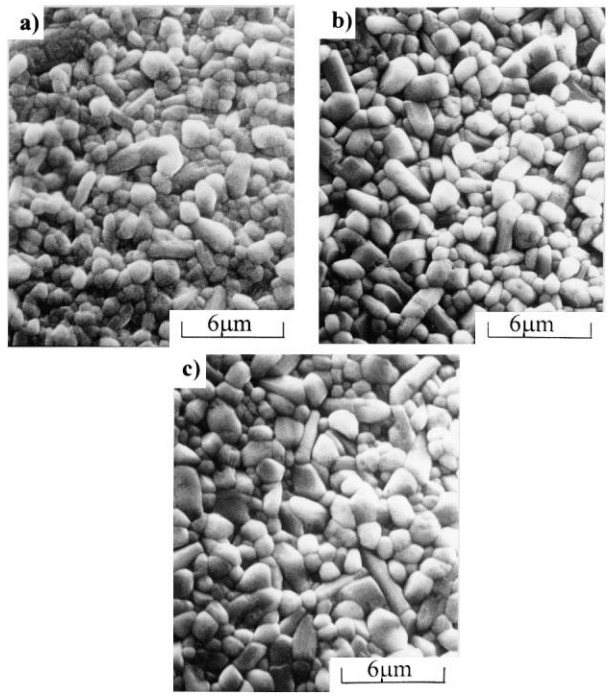

Fig. 2. SEM micrographs of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics ($y=0.8$) sintered at 1340 °C in air for 3 h, 6 h and 12 h.

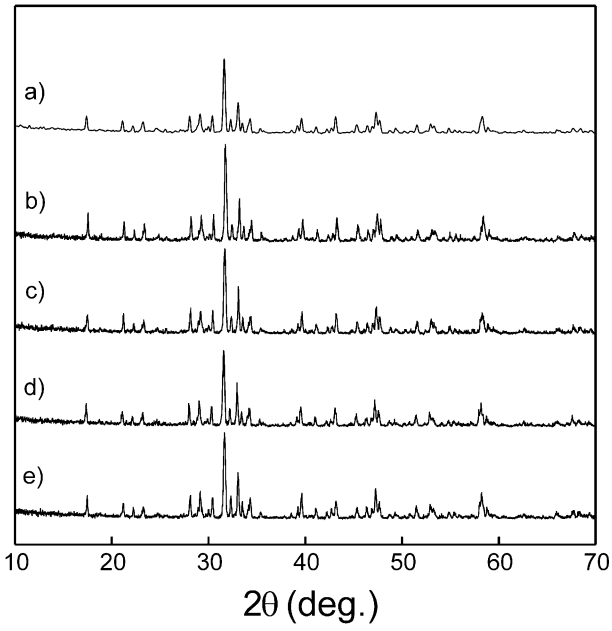

Fig. 3. XRD patterns of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics sintered at 1340 °C in air for 3h: (a) $y=0.0$, (b) $y=0.1$, (c) $y=0.3$, (d) $y=0.6$, (e) $y=0.8$.

since all the XRD patterns can be assigned to that of the orthorhombic tungsten bronze phase described in JCPDS card No.44-62, but the crystal parameters vary with y (see Table 1 and Fig. 4). Nd substitution for Sm leads to the complex variation of parameters a, b and c, but generally leads to the increase of unit cell volume. This is considered to be the result of the variation of crystallizability and ordering degree due to the Nd-substitution for Sm at A1-site in $[Ba_{2-3x}Sm_{8+2x}V_x]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$.[5] The smaller ion radius difference between Nd and Ba leads to the decrease of ordering degree at A1-site, therefor, the unit cell volume increases with Nd-substitution for Sm. Also, the larger ion radius of Nd will affect the crystal parameters directly. On the other hand, increasing sintering time does not change the phase constitution, but leads to the variation of crystal parameters as the results of the variation of crystallizability and ordering degree (Fig. 5). Prolonging sintering time generally leads to the increased crystallizability and the increased ordering degree, and subsequently the decreased unit cell volume is observed. The situation for Nd-rich composition ($y=0.8$) agrees well with this consideration. However, the compositions of $y=0.3$ and 0.5 show the more complex tendency, where the unit cell volume increases firstly then turns to decrease with increasing sintering time, such phenomenon has not been understood clearly and deserves further investigation.

As shown in Fig. 6, the dielectric constant increases with increasing y, while the high Qf factors (>9200 GHz) with slight variation are obtained for all compositions sintered for 3 h. The increase of dielectric constant with Nd substitution for Sm is originated from the larger ionic polarizibility of Nd^{3+}. Meanwhile, the temperature coefficient of dielectric constant τ_ε varies from +1.1 ppm/°C to −49.8 ppm/°C (Fig. 7), and therefore the temperature coefficient of resonant frequency τ_f is expected to vary from negative to positive according to Eq. (1) The zero temperature coefficient τ_f

Table 1
Crystal parameters vs composition in $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics

y	t (h)	a (Å)	b (Å)	c (Å)	V (Å^3)
0.0	3	22.3447	12.1770	3.8422	1045.441
0.1	3	22.2380	12.1445	3.8282	1033.887
0.3	3	22.2756	12.1590	3.8388	1039.745
0.3	6	22.3292	12.1806	3.8583	1049.380
0.3	12	22.3303	12.1867	3.8475	1047.035
0.5	3	22.2677	12.1533	3.8334	1037.410
0.5	6	22.2989	12.2166	3.8489	1053.210
0.5	12	22.3161	12.1835	3.8419	1044.579
0.6	3	22.2907	12.1861	3.8397	1042.990
0.8	3	22.3620	12.1935	3.8552	1051.276
0.8	6	22.3794	12.2124	3.8426	1050.203
0.8	12	22.3018	12.1766	3.8414	1043.154

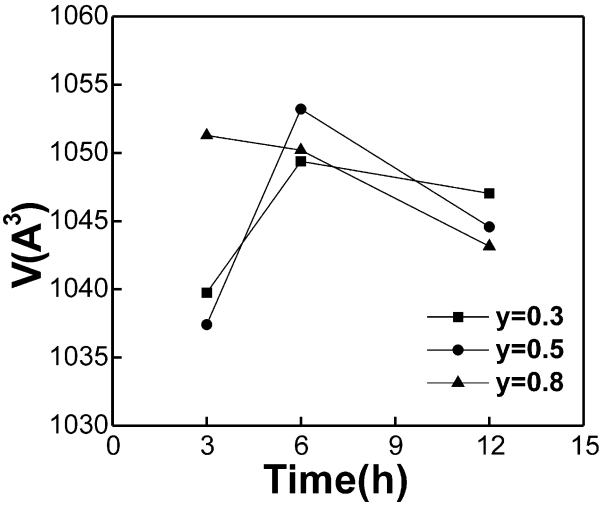

Fig. 5. Variation of cell volume in $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics with sintering time.

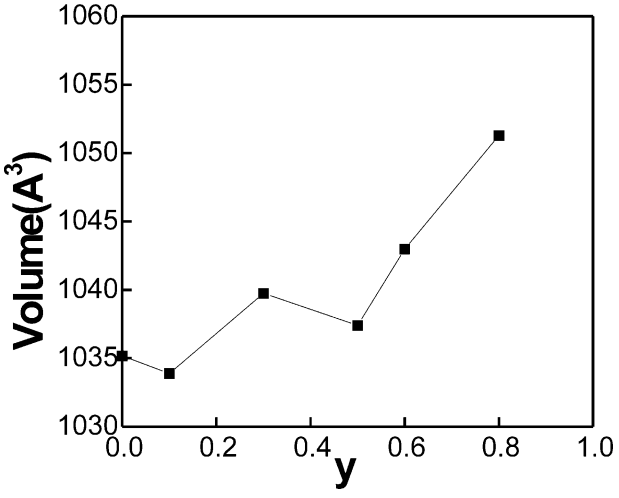

Fig. 4. Variation of cell volume vs composition in $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ solid solution.

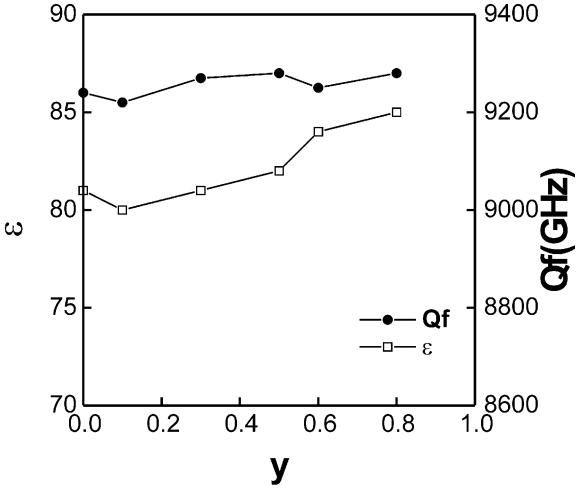

Fig. 6. Microwave dielectric characteristics of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics as functions of composition y.

is available by adjusting the composition to $y=0.5\sim0.6$ for the present ceramics sintered for 3 h.

Table 2 and Fig. 8 show the influence of sintering time upon the microwave dielectric properties of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ($x=2/3$) ceramics. Generally, the sintering time has no obvious influence on the dielectric constant, but affects Qf factor and temperature coefficient significantly. For compositions containing less Nd, the Qf factor initially increases sharply with extending sintering time, but it decreases when sintering time is longer than 6 h. On the other hand, when Nd content exceeds a critic value, the Qf factor increases continuously with prolonging sintering time. The interesting effects of sintering time upon the temperature coefficient τ_f should be emphasized. Generally, the prolonged sintering leads to the smaller positive or more negative temperature coefficient τ_f, and subsequently the zero temperature coefficient composition shifts to Nd-rich compositions. For 3 h sintering, the zero temperature coefficient τ_f is obtained at composition between $y=0.5$ and 0.6; but for 12h sintering, the zero temperature coefficient is achieved for composition near $y=0.8$. This phenomenon is very important because we can develop microwave dielectric ceramics with higher dielectric constant combined with high Qf value and near-zero temperature coefficient with the Nd-rich compositions in the present solid solution system.

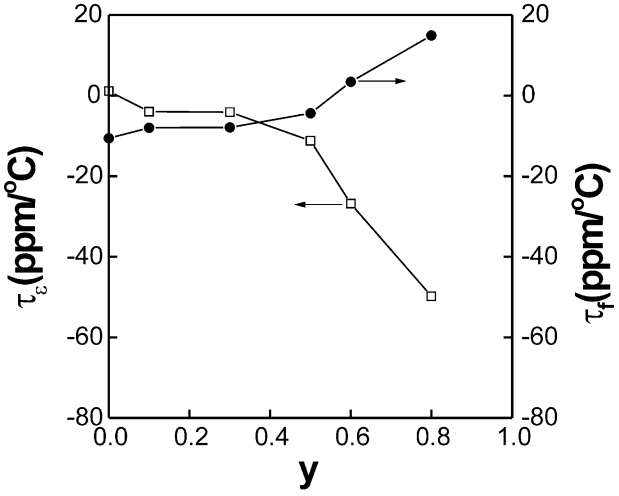

Fig. 7. Variation of temperature coefficients as functions of composition in $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics.

Table 2
Microwave dielectric properties of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics vs sintering time

	Sintering time (h)	f_0 (GHz)	ε	tanδ	Qf (GHz)
$y=0.0$	3	4.16	81	0.00045	9240
	6	4.52	81	0.00050	9040
	12	4.20	81	0.00046	9130
$y=0.1$	3	4.52	80	0.00049	9220
	6	3.75	80	0.00039	9620
	12	3.83	80	0.00041	9340
$y=0.3$	3	4.82	81	0.00052	9270
	6	3.90	81	0.00041	9510
	12	3.95	81	0.00041	9630
$y=0.5$	3	4.36	82	0.00047	9280
	6	3.61	82	0.00038	9500
	12	4.18	82	0.00045	9290
$y=0.6$	3	4.44	83	0.00048	9250
	6	4.22	83	0.00045	9380
	12	4.13	83	0.00044	9390
$y=0.8$	3	4.64	85	0.00050	9280
	6	4.20	85	0.00045	9330
	12	3.88	85	0.00041	9460

Among the influence of sintering time upon microwave dielectric characteristics discussed here, the best characteristics are obtained differently for different compositions. For $y=0.0$, sintering at 1340 °C for 3 h is the best sintering condition; for $y=0.1$, 6h is the best sintering time; for $y\geqslant0.3$, sintering at 1340 °C for 12 h can further increase Qf value. The best microwave

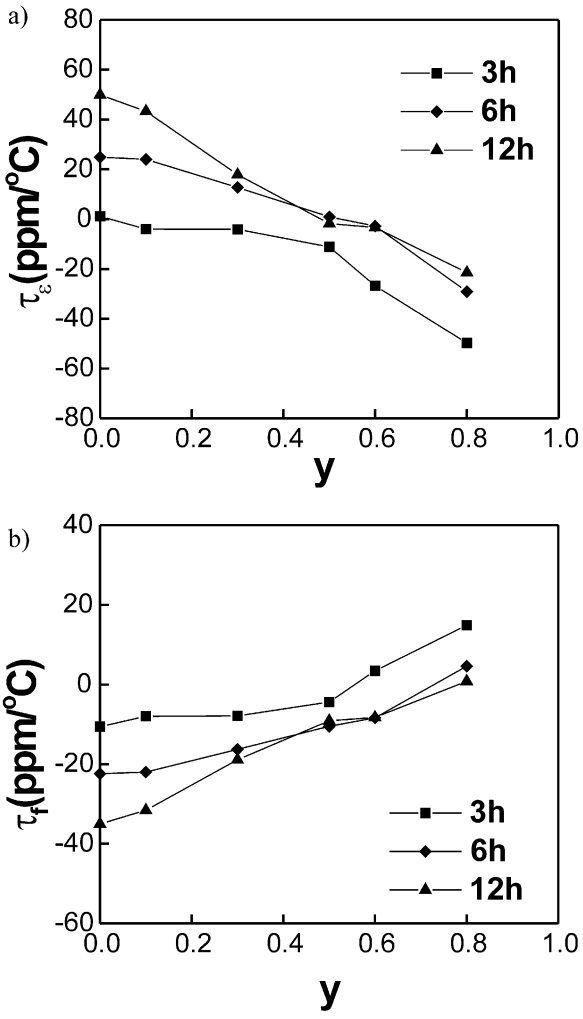

Fig. 8. Variation of temperature coefficients (a) τ_ε and (b) τ_f vs composition and sintering time in $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ceramics.

dielectric characteristics are obtained for ceramics with $y=0.8$ sintered at 1340 °C for 12 h: $\varepsilon=85$, $Qf=9460$ GHz, $\tau_f=+0.8$ ppm/°C.

Qf value is generally affected by crystallizability, oxygen vacancy, long-range ordering degree of cations, inner stress of the crystals and phase constitution. In the present situation, Nd substitution for Sm leads to increased unit cell volume which decreases the *Qf* value. However, since the crystallization temperature of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ is lower, better crystallization for Nd-rich compositions will lead to the improved *Qf* value. Therefore, Nd substitution just changes *Qf* value slightly in the present solid solution for short time sintering. The prolonged sintering has the complex influence on *Qf*, but it is generally beneficial. That is, properly prolonged sintering leads to improved *Qf* value probably due to the increased crystallizability and long-range ordering degree.

The variation tendency of temperature coefficients τ_ε and τ_f with Nd-substitution in $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ solid solution is originated from the compensation of the opposite temperature coefficients of $Ba_{6-3x}Nd_{8+2x}Ti_{18}O_{54}$ and $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$. The interesting variation tendency of temperature coefficients τ_ε and τ_f might be primarily concerned with the variation of crystallizability and long-range ordering degree of A-site cations, and the details are worth investigating further.

4. Conclusion

Composition and sintering conditions have significant effects upon the microstructures and microwave dielectric properties in the solid solution of $Ba_{6-3x}(Sm_{1-y}Nd_y)_{8+2x}Ti_{18}O_{54}$ ($x=2/3$). The dielectric constant increases and the temperature coefficient of resonant frequency τ_f changes from negative to positive with increasing Nd content, while the high *Qf* factor (>9000 GHz) can be obtained. It should be emphasized that the temperature coefficient of resonant frequency is profoundly affected by the sintering time and the zero-temperature coefficient composition shifted to Nd-rich side with increasing sintering time. Therefore, we can develop microwave dielectric ceramics with higher dielectric constant combined with high *Qf* value and near-zero temperature coefficient in the present system. The excellent microwave dielectric properties were achieved in the ceramics with y = 0.8 sintered at 1340 °C for 12 h: $\varepsilon=85$, $Qf=9{,}460$ GHz, and calculated $\tau_f=+0.8$ ppm/°C.

Acknowledgements

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