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Microstructure and microwave dielectric properties of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics

Fei Zhao, Zhenxing Yue*, Yingchun Zhang, Zhilun Gui, Longtu Li

State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

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Abstract

Microwave dielectric ceramics of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ($x = 0.40$–0.70) were prepared by solid-state reaction method. The microwave dielectric properties, such as dielectric constants, $Q \times f$ values and τ_f (temperature coefficient of resonant frequency) were studied as a function of composition and sintering temperature. In all the studied composition range, the sintered ceramics have orthorhombic perovskite structure in which the lattice parameters increase with increasing x. The substitution of Mg and Nb for Ti promotes the grain growth. With x increasing from 0.40 to 0.70, the dielectric constant decreases from 62.97 to 41.56, $Q \times f$ value increases from 12,213 to 29,428 GHz, and τ_f decreases from 92.6 to −12.6 ppm/°C. A near-zero τ_f was achieved at $x = 0.65$ with dielectric constant of 44.24 and $Q \times f$ value of 28,340 GHz. The change of dielectric constant and τ_f with x is related to the variation of the tolerance factor, which influences the tilting of oxygen octahedra in perovskite structure.

Keywords: $Ca(Ti,Mg,Nb)O_3$; Perovskites; Dielectric properties; Microwave dielectrics

1. Introduction

With the recent progress of microwave integrated circuits, low dielectric loss materials with a high dielectric constant and near-zero temperature coefficient of resonator frequency have been increasingly required for commercial microwave applications.[1] Most of the microwave dielectric ceramics with high dielectric constant have positive τ_f. Some titanate ceramics are of this kind. For instance, $CaTiO_3$ ceramics exhibited dielectric properties of $\varepsilon_r \sim 162$, $Q \times f$ value ~12,000 GHz and $\tau_f \sim 850$ ppm/°C.[2] Even though the titanate ceramics have very low quality factors and a high τ_f values, they have great potential because of their high dielectric constant. The effective way to achieve near-zero τ_f and optimize $Q \times f$ value is compensating the large positive temperature coefficient values using the compounds having negative temperature coefficient values with high quality factors. Several complex perovskites having the general formula $A(B'_{1/3}{}^{2+}B''_{2/3}{}^{5+})O_3$ have negative τ_f values.[3] Considering the quality factor and the dielectric constant, $Ca(Mg_{1/3}Nb_{2/3})O_3$ ($\varepsilon_r \sim 28$, $Q \times f$ value −58,000 GHz and $\tau_f \sim -48$ ppm/°C)[3] was selected to be the compensating compounds.

In this study, the microstructure and microwave dielectric properties of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics were investigated as a function of sintering temperature and composition.

2. Experimental procedure

Samples of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ with $x = 0.40$–0.70 were synthesized from high purity (more than 99.9%) powders of $CaCO_3$, MgO, TiO_2 and Nb_2O_5, using the conventional solid-state reaction method. The oxides and carbonate were weighed according to the compositions of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$. The mixtures were ball-milled

* Corresponding author. Tel.: +86 10 62784579; fax: +86 10 62771160.
E-mail address: yuezhx@mail.tsinghua.edu.cn (Z. Yue).

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in a polyethylene jar for 4 h using zirconia balls in alcohol medium. The milled powders were dried and then calcined at 1200 °C for 4 h. The calcined powders were remilled, dried, mixed with an appropriate amount of PVA (5 wt.%) as a binder and then screened by a 60 mesh. The screened powders were pressed into cylindrical disks of diameter 10 mm and height about 5 mm at a pressure of about 2000 kg/cm^2. These pellets were preheated at 600 °C for 2 h to expel the binder and then sintered at temperatures from 1350 to 1500 °C for 4 h in air.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystalline phase and the lattice constant of the sintered samples were determined by X-ray diffraction (XRD), using Cu Kα radiation. The microstructures of samples were observed by scanning electron microscopy (SEM). An HP8720ES network analyzer was employed in the measurement of microwave dielectric properties. The dielectric constant and unloaded quality factor were measured at microwave frequencies in room temperature using the Hakki–Coleman dielectric resonator method.[4,5] The temperature coefficients of resonant frequencies (τ_f) were measured in the temperature range of 25–100 °C. The τ_f value can be calculated by the following relationship:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)}$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

3. Results and discussions

To synthesize the phase pure perovskites, the mixed powders were calcined at temperature of 1200 °C for 4 h. The XRD characterization was performed on the synthesized powders. Fig. 1 shows the XRD patterns for the as-synthesized powders with compositions of x from 0.40 to 0.70. Two perovskite phases, corresponding to $CaTiO_3$ and $Ca(Mg_{1/3}Nb_{2/3})O_3$, respectively, can be identified from the patterns. This result indicates that two perovskites were formed for all compositions after calcination at 1200 °C.

In order to indicate the effects of the sintering temperature on the microstructure and phase transition of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics, XRD patterns for $x = 0.70$ composition sintered at temperature range of 1350–1500 °C are given in Fig. 2, which illuminates that orthorhombic perovskite structures were obtained for all cases. The comparison of XRD patterns between synthesized powders and sintered ceramics was made, as shown in Fig. 3. It indicates that the two perovskite phases, corresponding to $CaTiO_3$ and $Ca(Mg_{1/3}Nb_{2/3})O_3$, respectively, formed single solid-solution phases after sintered at 1450 °C.

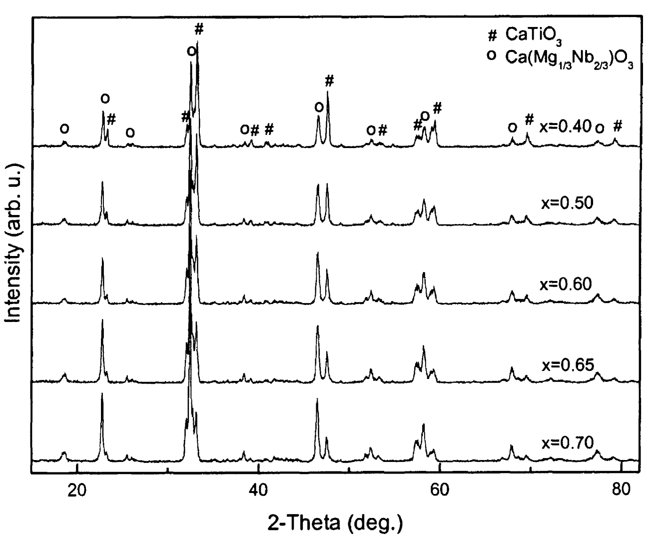

Fig. 1. XRD patterns of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ powders synthesized at 1200 °C for 4 h as a function of x.

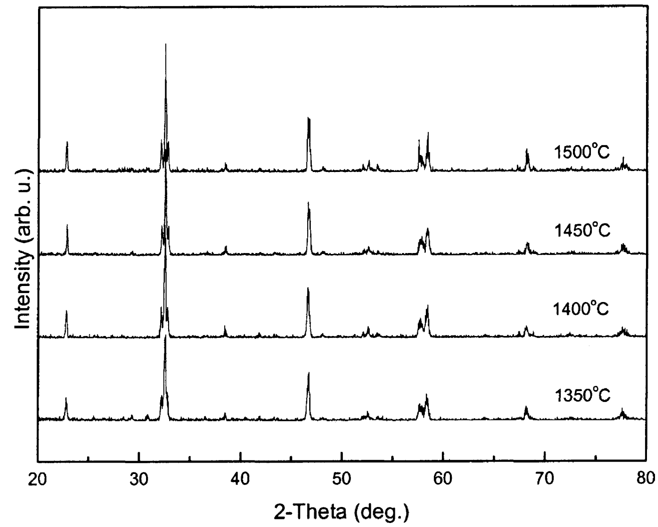

Fig. 2. XRD patterns for $x = 0.70$ composition sintered at temperature range of 1350–1500 °C.

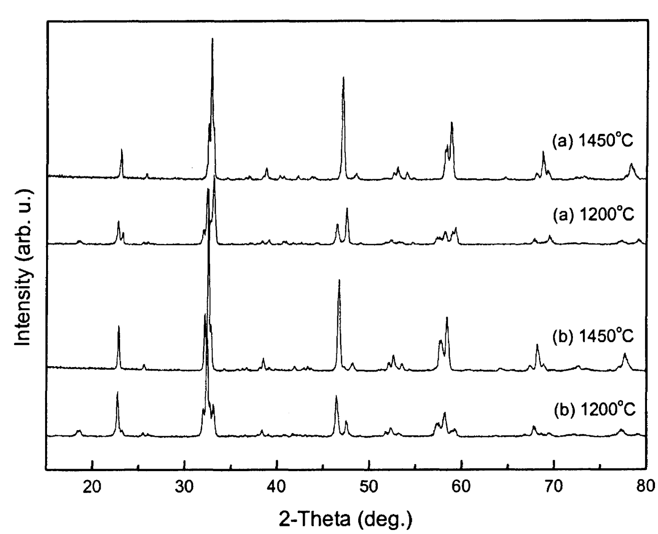

Fig. 3. The comparison of XRD patterns between synthesized powders and sintered ceramics: (a) $x = 0.40$ and (b) $x = 0.70$.

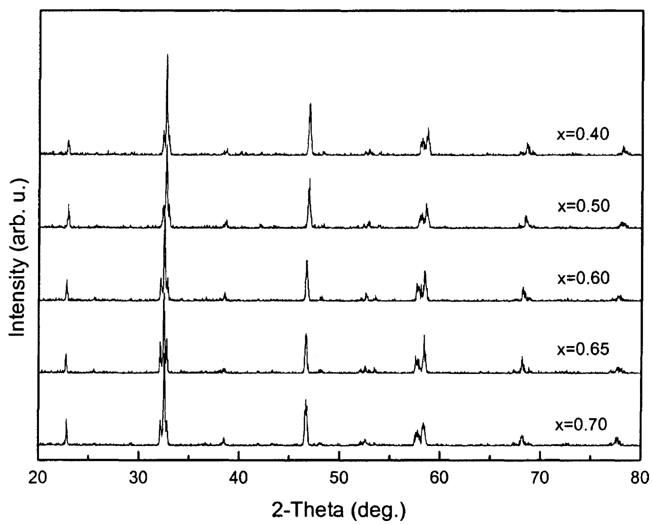

Fig. 4. XRD patterns of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics sintered at 1450 °C for 4 h as a function of *x*.

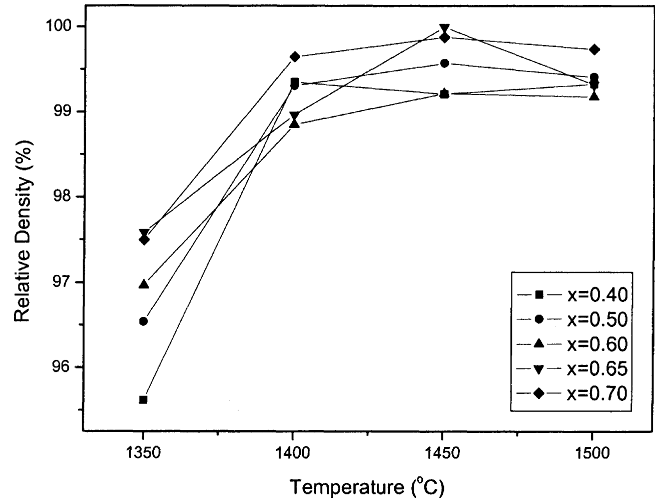

Fig. 6. The relative density of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics sintered at different temperatures as a function of *x*.

Fig. 4 shows the XRD patterns of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics for all compositions sintered at 1450 °C for 4 h. All compositions exhibited orthorhombic perovskite structures and no secondary phases were observed. These results suggest that the single solid-solution between $CaTiO_3$ and $Ca(Mg_{1/3}Nb_{2/3})O_3$ can be obtained at sintering temperature. Moreover, with increasing *x*, the lattice parameters of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics linearly increase (Fig. 5), which induce the peaks in XRD spectra shifted to lower angle. It is due to that the ionic radii of Mg^{2+} (0.72 Å) and Nb^{5+} (0.64 Å) are larger than that of Ti^{4+} (0.61 Å).[6] The substitution also influences the tolerance factor, which will be discussed later.

Fig. 6 demonstrates the relative densities of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics as a function of sintering temperature, through which the optimum sintering temperatures of the solid-solutions can be determined. It clearly reveals that the density saturation occurs at the temperature range of 1400–1450 °C.

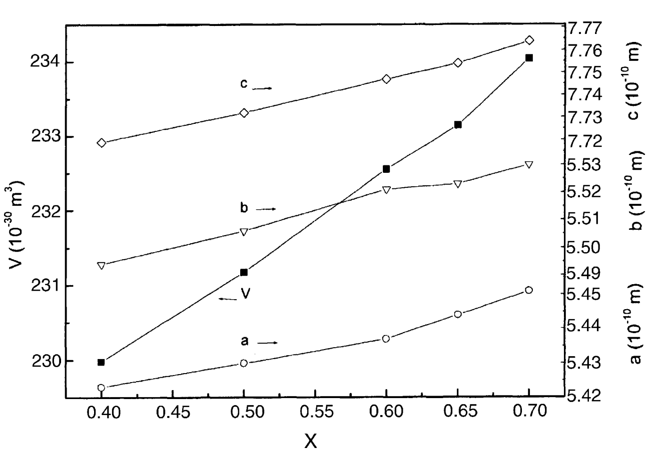

Fig. 5. The lattice parameter of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics as a function of *x*.

The microstructures of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics were observed using scanning electron microscopy. Fig. 7 illustrates the typical SEM photographs of sintered samples with various compositions, which were sintered at 1400° ($x = 0.40$), 1450 °C ($x = 0.50$, 0.60, 0.65 and 0.70) and 1500° ($x = 0.70$). Fig. 7a–e show that the well-densified microstructures were obtained and almost no porosities were observed in the sintered samples. With the increase of sintering temperature, the exaggerated grains with tiny cracks were observed, as shown in Fig. 7f. This is in well agreement with the relative density shown in Fig. 6. Moreover, the grain size is significantly increased with increasing *x*. This implies that the substitution of Mg and Nb for Ti in perovskite lattice can promote the grain growth.

The tolerance factor of perovskite structure is one of the factors which affect the microwave dielectric properties. The ideal cubic structure corresponds to $t = 1$. For $t > 1$, B-site ion is much smaller so that larger room exists for that ion to rattle about. For $t > 1$, the octahedra rotate in order to reduce the size of the octahedral interstices of oxygen sublattice because A-site ion is too small to occupy the available volume at a given temperature. As a result, the tolerance factor indirectly influences the ionic polarizability through tilting of octahedra.[7,8] The magnitude of tilting increases with decrease in the tolerance factors.[9] For the $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics, the tolerance factors were calculated by the following relationship:

$$t = \frac{R_{Ca} + R_O}{\sqrt{2}[(1-x)R_{Ti} + (x/3)(R_{Mg} + 2R_{Nb} + R_O)} \quad (2)$$

where R_{Ca}, R_{Ti}, R_{Mg}, R_{Nb} and R_O are the radii of Ca^{2+}, Ti^{4+}, Mg^{2+}, Nb^{5+} and O^{2-} ions, respectively. The tolerance factors decrease with the increase of *x*, as shown in Fig. 8. This implies that the magnitude of tilting of octahedra increases with increasing Mg and Nb content.

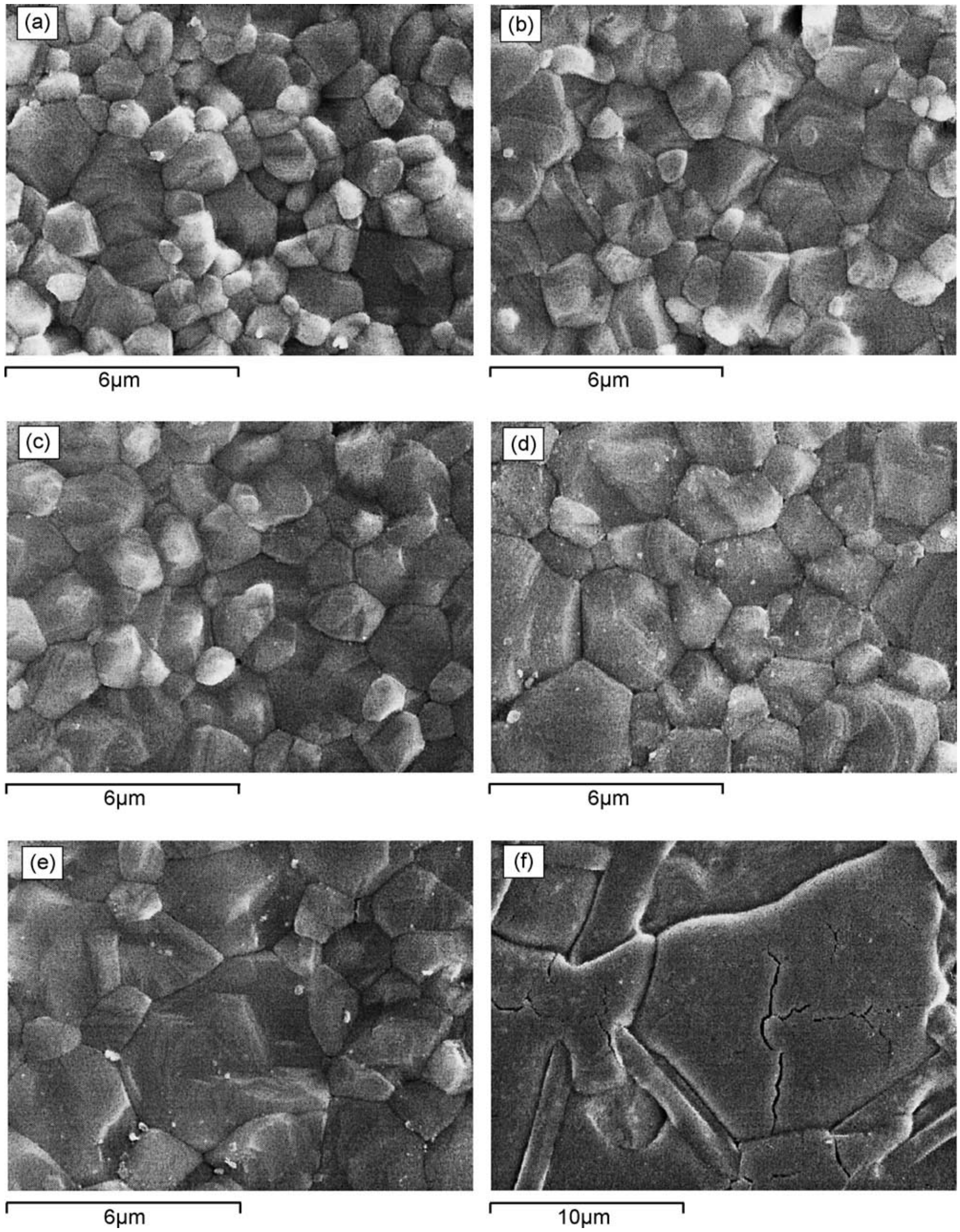

Fig. 7. SEM photographs of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics: (a) sintered sample $x = 0.40$ at 1400 °C, (b) sintered sample $x = 0.50$ at 1450 °C, (c) sintered sample $x = 0.60$ at 1450 °C, (d) sintered sample $x = 0.65$ at 1450 °C, (e) sintered sample $x = 0.70$ at 1450 °C, and (f) sintered sample $x = 0.70$ at 1500 °C.

The dielectric properties of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics at microwave frequencies were measured on the sintered ceramics and the results are listed in Table 1. The dependence of the dielectric constant and the temperature coefficient of resonant frequency (τ_f) on the tolerance factor is shown in Fig. 9. It can be seen that both the dielectric constant and τ_f value increase with increasing tolerance factor. It is well-known that the dielectric constant is markedly depended on the relative density and ionic polarizablity at microwave frequencies. However, the relative density does not largely affect the dielectric constant if the relative densities of the samples are higher than 96%.[10] So in present research, the ionic polarizablity is the more important factor affecting the dielectric constant. Although the total polarizabilities due to the substitution increases from 2.93 to (1.32 + 2 × 3.97)/3 Å[3,11] in reality the effective ionic polarizabilities decrease with the increase of x. It is probable that the

Table 1
Dielectric properties of sintered $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics

x	f_0 (GHz)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)
0.40	6.123	62.97	12213	92.6
0.50	6.528	54.31	22900	39.3
0.60	6.726	47.25	25631	8.2
0.65	6.893	44.24	28340	−2.1
0.70	6.665	41.56	29428	−12.6

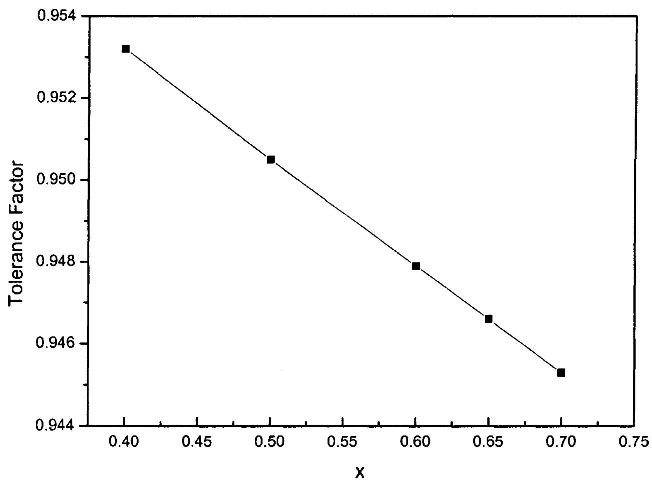

Fig. 8. The variation of the tolerance factors as a function of *x*.

tilting of octachedra increased with the decrease of the tolerance factors has a much stronger effect on ionic polarizabilities. The temperature coefficient of resonant frequency (τ_f) is also closely related with tilting of octahedra. The τ_f value increases with the increase of the tolerance factor.

In order to illuminate the effects of sintering temperature on the microwave dielectric properties, the variations of dielectric constant and $Q \times f$ value of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics with sintering temperature are shown in Figs. 10 and 11, respectively. The dielectric constant is not largely affected by the sintering temperature, which is owing to the high relative densities at all sintering temperatures shown in Fig. 6. Nevertheless, the sintering temperature has an obvious effect on the $Q \times f$ value. In general, the $Q \times f$ value depends on the secondary phase, density and microstructure. The effect of secondary phase may be neglected because there was no secondary phase observed in XRD patterns, neither in SEM photographs. With the increase of sintering temperature, the relative density slightly increases. In addition, the increase of grain size reduces the

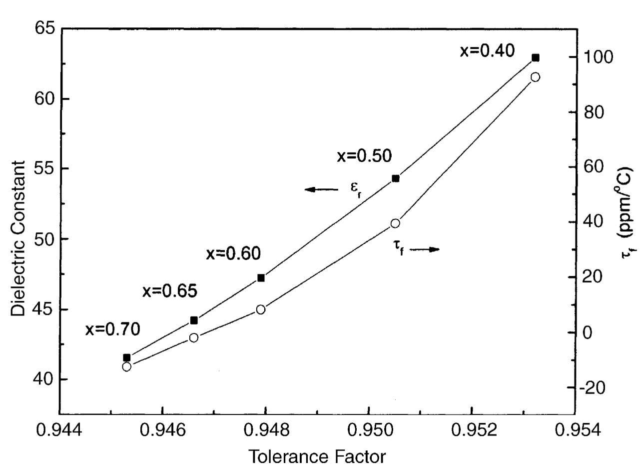

Fig. 9. The dependence of the dielectric constant and temperature coefficient of resonant frequency on the tolerance factor.

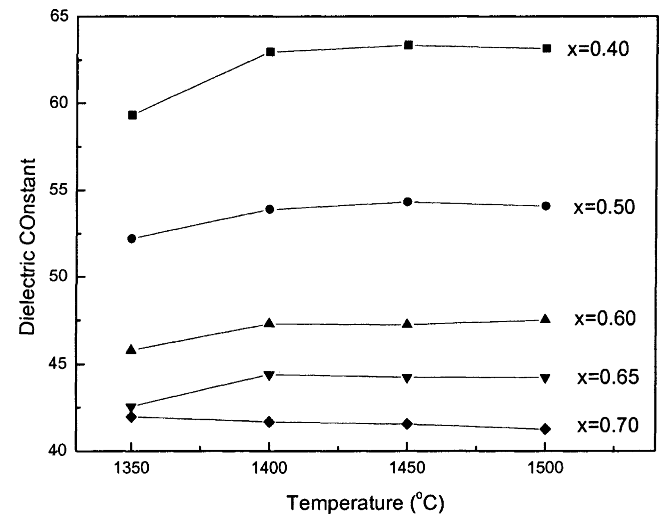

Fig. 10. The dielectric constant of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics sintered at different temperatures as a function of *x*.

grain boundaries and structural defects. All mentioned above may enhance the $Q \times f$ value. However, the $Q \times f$ values of ceramics sintered at 1500 °C decrease, which is owing to the appearance of exaggerated grain with tiny cracks, as shown in Fig. 7f.

The variations of dielectric constant, $Q \times f$ value and τ_f value with x for $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics are shown in Fig. 12. With x increasing from 0.40 to 0.70, $Q \times f$ value increases from 11,213 to 29,428 GHz, while dielectric constant decreases from 62.97 to 41.56, and τ_f from 92.6 to −12.6 ppm/°C. The change of microwave dielectric properties can be understood because $CaTiO_3$ ceramics have higher dielectric constant and lower $Q \times f$ value with a large positive τ_f than that of $Ca(Mg_{1/3}Nb_{2/3})O_3$ ceramics as reported in reference.[3] From the present results, we can conclude that the microwave dielectric properties of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics can be easily modified

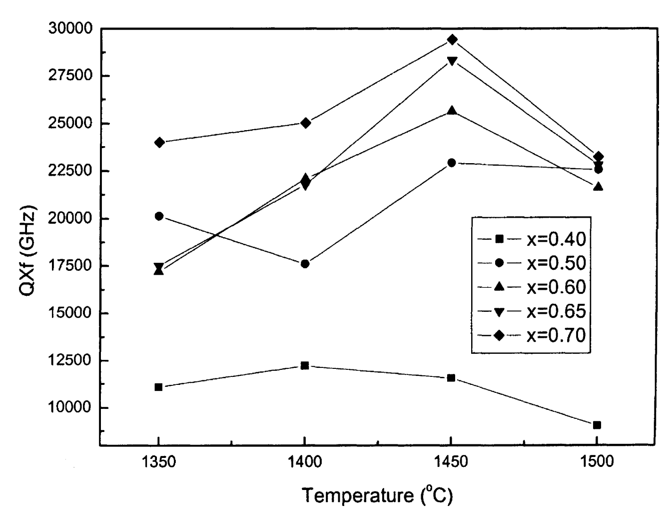

Fig. 11. $Q \times f$ value of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics sintered at different temperatures as a function of *x*.

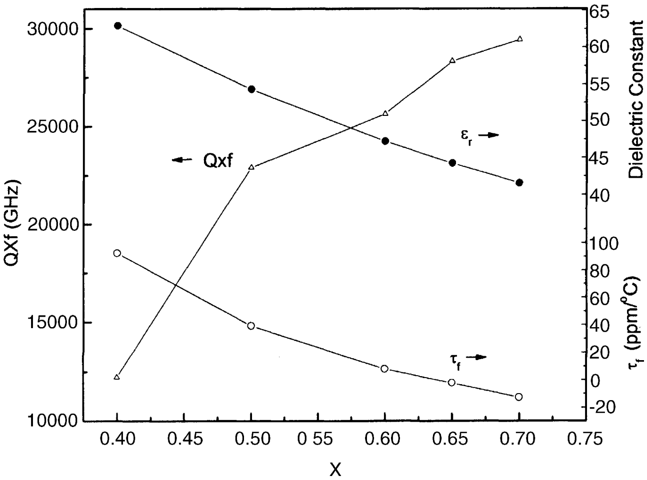

Fig. 12. The variations of dielectric constant, $Q \times f$ value and τ_f value with x for $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics.

in a large range by changing the relative content of Mg and Nb to Ti. As a result, a near-zero τ_f ceramic with dielectric constant of 44.34 and $Q \times f$ value of 28,340 GHz was obtained at $x = 0.65$ in the present experiment.

4. Conclusions

The microstructure and microwave dielectric properties of $Ca[Ti_{1-x}(Mg_{1/3}Nb_{2/3})_x]O_3$ ceramics ($x = 0.40$–0.70) were investigated as a function of composition and sintering temperature. In all the studied composition range, the sintered ceramics have orthorhombic perovskite structure. The effect of substitution Mg and Nb for Ti on dielectric properties is discussed in terms of the tolerance factor, which influences the tilting of octahedra in perovskite structure. With x increasing from 0.40 to 0.70, the dielectric constant linearly decreases from 62.97 to 41.56 and τ_f from 92.6 to -12.6 ppm/°C, whereas the $Q \times f$ value increases from 12,213 to 29,428 GHz. A near-zero τ_f ceramic with dielectric constant of 44.24 and $Q \times f$ value of 28,340 GHz was obtained at $x = 0.65$. The sintering temperature has significant effect on $Q \times f$ value. A $Q \times f$ maximum is achieved at a specific sintering temperature for every composition.

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References

1. Takada, T., Wang, S. E., Yoshikawa, S., Yang, S. J. and Newnham, R. E., Effect of glass additions on BaO–TiO_2–WO_3 microwave ceramics. *J. Am. Ceram. Soc.*, 1994, **77**, 1904–1916.
2. Wise, P. L., Reaney, I. M., Lee, W. E., Price, T. J., Iddles, D. M. and Cannell, D. S., Structure-microwave property relations in $(Sr_xCa_{(1-x)})_{n+1}Ti_nO_{3n+1}$. *J. Eur. Ceram. Soc.*, 2001, **21**, 1723–1726.
3. Kagata, H. and Kato, J., Dielelctric properties of Ca-based complex perovskite at microwave frequencies. *Jpn. J. Appl. Phys.*, 1994, **33**, 5463–5465.
4. Hakki, B. W. and Coleman, P. D., A dielectric resonator method of measuring inductive in the millimetre range. *IRE Trans. Microwave Theory Tech.*, 1970, **MMT-18**, 476–485.
5. Courtney, W. E., Analysis and evaluation of a method of measuring the complex permittivity and permeability of microwave insulators. *IRE Trans. Microwave Theory Tech.*, 1970, **MMT-18**, 476–485.
6. Shannon, R. D., Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallogr.*, 1976, **A32**, 751–767.
7. Colla, E. L., Reaney, I. M. and Setter, N., Effect of structural changes in complex perovskites on the temperature coefficient of the relative permittivity. *J. Appl. Phys.*, 1993, **74**, 3414–3425.
8. Reaney, I. M., Colla, E. L. and Setter, N., Dielectric and structural characteristics of Ba-based and Sr-based complex perovskites as a function of tolerance factor. *Jpn. J. Appl. Phys.*, 1994, **33**, 3984–3990.
9. Venkatesh, J. and Murthy, V. R. K., Microwave dielectric properties of $(Ba,Sr)(Zn_{1/3}Ta_{2/3})O_3$ dielectric resonators. *Mater. Chem. Phys.*, 1999, **58**, 276–279.
10. Iddles, D. M., Bell, A. J. and Moulson, A. J., Relationships between dopants, microstructure and the microwave dielectric properties of ZrO_2–TiO_2–SnO_2 ceramics. *J. Mater. Sci.*, 1992, **27**, 6303–6310.
11. Shannon, R. D., Dielectric polarizabilities of ions in oxides and fluorides. *J. Appl. Phys.*, 1993, **73**, 348–366.