

# Microstructure and microwave dielectric properties of $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$ complex perovskite ceramics

M. S. Fu · X. M. Chen · D. Liu

Published online: 26 October 2007  
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**Abstract** Ceramics in the  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  system were prepared and characterized. Single phase solid solutions were obtained up to  $x=0.4$ , and the crystal structure belonged to monoclinic space group  $P21$  (4) for  $x=0.1$  and orthorhombic space group  $Pbnm$ (62) for  $x$  above 0.1. The secondary phase of  $\text{Ca}_2(\text{Ti,Nb})_2\text{O}_6$  was observed for  $x=0.6$  and 0.8. Good combination of microwave dielectric properties was achieved in the present ceramics with  $x=0.4$ :  $\epsilon_r=46.5$ ,  $Qf=14,136$  GHz,  $\tau_f=-12.5$  ppm/°C.

**Keywords** Perovskite · Microwave dielectric properties · Microstructure

## 1 Introduction

Ca-based complex perovskite oxides  $\text{Ca}(\text{B},\text{B}')\text{O}_3$  ( $\text{B}=\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ;  $\text{B}'=\text{Nb}^{5+}$ ,  $\text{Ta}^{5+}$ ) are recognized as good candidates for the microwave dielectric ceramics with moderate dielectric constant [1, 2]. These materials generally have a dielectric constant  $\epsilon$  of 25–35, a very high  $Q$  value and a relative large negative temperature coefficient of resonant frequency  $\tau_f$ . Whereas,  $\text{CaTiO}_3$  exhibits high  $\epsilon$  of 170 and a large positive  $\tau_f$  values (+800 ppm/°C) [3]. Thus, potential ceramics with near zero  $\tau_f$  value and  $\epsilon$  of 40~60 are expected by preparing solid solution or mixed phases between Ca-based complex perovskites with negative  $\tau_f$  and  $\text{CaTiO}_3$  with positive  $\tau_f$ . Several studies on such

solid solution systems have been reported [3–7], where the microwave dielectric characteristics were discussed together with crystal structures and phase transitions. On the other hand, the A-site deficient perovskites  $\text{Ca}_{1-x}\text{Ln}_{2x/3}\text{TiO}_3$  ( $\text{Ln}=\text{La}$ ,  $\text{Nd}$  and  $\text{Sm}$ ) have much higher  $Q$  value and smaller  $\tau_f$  than those of  $\text{CaTiO}_3$  [8–10]. Therefore, one can expect to obtain the temperature stable microwave dielectric ceramics combined with a higher dielectric constant and a higher  $Q$  value in the systems of  $\text{Ca}(\text{B},\text{B}')\text{O}_3\text{--Ca}_{1-x}\text{Ln}_{2x/3}\text{TiO}_3$ .

$\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  ceramics were reported to have good microwave dielectric properties ( $\epsilon=28$ ,  $Qf=58,000$  GHz,  $\tau_f=-48$  ppm/°C) [11]. It was refined in  $P2_1/c$  (14), resulting from  $b^-b^-c^+$  titling system, and 1:2 long-range ordering of B-site ions was observed [12]. On the other hand,  $\text{Ca}_{1-x}\text{Nd}_{2x/3}\text{TiO}_3$  ceramics indicate the best combination of microwave dielectric characteristics at  $x=0.39$ :  $\epsilon=108$ ,  $Qf=17,200$  GHz,  $\tau_f=+270$  ppm/°C [9]. It should be an interesting issue to investigate the possible solid solution in  $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  (CMN–CNT) system, and a moderate dielectric constant combined with the near-zero temperature coefficient of resonant frequency and high  $Q$  value are expected.

In the present work, the modification of  $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  ceramics by incorporating  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  is investigated to achieve higher dielectric constant (40~60) and near-zero temperature coefficient of resonant frequency. The microwave dielectric properties are discussed through the property-structure relationship.

## 2 Experimental procedures

$(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  powders were prepared by a solid-state reaction process where reagent-

M. S. Fu · X. M. Chen (✉) · D. Liu  
Department of Materials Science and Engineering,  
Zhejiang University,  
Hangzhou 310027, China  
e-mail: xmchen@cmsce.zju.edu.cn

grade  $\text{CaCO}_3$  (99.99%),  $\text{MgO}$  (99.9%),  $\text{Nb}_2\text{O}_5$  (99.99%),  $\text{Nd}_2\text{O}_3$  (99.9%) and  $\text{TiO}_2$  (99.5%) powders were adopted as the raw materials. The weighed raw materials were mixed by ball milling with zirconia media in distilled water for 24 h, and the mixtures were heated at 1100 °C in air for 3 h after drying. The calcined powders with 6 wt% of PVA, were pressed into disks measuring 12 mm in diameter and 2–6 mm high and then sintered at 1400–1500 °C in air for 3 h. After cooling from the sintering temperature to 1100 °C at a rate of 2 °C/min, the ceramics were cooled inside the furnace.

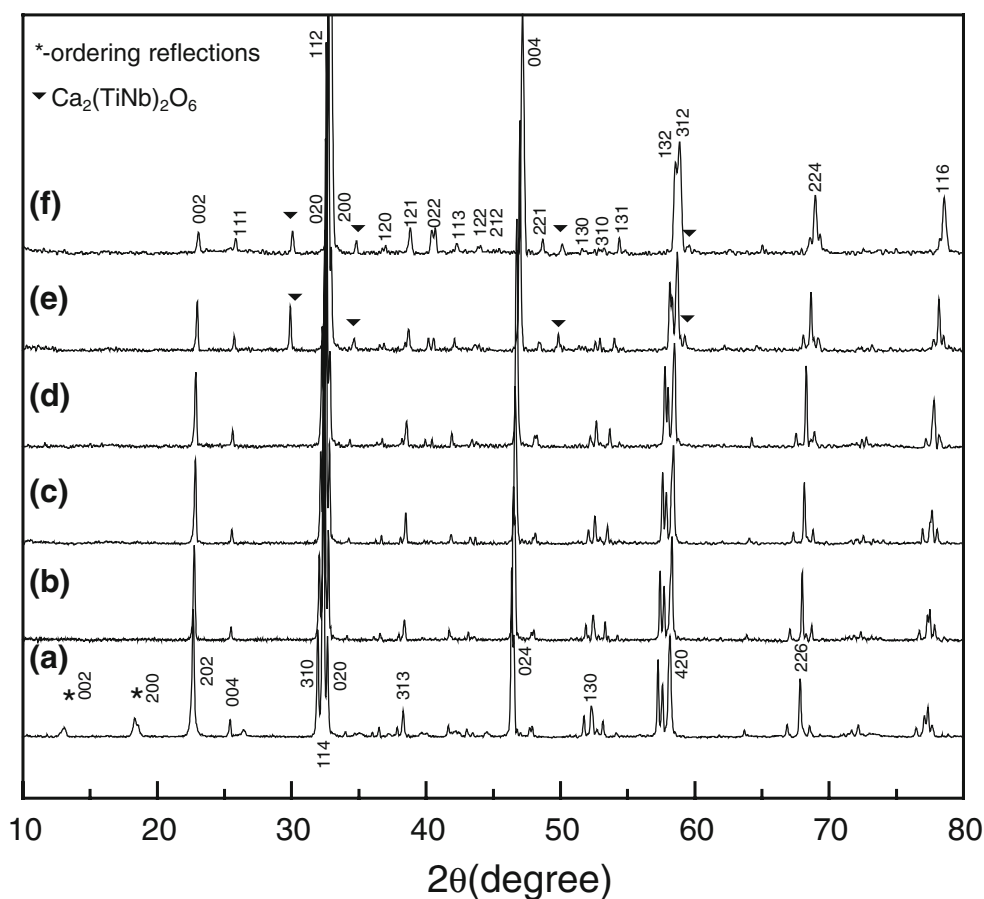
The bulk density of specimens with regular shape was calculated by Archimedes method. The crystal phases of the sintered samples after crushing and grinding were determined by powder X-ray diffraction (XRD) analysis, using  $\text{CuK}\alpha$  radiation. The microstructure observation was performed by SEM (JEOL-JSM-5610LV). The microwave dielectric constant  $\epsilon_r$  and quality factor  $Q$  were evaluated using the Hakki–Coleman method and cavity method, respectively [13]. Because  $Q$  factor generally varies inversely with the frequency, in the microwave region, the product of  $Qf$  was used to evaluate the dielectric loss instead of  $Q$ . The temperature coefficient of resonant frequency  $\tau_f$  at micro-

wave frequency was measured in the temperature range from 20 to 85 °C.

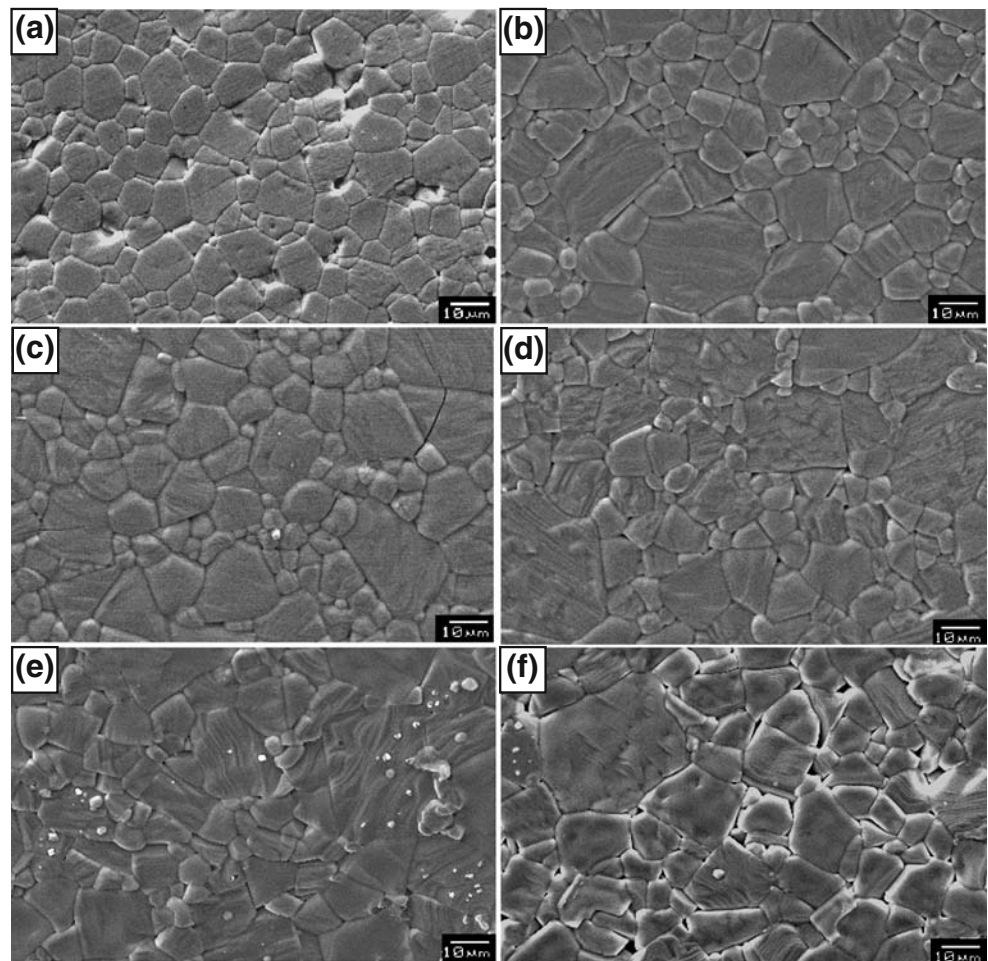
### 3 Results and discussion

$\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  can be refined in the monoclinic space group  $P2_1/c$  (14), resulting from  $b^-b^+c^+$  titling system. The difference of ionic radius and electronegativity between the  $\text{Mg}^{2+}$  and  $\text{Nb}^{5+}$  in B-site originates the 1:2 ordering structure in  $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  [12]. On the other hand, Masashi et al. have suggested that  $\text{Ca}_{1-x}\text{Nd}_{2x/3}\text{TiO}_3$  ( $x \leq 0.69$ ) could be refined as orthorhombic structure with space group  $Pnma$ (62) [9]. Figure 1 shows the XRD patterns of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics sintered at 1450 °C for 3 h. A single perovskite phase is obtained up to  $x=0.4$ , and  $\text{Ca}_2(\text{Ti,Nb})_2\text{O}_6$  with space group  $Fd\bar{3}m$ (227) is detected for  $x=0.6-0.8$  as a secondary phase. Spectrum of the sample with  $x=0.1$  shows the same structure as  $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  with peaks at 12.8° and 18.2° indicated the 1:2 ordering of B site cations. However, for ceramics with  $x=0.2$  to 0.8, spectra of the major phase show  $Pbnm$ (62) orthorhombic structure with absence of ordering peaks. The diffraction

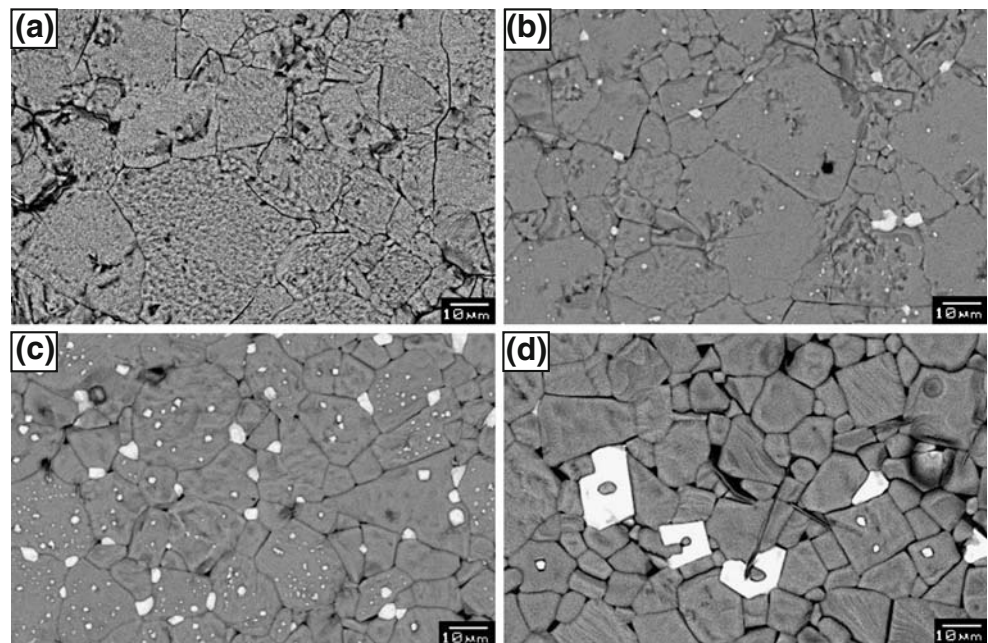
**Fig. 1** XRD patterns of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics: (a)  $x=0.1$ , (b)  $x=0.2$ , (c)  $x=0.3$ , (d)  $x=0.4$ , (e)  $x=0.6$ , (f)  $x=0.8$



**Fig. 2** SEM micrographs of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics: (a)  $x=0.1$ , (b)  $x=0.2$ , (c)  $x=0.3$ , (d)  $x=0.4$ , (e)  $x=0.6$ , (f)  $x=0.8$



**Fig. 3** Electron back scattering micrographs of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics: (a)  $x=0.3$ , (b)  $x=0.4$ , (c)  $x=0.6$ , (d)  $x=0.8$



peaks are displaced to higher  $2\theta$  angles with increasing  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  content. This reflects the decrease in the unit-cell volume upon substitution of  $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$  ( $r^6=0.0667 \text{ \AA}$ ) by the smaller  $\text{Ti}^{4+}$  ( $r^6=0.0605 \text{ \AA}$ ) [14] cations in B sites and the introduced vacancies in A sites.

SEM micrographs of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics after sintered at  $1450 \text{ }^\circ\text{C}$  for 3 h are illustrated in Fig. 2. The grain growth is approximately uniform at  $x=0.1$ , but as  $x$  increases it becomes abnormal and the amount of porosity increases. Figure 3 shows the electron back scattering micrographs of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics. Secondary phases are clearly showed at the graphs of ceramics with  $x=0.4$  to  $0.8$ . According to further analysis using step scanning XRD data, no secondary phase is detected in the sintered ceramics with  $x=0.4$ , and this means that the amount of the secondary phase is small.

Figure 4 shows the dielectric constant and temperature coefficient of resonant frequency of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics sintered at different temperatures for 3 h. Both dielectric constant and temperature coefficient of resonant frequency of the present ceramics increase with increasing  $x$  nonlinearly and the a small temperature coefficient of resonant frequency ( $-12.5 \text{ ppm}/^\circ\text{C}$ ) is obtained at  $x=0.4$ . This behavior can be explained by considering the Clausius–Mossotti equation [15] which relates the dielectric constant with macroscopic sphere having volume  $V_m$  and the macroscopic polarizability  $\alpha_m$ .

$$\left(\frac{\epsilon_r - 1}{\epsilon_r + 2}\right) = \frac{4\pi\alpha_m}{3V_m} \tag{1}$$

Since the macroscopic polarizability  $\alpha_m$  is not a simple sum of ionic polarizabilities, the  $\epsilon_r$  exhibits nonlinear dependence on the  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  content. Similarly, the

expression of temperature coefficient of resonant frequency can be obtained by Eqs. 2 (differentiating the macroscopic Clausius–Mossotti equation) and 3 [16].

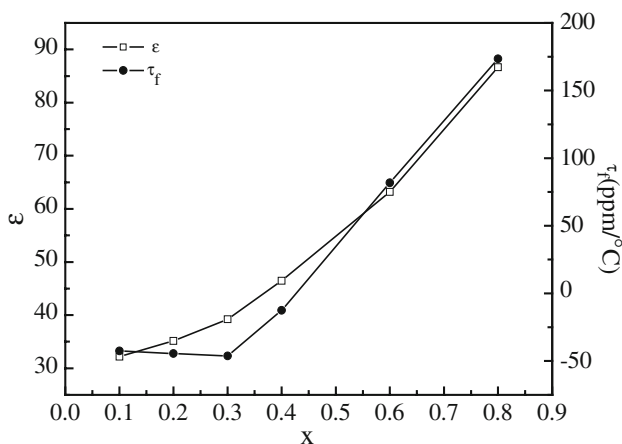
$$\tau\epsilon_r = \frac{1}{\epsilon_r} \left(\frac{\partial\epsilon}{\partial T}\right)_P = \frac{(\epsilon_r - 1)(\epsilon_r + 2)}{\epsilon_r} (A + B + C) \tag{2}$$

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

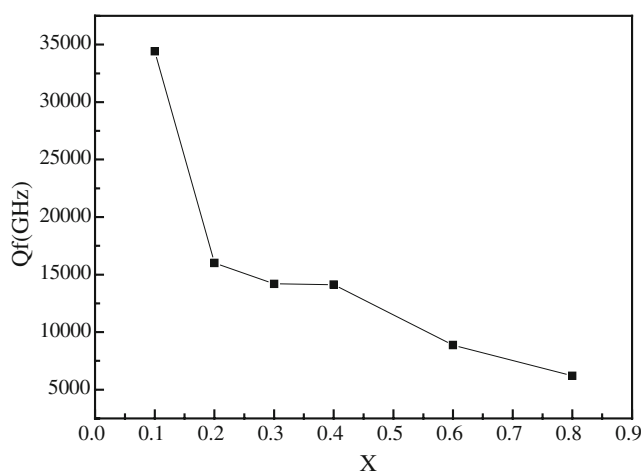
$$= \frac{1}{3\alpha_m} \left(\frac{\partial\alpha_m}{\partial T}\right)_V, \tau_f = -\frac{\tau\epsilon_r}{2} - \alpha \tag{3}$$

where,  $\alpha$  is the thermal expansion coefficient. The  $C$  term is always negative for materials with  $\epsilon_r > 10$ , while the  $(A + B)$  term is always positive. [16] Since the  $(A + B)$  term nearly remains constant with variation in composition [17], the change in sign and magnitude of  $\tau\epsilon_r$  is a direct outcome of the increasing magnitude of the  $|C|$  term related to  $(A + B)$ . So as  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  content increase, the contribution from the  $C$  term increase,  $\tau\epsilon_r$  become more negative and the magnitude of the change is amplified by larger  $\epsilon_r$  values. The variation tendency of  $\tau_f$  with  $x$  can also be interpreted by the different tilting degrees.  $\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  with significant tilting indicates the negative  $\tau_f$ , while  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  with slight tilting shows the positive  $\tau_f$ . [9, 12] Since the tilting become weak with increasing  $x$ ,  $\tau_f$  of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  varies from negative towards positive.

$Q_f$  value decreases monotonously with increasing  $\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  content as shown in Fig. 5. The highest  $Q_f$  value of 34,421 GHz is achieved in ceramics for  $x=0.1$  but reduces to 6,190 GHz for  $x=0.8$ . The sharp decrease of  $Q_f$  value of the present ceramics with  $x=0.1 \sim 0.2$  is due to the change from order to disorder of  $B$  site ions and



**Fig. 4** Dielectric constant and temperature coefficient of resonant frequency of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  microwave dielectric ceramics as functions of  $x$



**Fig. 5**  $Q_f$  values of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  microwave dielectric ceramics as functions of  $x$

abnormal grain growth as shown in Figs. 1 and 2, respectively. Slight decrease of  $Qf$  value from  $x=0.2$  to 0.4 might due to the increase of degree of abnormal grain growth and the amount of porosity. The  $\text{Ca}_2(\text{Ti,Nb})_2\text{O}_6$  secondary phase should be responsible for the low  $Qf$  values achieved in ceramics with  $x=0.6$  and 0.8. As the present ceramics sintered in air, it would cause the reduction of  $\text{Ti}^{4+}$  and the formation of oxygen vacancies in the abnormal large size grains, which result in the increase of dielectric loss. This implies that the  $Qf$  value could be improved by annealing in oxygen atmosphere.

#### 4 Conclusions

The microwave dielectric properties, crystal structure and microstructures of  $(1-x)\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3/x\text{Ca}_{0.61}\text{Nd}_{0.26}\text{TiO}_3$  ceramics have been investigated. Crystal structure of the present ceramics changed from monoclinic for  $x=0.1$  to orthorhombic for  $x$  above 0.1.  $\text{Ca}_2(\text{Ti,Nb})_2\text{O}_6$  second phase formed in ceramics with  $x=0.6$  and 0.8, which caused the low  $Qf$  values. Both the dielectric constant and temperature coefficient of resonant frequency of the present ceramics increased with increasing  $x$  nonlinearly while the  $Qf$  value decreased monotonously. The order–disorder transition, abnormal grain growth and oxygen vacancies should be responsible for the decrease of  $Qf$  values. The good combination of microwave dielectric properties was achieved in the present ceramics with  $x=0.4$ :  $\epsilon_r=46.5$ ,  $Qf=14,136$  GHz,  $\tau_f=-12.5$  ppm/°C. Further improvement of microwave dielectric properties would be achieved by annealing in oxygen atmosphere.

**Acknowledgment** This work was financially supported by the Primary Project of National Science Foundation of China under grant number 50332030 and Chinese National Key Project for Fundamental Researches under grant number 2002CB613302.

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