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Sintering and compositional effects on the microwave dielectric characteristics of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics with $0.25 \leqq x \leqq 0.35$

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Abstract 1,500 °C−sintered $MgTa_2O_6$ ceramic exhibits microwave dielectric characteristics of ε_r=30.5, $Q\times f$= 56,900 GHz, and τ_f=28.3 ppm/°C, whereas 1,400 °C-sintered $MgNb_2O_6$ ceramic exhibits microwave dielectric characteristics of ε_r=21.7, $Q\times f$=89,900 GHz, and τ_f= −68.5 ppm/°C. In order to find the dielectric resonators with τ_f value close to 0 ppm/°C, the effects of sintering condition and composition on the microwave dielectric characteristics of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics ($0.25\leqq x\leqq 0.35$) prepared under sintering temperature of 1,300–1,450 °C are investigated. The results show that as the sintering temperature increases from 1,300 to 1,450 °C, the ε_r, $Q\times f$ and τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics all increase and saturate at 1,450 °C. On the other hand, as the Nb_2O_5 content decreases, the τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics will shift to near 0 ppm/°C. The optimized sintering conditions and composition to obtain the $Mg(Ta_{1-x}Nb_x)_2O_6$ dielectrics with τ_f close to 0 ppm/°C are sintering temperature of 1,450 °C, sintering duration of 4 h, and composition of x=0.25, which exhibits the microwave dielectric characteristics of ε_r=27.9, $Q\times f$=33,100 GHz, and τ_f=−0.7 ppm/°C.

Keywords $Mg(Ta_{1-x}Nb_x)_2O_6$ · Microwave characteristics · Orthorhombic

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1 Introduction

High quality AB_2O_6 (A=Ca, Mg, Mn, Co, Ni, Zn and B= Nb, Ta) compounds had been investigated as microwave dielectric resonators by Lee et al. [1] and Kan et al. [2]. Lee et al. reported that $MgNb_2O_6$ sintered at 1,300 °C exhibited relative dielectric constant (ε_r) of 21.4, quality factor ($Q\times f$) of 93,800 GHz, and temperature coefficient of resonant frequency (τ_f) of −70 ppm/°C and $MgTa_2O_6$ sintered at 1,550 °C exhibited ε_r=30.3, $Q \times f = 59,600$ GHz, and τ_f= 30 ppm/°C. Both had high $Q\times f$ values and dielectric constants of higher than 20, but both also revealed large τ_f values. To adjust τ_f value of microwave dielectric resonators close to 0 ppm/°C, two or more compounds having negative and positive τ_f values are employed to form a solid solution or mixed phases in order to obtain the desired τ_f values. Kucheiko reported that zero τ_f value could be achieved in $CaTiO_3$–$Ca(Al_{1/2}Ta_{1/2})O_3$ system [3]. Chen et al. reported that small τ_f value was achieved in $CaO-Li_2O-Sm_2O_3-TiO_2$ (CLST) system [4], in which the $Li_{1/2}Sm_{1/2}TiO_3$ (ε_r=52, $Q \times f = 2,280$ GHz, and τ_f=−260 ppm/°C) and $CaTiO_3$ (ε_r=170, $Q \times f = 3,600$ GHz, and τ_f=800 ppm/°C) dielectrics were employed [5].

The substitution of similar ions in dielectric resonators can improve the microwave dielectric characteristics. For example, in the $BiNbO_4$ system, Nd_2O_3 and Sm_2O_3 can be used to substitute Bi_2O_3 to form $(Bi_{1-x}Nd_x)NbO_4$ and $(Bi_{1-x}Sm_x)NbO_4$ compositions [6, 7], Ta_2O_5 can be used to substitute

Nb_2O_5 to form $Bi(Nb_{1-x}Ta_x)O_4$ compositions [8], and all the three compositions possess high $Q\times f$ and low τ_f values. In the $BaSm_2Ti_4O_{12}$ system, SrO and Nd_2O_3 can be used to substitute BaO and Sm_2O_3 to form $(Ba,Sr)Sm_2Ti_4O_{12}$ and $Ba(Sm,Nd)_2Ti_4O_{12}$ compositions [4,9], and the microwave dielectric characteristics can also be improved, especially, the τ_f values can be adjusted to near 0 ppm/°C.

In our preliminary study, $MgTa_2O_6$ ceramics sintered at 1,500 °C exhibited the microwave dielectric characteristics of τ_f=28.3 ppm/°C, ε_r=30.5 and $Q\times f=56,900$ GHz, whereas $MgNb_2O_6$ ceramics sintered at 1,400 °C exhibited the microwave dielectric characteristics of τ_f=−68.5 ppm/°C, ε_r= *21.7, and* $Q\times f=89,900$ GHz, as shown in Table 1. In order to obtain the microwave dielectrics with τ_f close to 0 ppm/°C, the compositions of $Mg(Ta_{1-x}Nb_x)_2O_6$ were investigated in this study. The empirical method was adopted to combine the microwave dielectric characteristics of $MgTa_2O_6$ (with positive τ_f) and $MgNb_2O_6$ (with negative τ_f), and the results showed that the zero τ_f value would exist within the range of $0.25\leqq x\leqq 0.35$. As a result, the compositions of $Mg(Ta_{1-x}Nb_x)_2O_6$ ($0.25\leqq x\leqq 0.35$) were developed and their sintering behaviors and microwave dielectric characteristics were investigated.

2 Experimental

Proportional amounts of reagent-grade starting materials of MgO, Ta_2O_5, and Nb_2O_5 were mixed according to the compositions of $Mg(Ta_{1-x}Nb_x)_2O_6$, (x=0.25, 0.3, and 0.35, abbreviated as MTN1, MTN2, and MTN3, respectively), and ball-milled for 5 h with deionized water. After drying, the powder was ground and calcined at 1,100 °C for 2 h. After mixing with polyvinyl alcohol (PVA) as binder, the mixed powder was pressed into pellets in a steel die. After debindering, sintering of these pellets was carried out at temperature between 1,300 and 1,450 °C under ambient conditions for 4 h.

Table 1 The microwave dielectric properties of $MgTa_2O_6$ and $MgNb_2O_6$ ceramics.

Material	Sintering temperature (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
$MgTa_2O_6$	1,400	25.2	28,500	22.4
	1,450	28.9	44,300	27.1
	1,500	30.5	56,900	28.3
	1,550	30.6	58,200	28.5
$MgNb_2O_6$	1,300	15.7	34,100	−78.0
	1,350	20.5	66,500	−69.1
	1,400	21.7	89,900	−68.5
	1,450	21.8	91,500	−68.3

The crystal structures were analyzed by means of X-ray powder diffraction method using CuK_α radiation (Rigaku D-max/IIB). The densities of sintered specimens, as a function of sintering temperature, were measured by the liquid displacement method using deionized water as the liquid (Archimedes's method). To investigate the morphologies of the samples, the surfaces of sintered specimens were observed by SEM (Hitachi S-2500). Dielectric characteristics at microwave frequency were measured by Hakki and Coleman's dielectric resonator method [10], which was improved by Courtney [11]. An HP8720ET network analyzer was used for the measurements of microwave dielectric characteristics. The dielectric constant can be accurately determined by measuring the resonant frequency of the TE_{011} mode and verified by the $TE_{01\delta}$ resonant modes. The temperature variation of resonant frequency $\Delta f_0/f_0$ and the temperature coefficient of resonant frequency τ_f are defined as:

$$\Delta f_0/f_0=(f_T-f_0)/f_0 \quad (1)$$

and

$$\tau_f=\Delta f_0/(f_0\times\Delta T) \quad (2)$$

where f_T and f_0 are the resonant frequencies at 85 and 25°C, respectively, and ΔT is 60°C.

3 Results and discussion

Typical X-ray diffraction patterns of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics are shown in Fig. 1. $MgTa_2O_6$ ceramic exists a single phase with tetragonal structure, whereas, $MgNb_2O_6$ ceramic exists a single phase with orthorhombic structure. The results show that the lattice constants of $MgNb_2O_6$ ceramic sintered at 1,300°C are a=5.720 Å, b=5.306 Å, and c=14.1780 Å. On the other hand, $MgTa_2O_6$ ceramics sintered at 1,500 °C exhibit the lattice constants of a=b=4.7173 Å and c=9.2094 Å. The $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics have the crystal structure of orthorhombic, which is similar to that of $MgNb_2O_6$ ceramic; however, their lattice constants are smaller than those of $MgNb_2O_6$ ceramic. In our previous report, the $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics were revealed to exist a phase transition within x=0.1–0.2 from tetragonal to orthorhombic phase [12], hence, no tetragonal phase appeared in Fig. 1 with $0.25\leqq x\leqq 0.35$. The results also show that as the Nb_2O_5 content increases form x=0.25 to x=0.35, the lattice constants of a, b, and c slightly increase from 5.484 Å, 4.998 Å, and 13.724 Å to 5.507 Å, 5.109 Å, and 13.948 Å, which is due to the smaller ionic radius of Ta^{5+} (0.64 Å) than that of Nb^{5+} (0.69 Å).

The variations in the morphologies of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics under different sintering temperatures and compositions can be observed by SEM photographs. The changes

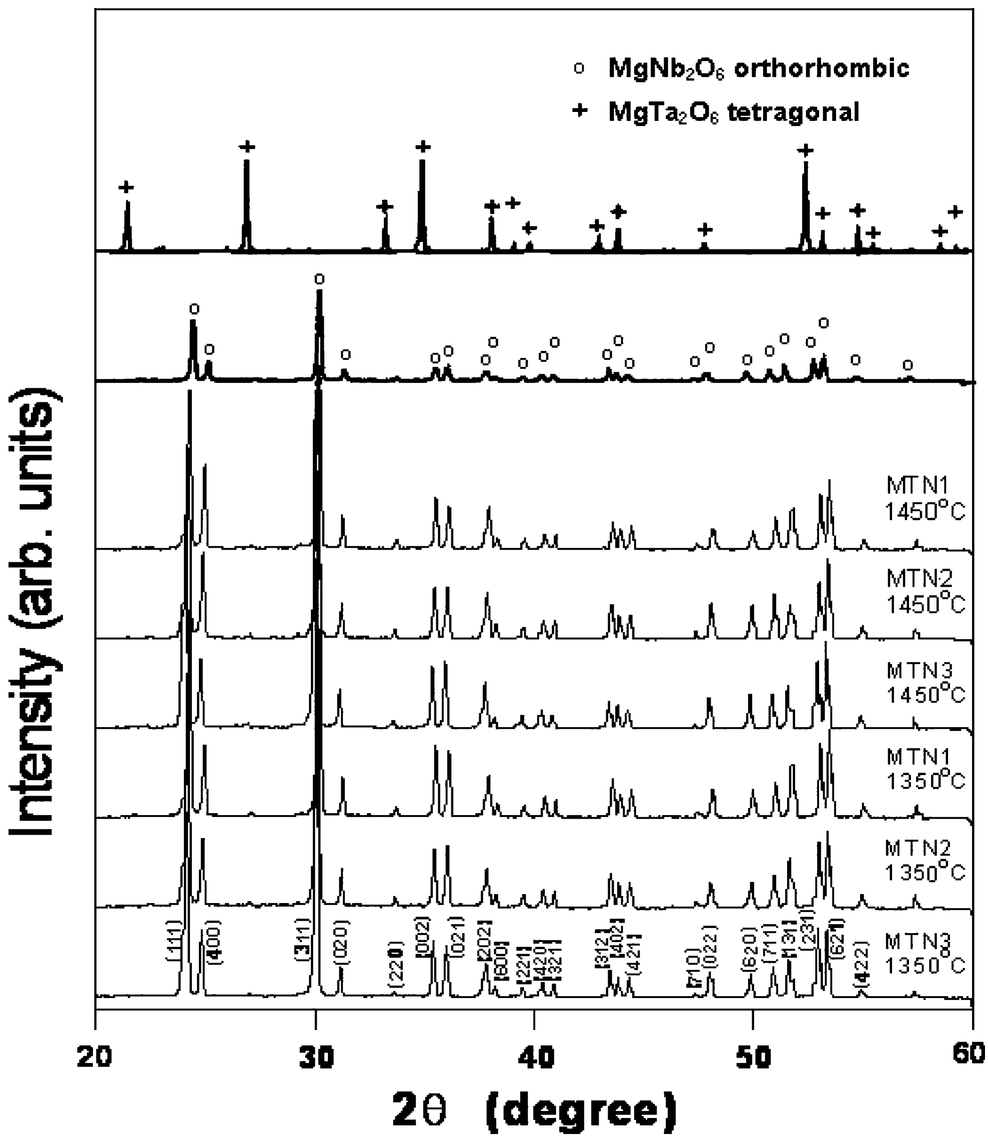

Fig. 1 The X-ray patterns of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics sintered at different temperatures

in density and grain size of selected $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics are shown in Fig. 2. For 1,300 °C-sintered $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics, isolated $Mg(Ta_{1-x}Nb_x)_2O_6$ grains and pores can be revealed, as shown in Fig. 2a. Further increasing of sintering temperature to 1,350 °C, homogeneous fine microstructures with fewer pores are observed, which is shown in Fig. 2b. The pores of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics decrease and the grain sizes increase with the increase of sintering temperature, which are independent of Nb_2O_5 content. As sintered at 1,400 °C, the grain sizes are enlarged for samples with larger Nb_2O_5 content, this result is obvious by comparing the Fig. 2c, d, and e. This appears that the grain growth is improved due to the increase of sinterability induced by the Nb_2O_5 substitution.

The ε_r values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics were measured as functions of sintering temperature and composition, and the results are shown in Fig. 3. The ε_r values of all $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics increased with sintering temperature and saturated at about 1,400 °C, independent of the Nb_2O_5 content. The relationships between ε_r values and sintering temperature revealed the same trend with those between densities and sintering temperatures since higher sintering temperature caused grain growth and fewer pores. The saturated ε_r values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics linearly decrease from 27.94 to 26.2 as x varied from 0.25 to 0.35. This result implies that the effect of Nb_2O_5 substitution on the ε_r values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics is apparent.

Figure 4 shows the $Q\times f$ values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics as functions of sintering temperature and composition. As sintering temperature increases, the $Q\times f$ values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics increase and then reach the saturation values at 1,400 °C. The increase in grain growth and decrease in pores may cause this result. In the $Mg(Ta_{1-x}Nb_x)_2O_6$ system, even the dielectric constant decreases with the increase of Nb_2O_5 content, the $Q\times f$

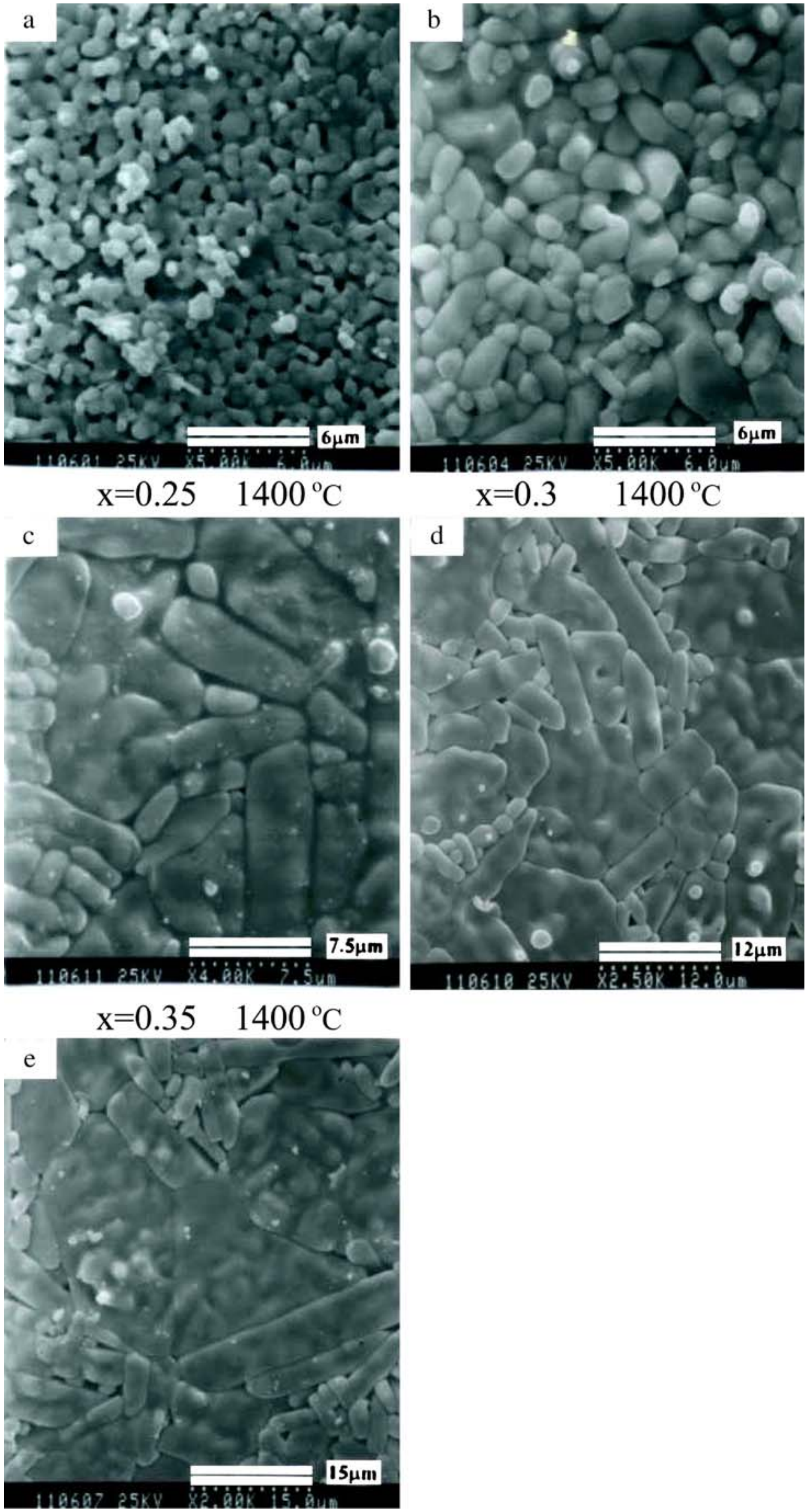

Fig. 2 The microstructures of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics sintered at, **a** 1,300 °C, and **b** 1,350 °C for x=0.35, and sintered at 1,400 °C for **c** x=0.25, **d** x=0.3, and **e** x=0.35

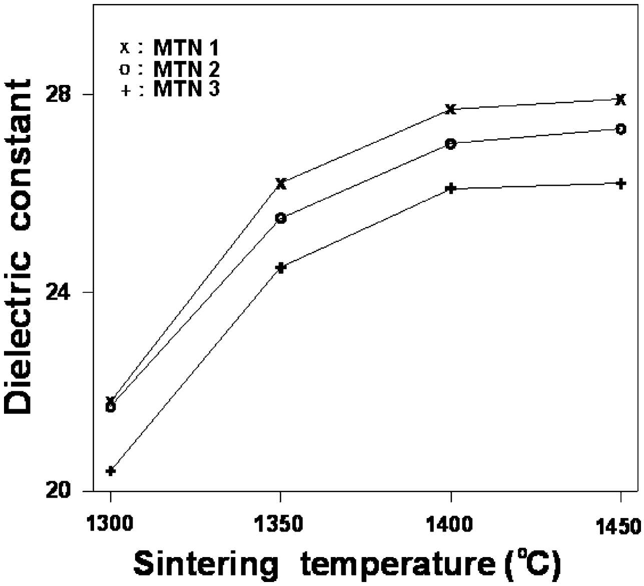

Fig. 3 The dielectric constants of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics as a function of sintering temperature

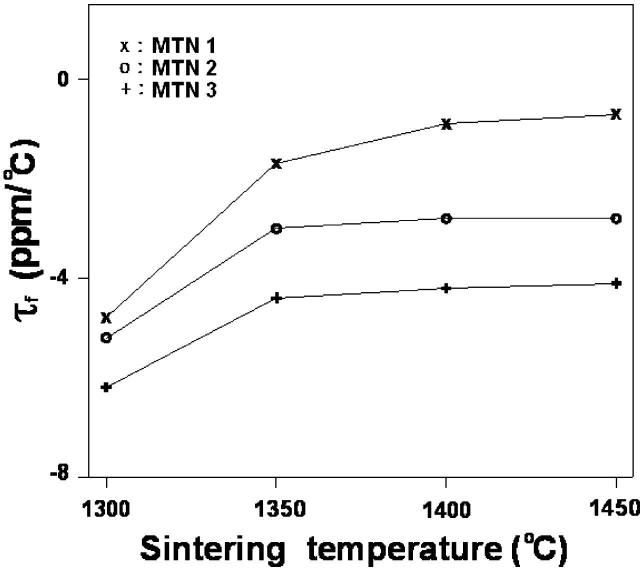

Fig. 5 The temperature coefficient of resonant frequency of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics as a function of sintering temperature

value increases apparently with the increase of Nb_2O_5 content. For $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics sintered at 1,400 °C, the $Q\times f$ values increase from 29,500 for x=0.25 to 40,100 for x=0.35.

The τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics with various Nb_2O_5 content at different sintering temperatures are demonstrated in Fig. 5. Both Nb_2O_5 content and sintering temperature have large influences on the τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics. For the sintering temperature ranged 1,300–1,450 °C, the τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics vary from a larger negative value to a smaller negative one, which may due to the decreased pores in $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics as sintered at higher temperature. In essence, the temperature coefficient of resonant frequency τ_f of a dielectric is a function of the thermal expansion coefficient (α) and the temperature coefficient of dielectric constant (τ_ε), that is $\tau_f \cong -\left(\alpha + {}^1\!/_2\tau_\varepsilon\right)$, which is revealed to be a negative value for air [13]. Because the air is enclosed in the pores, the τ_f value will vary steadily from a larger negative value to a smaller negative one as the pores decrease with the increased sintering temperature for $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics. On the other hand, as the Nb_2O_5 content decreases, the τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics will also shift to near 0 ppm/°C. The results show that the saturated τ_f values for MTN3, MTN2, and MTN1 ceramics sintered at 1,450 °C are −4.1 ppm/°C, −2.8 ppm/°C,

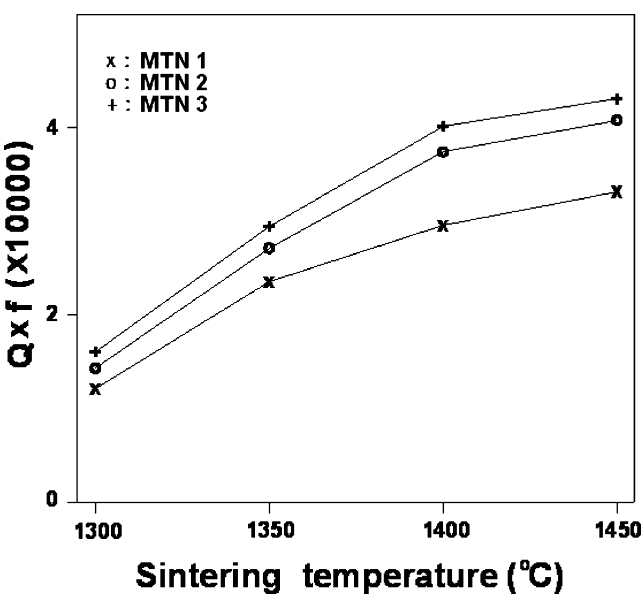

Fig. 4 The quality values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics as a function of sintering temperature

Table 2 The microwave dielectric properties of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics.

Material	Sintering temperature (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
$MgTa_{1.5}Nb_{0.5}O_6$ (MTN1, x=0.25)	1,300	21.8	12,100	−4.8
	1,350	26.2	23,500	−1.7
	1,400	27.7	29,500	−0.9
	1,450	27.9	33,100	−0.7
$MgTa_{1.4}Nb_{0.6}O_6$ (MTN2, x=0.3)	1,300	21.7	14,300	−5.2
	1,350	25.5	27,100	−3.0
	1,400	27.0	37,400	−2.8
	1,450	27.3	40,800	−2.8
$MgTa_{1.3}Nb_{0.7}O_6$ (MTN3, x=0.35)	1,300	20.4	16,100	−6.2
	1,350	24.5	29,400	−4.4
	1,400	26.1	40,100	−4.2
	1,450	26.2	43,100	−4.1

and −0.7 ppm/°C, respectively. Finally, all the microwave dielectric characteristics for various $Mg(Ta_{1x}Nb_x)_2O_6$ compositions and sintering temperatures are listed in Table 2. The optimized sintering conditions and composition to obtain the $Mg(Ta_{1-x}Nb_x)_2O_6$ dielectrics with τ_f close to 0 ppm/°C are sintering temperature of 1,450 °C, sintering duration of 4 h, and composition of x=0.25, which exhibits the microwave dielectric characteristics of ε_r=27.9, $Q \times f = 33,100$ GHz, and τ_f=−0.7 ppm/°C.

4 Conclusion

The sintering behaviors and microwave dielectric characteristics of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics ($0.25 \leqq x \leqq 0.35$) are influenced by the sintering temperature and Nb_2O_5 content, including grain growth, dielectric constant, quality factor, and τ_f value. In this system, the dielectric constant increases, the quality factor decreases, and the τ_f value shift to near 0 ppm/°C as the Nb_2O_5 content decreases. However, the saturated τ_f values of $Mg(Ta_{1-x}Nb_x)_2O_6$ ceramics ($0.25 \leqq x \leqq 0.35$) are all within the range of −4.1–−0.7 ppm/°C, which indicates that the $Mg(Ta_{1-x}Nb_x)_2O_6$ system is available to be adopted as microwave dielectric resonators. In this report, the optimized sintering conditions and composition to obtain the $Mg(Ta_{1-x}Nb_x)_2O_6$ dielectrics with τ_f close to 0 ppm/°C are sintering temperature of 1,450 °C, sintering duration of 4 h, and composition of x=0.25, which exhibits the microwave dielectric characteristics of ε_r=27.9, $Q \times f = 33,100$ GHz, and τ_f=−0.7 ppm/°C.

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