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Temperature-stable dielectric ceramics in $Pb(Mg_{1/3}Nb_{2/3})O_3$–$CaTiO_3$–$Bi_4Ti_3O_{12}$ pseudo-ternary system

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Abstract

Ceramics in the $Pb(Mg_{1/3}Nb_{2/3})O_3$–$CaTiO_3$–$Bi_4Ti_3O_{12}$ pseudo-ternary system were investigated to search for new temperature-stable dielectrics for high frequency applications. A near-zero temperature coefficient was obtained combined with a high dielectric constant (124) and a low dielectric loss (10^{-3} at 1 MHz) where a complex phase constitution was observed. The dielectric properties were significantly sensitive to the sintering conditions due to the variation of phase constitution. © 2002 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: Dielectric ceramics; Pb $(Mg_{1/3}Nb_{2/3})$ O_3–$CaTiO_3$–$Bi_4Ti_3O_{12}$ system

1. Introduction

It is well known that relaxor ferroelectries of lead-based complex perovskites unusually exhibit high dielectric constants [1]. If the temperature coefficient and dielectric loss can be suppressed efficiently, such modified relaxor ferroelectrics will have great potential as high-ϵ microwave materials [2–6].

Recently, Chen and Lu [7] reported that the dielectric loss and temperature coefficient could be pronouncedly reduced by incorporating $CaTiO_3$ into $Pb(Mg_{1/3}Nb_{2/3})O_3$. By this means, good microwave dielectric properties, $\varepsilon = 172.6$ and $Qf = 1930$ GHz were achieved in a $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$ composition, where the temperature coefficient of resonant frequency is $+470$ ppm/°C. It is very interesting to search for alternative approach to further modify the temperature coefficient in $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$ ceramics.

In the present work, $Bi_4Ti_3O_{12}$ with a positive temperature coefficient of dielectric constant (τ_ε) [8] has been incorporated into $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6$ $CaTiO_3$ ceramics to cerate near-zero temperature coefficient dielectric materials. The influences of composition and sintering condition on the dielectric properties and the structure evolution have been investigated.

2. Experimental procedure

A two-step solid-state reaction method was used. Reagent grade $CaCO_3$, MgO, Nb_2O_5, PbO and TiO_2 powders were adopted as raw materials to prepare $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$ at first. The raw powders were mixed and ball-milled with zirconia media in ethanol for 24 h, then dried and calcined at 850 °C in air for 3 h. The calcined powders were remilled for one day and dried. $Bi_4Ti_3O_{12}$ powders were synthesized by a similar method, where the starting materials were reagent grade oxide powders of Bi_2O_3 and TiO_2 and the mixed powers were calcined at 850 °C in air for 3 h.

The above powders were batched for the compositions $(1-x)[0.4Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.6CaTiO_3]/xBi_4Ti_3O_{12}$ with $x = 0.1$, 0.2, 0.3, 0.4 and 0.5 and ball-milled for 24 h and dried. Then the mixed powders with an organic binder (PVA) were pressed under 98 MPa into compacts of 12mm in diameter, and finally sintered at 1050–1200 °C in air for 3 and 6 h.

Bulk density was measured by dimensional method for the sintered samples. The microstructures of sintered samples and phase constitution were studied by scanning electron microscope (SEM) and X-ray diffraction (XRD) using CuK_α radiation, respectively.

Dielectric constant and dielectric loss were determined from capacitance measurements over the frequency range 100 KHz–10 MHz at room temperature by an

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HP4285A LCR meter. The temperature coefficient of dielectric constant was evaluated by another LCR meter (HP4284A) at 10 KHz to 1 MHz. Silver paste was used for the electrodes. The microwave dielectric properties were evaluated by the Hakki and Coleman's dielectric resonator method [9].

3. Results and discussion

Compared with $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$ end-member, the present ceramics can sinter satisfactorily at lower temperatures (1100–1150 °C). As shown in Figs. 1 and 2, the addition of $Bi_4Ti_3O_{12}$ into $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$ has significant effects on the dielectric properties. The dielectric constant generally decreases with increasing $Bi_4Ti_3O_{12}$ content, except for the slight increase for the composition of $x \leqslant 0.2$ sintered at 1100 °C. $Bi_4Ti_3O_{12}$ addition generally leads to a higher dielectric loss than for the end-member. On the other hand, the temperature coefficient can be adjusted from negative to positive by increasing $Bi_4Ti_3O_{12}$ content and a near-zero temperature coefficient is obtained for the compositions of $x = 0.4$–0.5 sintered under the appropriate conditions (at 1150 °C for 6 h). The dielectric properties are also pronouncedly affected by the sintering conditions. The higher temperature and prolonged sintering generally lead to a decreased dielectric constant, lower dielectric loss and smaller positive or more negative τ_ε. A good combination of dielectric properties (at 1 MHz) is achieved in the composition with $x = 0.4$ sintered at 1150 °C in air for 6 h: $\varepsilon = 124$, $\tan\delta = 0.0044$, $\tau_\varepsilon = -15$ ppm/°C.

The above variation tendency of dielectric properties is primary linked to the phase constitution. XRD patterns of the present materials with various compositions are shown in Figs. 3 and 4. The XRD results suggest that the following reactions may occur during sintering:

$$3(Pb_{0.4}Ca_{0.6})\left[\left(Mg_{1/3}Nb_{2/3}\right)_{0.4}Ti_{0.6}\right]O_3 + Bi_4Ti_3O_{12} \rightarrow 3\left[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}\right]_2\left[Ti_{0.8}\left(Mg_{1/3}Nb_{2/3}\right)_{0.2}\right]_2O_7 \quad (1)$$

$$(Pb_{0.4}Ca_{0.6})\left[\left(Mg_{1/3}Nb_{2/3}\right)_{0.4}Ti_{0.6}\right]O_3 + Bi_4Ti_3O_{12} \rightarrow (Pb_{0.4}Ca_{0.6})Bi_4\left[Ti_{0.9}\left(Mg_{1/3}Nb_{2/3}\right)_{0.1}\right]_4O_{15} \quad (2)$$

$$3(Pb_{0.4}Ca_{0.6})\left[\left(Mg_{1/3}Nb_{2/3}\right)_{0.4}Ti_{0.6}\right]O_3 + Bi_4Ti_3O_{12} \rightarrow (Pb_{0.4}Ca_{0.6})_3Bi_4\left[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.2}\right]_6O_{21} \quad (3)$$

$$4(Pb_{0.4}Ca_{0.6})\left[\left(Mg_{1/3}Nb_{2/3}\right)_{0.4}Ti_{0.6}\right]O_3 + Bi_4Ti_3O_{12} \rightarrow (Pb_{0.4}Ca_{0.6})_4Bi_4\left[Ti_{0.9}\left(Mg_{1/3}Nb_{2/3}\right)_{0.228}\right]_7O_{24} \quad (4)$$

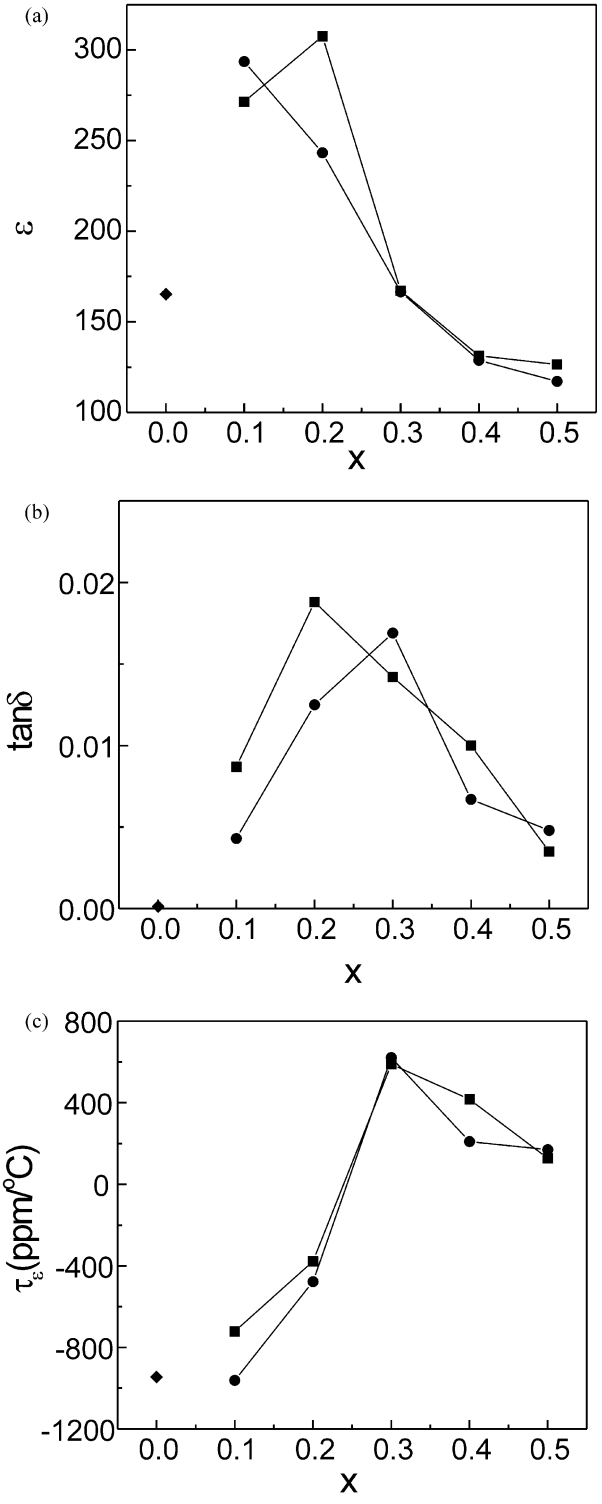

Fig. 1. Dielectric properties at 1 MHz of $(1-x)[0.4Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.6CaTiO_3]/xBi_4Ti_3O_{12}$ ceramics sintered at 1100–1150 °C for 3 h as function of x: (a) temperature coefficient of dielectric constant; (b) dielectric loss; (c) dielectric constant; (■, 1100 °C/3 h; ●, 1150 °C/3 h; ◆, 1300 °C/4 h).

Occurrence of any specific reaction among (1) to (4) and the final phase constitution are largely dependent on the composition, sintering temperature and sintering

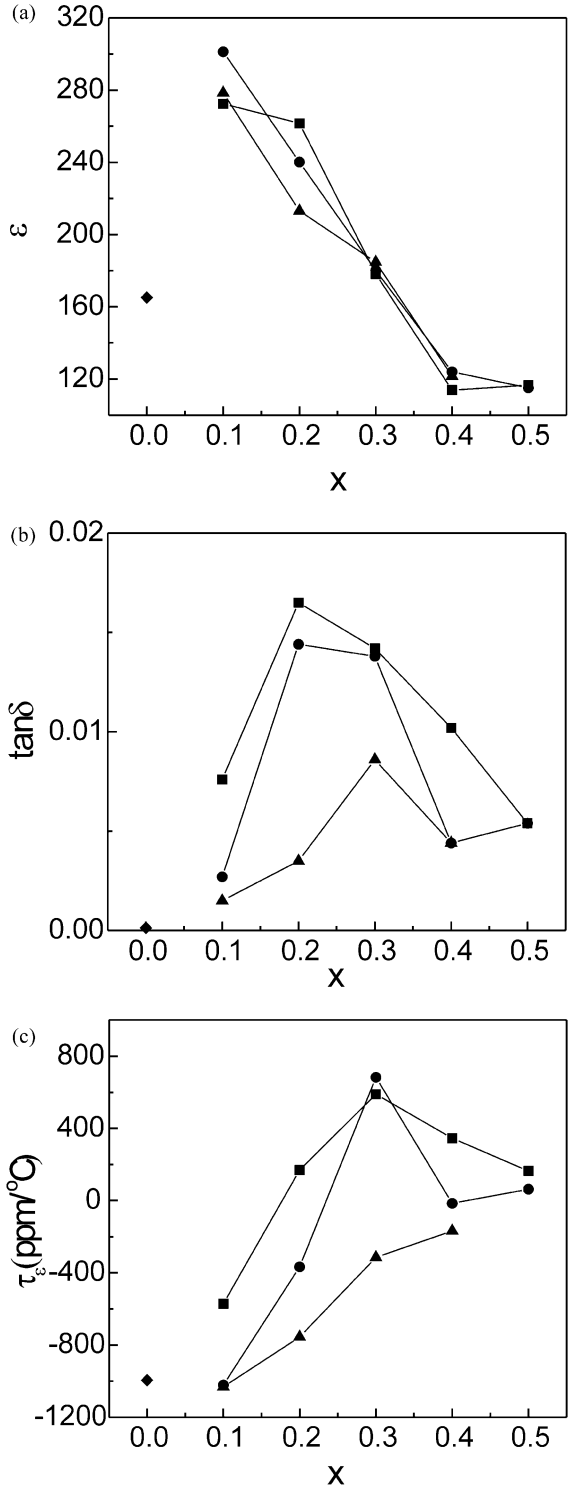

Fig. 2. Dielectric properties (at 1MHz) of $(1-x)[0.4Pb(Mg_{1/3}Nb_{2/3})O_3–0.6CaTiO_3]/xBi_4Ti_3O_{12}$ ceramics sintered at 1100–1200 °C for 6 h as function of x: (a) temperature coefficient of dielectric constant; (b) dielectric loss; (c) dielectric constant; (■, 1100 °C/6 h; ●, 1150 °C/6 h, ▲, 1200 °C/6 h; ◆, 1300 °C/4 h).

time. For all compositions, no $Bi_4Ti_3O_{12}$ is observed in the sintered ceramics, as it dissolves into or reacts with $Pb_{0.4}Ca_{0.6}[(Mg_{1/3}Nb_{2/3})_{0.4}]Ti_{0.6}O_3$. Compositions with

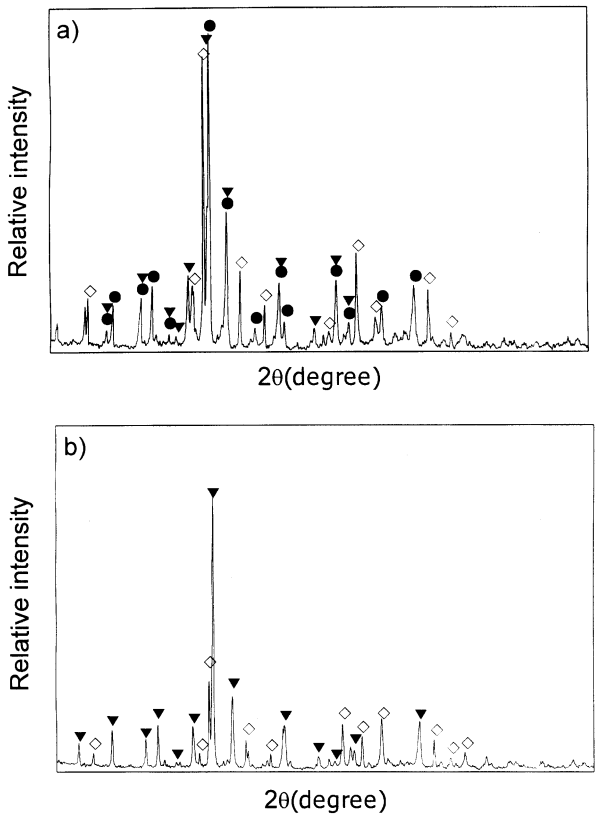

Fig. 3. XRD patterns of the ceramics sintered at 1150 °C for 3 h: (a) $x=0.4$; (b) $x=0.5$; (◇, $[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}]_2[Ti_{0.8}(Mg_{1/3}Nb_{2/3})_{0..2}]_2O_7$; ▼, $(Pb_{0.4}Ca_{0.6})Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.1}]_4O_{15}$; ◇, $(Pb_{0.4}Ca_{0.6})_3Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.2}]_6O_{21}$).

Table 1
Microwave dielectric properties of $(1-x)[0.4Pb(Mg_{1/3}Nb_{2/3})O_3–0.6CaTiO_3]/xBi_4Ti_3O_{12}$ multiphase ceramics

x	Sintering condition	f_0 (GHz)	ε	Qf (GHz)
0.4	1150 °C/6 h	3.68	134	120
0.5	1150 °C/6 h	3.92	124	260

$x=0.1$ and $x=0.5$ result in a relatively simple phase constitution, whereas for $0.2\leqslant x\leqslant 0.4$ phase composition is more complex. The end-member $Pb_{0.4}Ca_{0.6}[(Mg_{1/3}Nb_{2/3})_{0.4}]Ti_{0.6}O_3$ is observed in the composition of $x=0.1$ combined with a pyrochlore solid solution phase of $[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}]_2[Ti_{0.8}(Mg_{1/3}Nb_{2/3})_{0..2}]_2O_7$. The latter will become the major phase with increasing x or increasing sintering temperature. For the composition $x=0.5$, no original end-member phase is observed, and the more complex solid solution of $(Pb_{0.4}Ca_{0.6})Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.1}]_4O_{15}$ becomes the major phase according to reaction (2), pyrochlore solid solution of $[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}]_2[Ti_{0.8}(Mg_{1/3}Nb_{2/3})_{0..2}]_2O_7$ being observed as a secondary phase. Both $[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}]_2$ $[Ti_{0.8}(Mg_{1/3}Nb_{2/3})_{0..2}]_2O_7$ or $(Pb_{0.4}Ca_{0.6})_3Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.2}]_6O_{21}$ may become the major phase

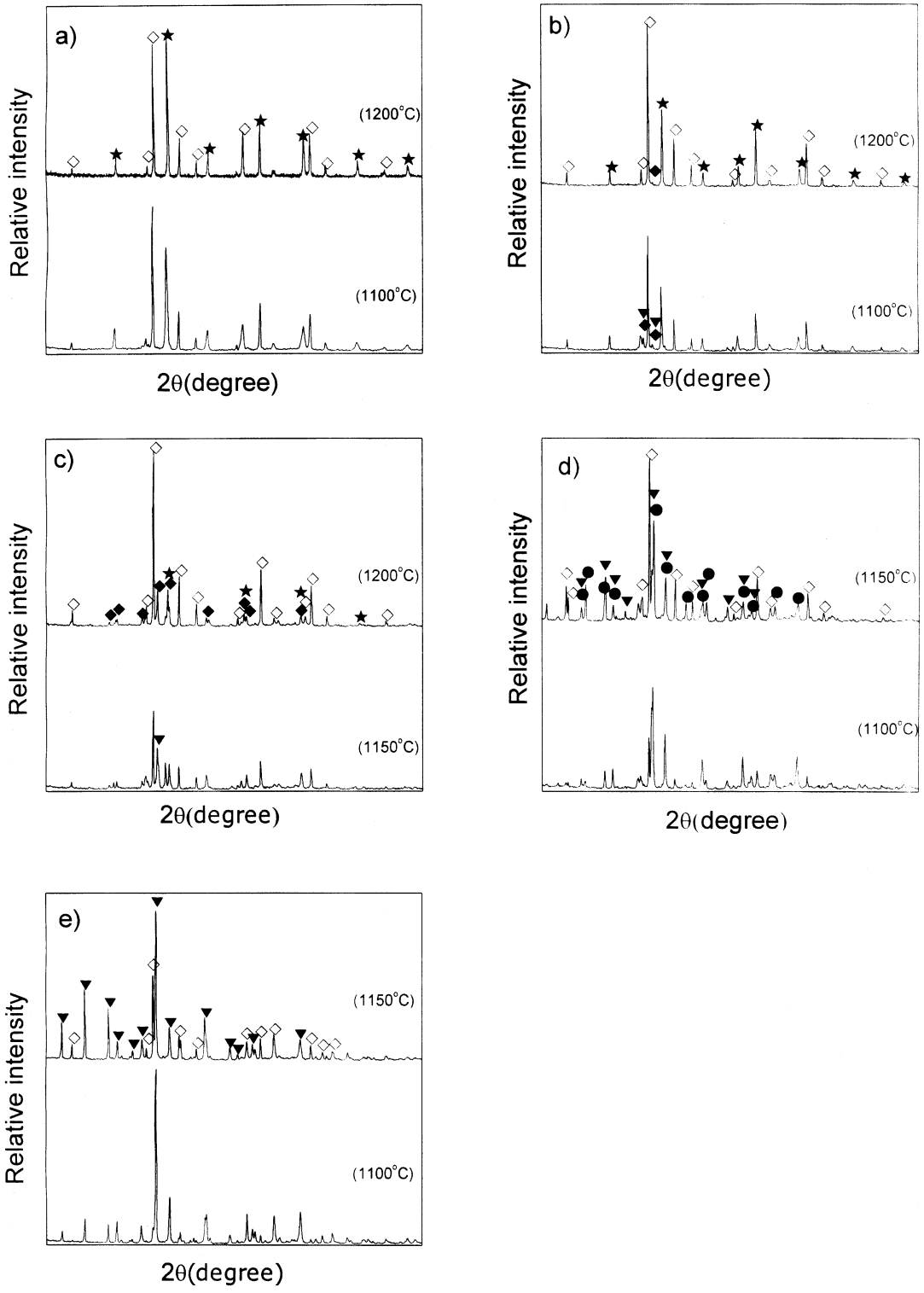

Fig. 4. XRD patterns of the ceramics sintered at different temperature for 6 h: (a) $x=0.1$; (b) $x=0.2$; (c) $x=0.3$; (d) $x=0.4$; (e) $x=0.5$. (⋆, $(Pb_{0.4}Ca_{0.6})[(Mg_{1/3}Nb_{2/3})_{0.4}Ti_{0.6}]O_3$; ◇, $[Bi_{2/3}(Pb_{0.4}Ca_{0.6})_{0.5}]_2[Ti_{0.8}(Mg_{1/3}Nb_{2/3})_{0..2}]_2O_7$; ▼, $(Pb_{0.4}Ca_{0.6})Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.1}]_4O_{15}$; ●, $(Pb_{0.4}Ca_{0.6})_3Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.2}]_6O_{21}$; ◆, $(Pb_{0.4}Ca_{0.6})_4Bi_4[Ti_{0.9}(Mg_{1/3}Nb_{2/3})_{0.228}]_7O_{21}$).

for $x=0.4$ according to reaction (1) and (3), depending on the sintering conditions.

Table 1 lists the microwave dielectric properties of some selected compositions. Because of the complex phase constitution based on pyrochlore phase and bismuth layered structure compound, a poor Qf value is obtained for the present multiphase ceramics.

Generally, a good combination of high dielectric constant and near-zero temperature coefficient can be achieved in the present pseudo-ternary system, but the increased dielectric loss limits microwave applications. However, the present multiphase ceramics may find promising application in high-frequency capacitors or temperature-compensated capacitors.

4. Conclusions

Temperature-stable dielectric ceramics with high dielectric constant have been obtained by balancing a positive temperature coefficient material $Bi_4Ti_3O_{12}$ and a negative temperature coefficient material $0.4Pb(Mg_{1/3}Nb_{2/3})O_3/0.6CaTiO_3$. A near-zero temperature coefficient can be obtained in the present multiphase ceramics combined with a high dielectric constant (124) and relatively low dielectric loss (0.0044 at 1 MHz). The dielectric properties are significantly affected by the sintering conditions due to the variation of phase constitution.

Though the present multiphase ceramics are not suitable for microwave resonator application due to their increased dielectric loss, they may find promising application in high frequency capacitors and temperature-compensated capacitors.

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