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Tunable dielectric properties of $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composite ceramics

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ABSTRACT

$BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites were prepared by a solid-state reaction method, and their dielectric and tunable characteristics were investigated for the potential application as microwave tunable materials. It is observed that the addition of Mg_2SiO_4–MgO into $BaZr_{0.2}Ti_{0.8}O_3$ form ferroelectric ($BaZr_{0.2}Ti_{0.8}O_3$)–dielectric (Mg_2SiO_4–MgO) composites. The dielectric constant and loss tangent of $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites have been reduced and the overall tunability is maintained at a sufficiently high level. An anomalous relation between dielectric constant and tunability was observed: with the increase of Mg_2SiO_4 content (>30 wt%), the dielectric constant of composite decreases and the tunability increases. The anomalous increased tunability can be attributed to redistribution of the electric field. $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites have tunability of 14.2–17.9% at 100 kHz under 2 kV/mm, indicating that it is a promising candidate material for tunable microwave applications requiring low dielectric constant.

1. Introduction

Electric field tunable ferroelectric materials have attracted extensive attention in recent years due to their potential applications for tunable microwave device such as tunable filters, phased array antennas, delay lines and phase shifters. These applications require a material that demonstrates high tunability, low dielectric loss, and suitable permittivity. High dielectric constant ferroelectric materials tend to have higher loss tangents and, therefore, higher insertion loss. Furthermore, a high dielectric constant can cause substantial impedance mismatch issues. Of all the ferroelectric materials investigated for tunable microwave applications, (Ba, Sr)TiO_3 solid solution has received the most attention [1–8] due to its intrinsic high dielectric tunability. Some dielectric materials with relatively low dielectric constant and loss tangent were added into (Ba, Sr)TiO_3 to reduce the effective dielectric constant and loss tangent of the (Ba, Sr)TiO_3 while maintaining respectable tunability [3–8].

Recently $BaZr_xTi_{1-x}O_3$ solid solution has shown great potential for the application in tunable microwave devices [9–15]. With increasing Zr content, phase transition peak shifts to lower temperature and the tunability and loss tangent decrease. The dielectric constant of $BaZr_{0.2}Ti_{0.8}O_3$ at room temperature at 1 MHz is as high as ~22,000 [12,16]. High dielectric constant has restricted its application in tunable microwave device. It is necessary to decrease the dielectric constant of $BaZr_xTi_{1-x}O_3$. It is reported that forming ferroelectric–dielectric composite is an efficient method to decrease dielectric constant and loss tangent while maintaining the tunability at a sufficiently high level [3,4]. Maiti et al. [12,16,17] have reported high tunability and low loss tangent of the $Ba(Zr_xTi_{1-x})O_3$:MgO composites which show the dielectric constant <400 in the temperature range from 300 K to 11 K. 50 wt% $BaZr_{0.2}Ti_{0.8}O_3$–50 wt% MgO has a tunability 22% under 3 kV/mm biasing versus a dielectric constant 219 (10 kHz) and the sintering temperature is as high as 1500 °C.

In this paper, MgO and Mg_2SiO_4 have been introduced to fabricate the $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites for tunable microwave devices applications. MgO and Mg_2SiO_4 are microwave dielectric materials with low dielectric constant and loss tangent, and their combination tailored the dielectric properties of $BaZr_{0.2}Ti_{0.8}O_3$ ceramics to make it useful in an array of different applications similar to the (Ba, Sr)TiO_3:MgO [3,4], furthermore, the sintering temperature can be reduced. $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO (where $x = 48$, 36, 30, 24 and 12 wt%) composite ceramics have been prepared and their microstructure and dielectric tunable characteristics have been studied for the potential application as microwave tunable materials.

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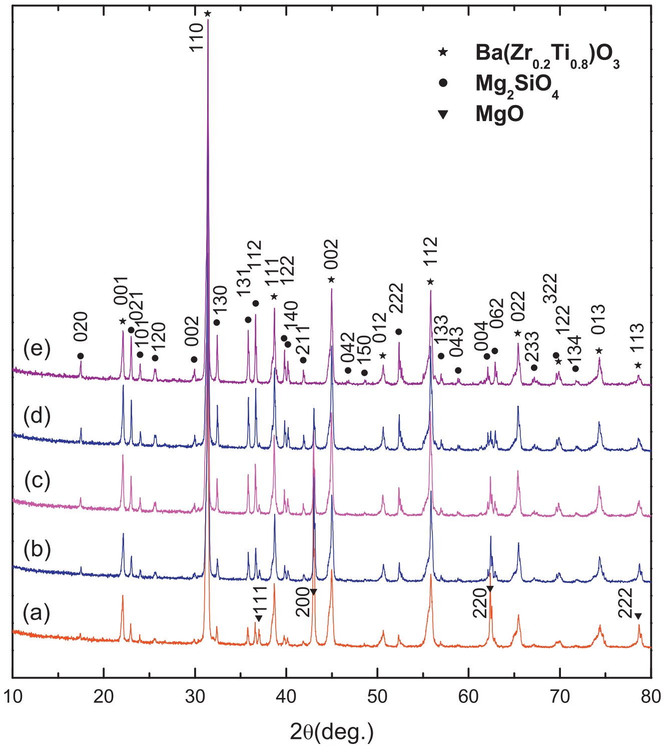

Fig. 1. The XRD patterns of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO composite ceramics sintered at 1350 °C for 3 h. (a) $x = 48$ wt%, (b) $x = 36$ wt%, (c) $x = 30$ wt%, (d) $x = 24$ wt%, and (e) $x = 12$ wt%.

2. Experimental procedures

2.1. Synthesis of composite ceramics

Ceramic samples were prepared by the conventional solid-state route. $BaZr_{0.2}Ti_{0.8}O_3$ and Mg_2SiO_4 powders were prepared first from $BaCO_3$, ZrO_2, TiO_2 and MgO, SiO_2 powders at 1200 °C, respectively. The $BaZr_{0.2}Ti_{0.8}O_3$ powders were mixed with Mg_2SiO_4 and MgO according to the formalism $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO (where $x = 48$, 36, 30, 24 and 12 wt%) and milled with agate balls for 6 h. After adding the binder the composite powders were pressed into pellets and subsequently sintered at temperatures 1300–1350 °C for 3 h. Silver paste was coated to form electrodes on both sides of the sintered ceramic samples for dielectric measurements.

2.2. Characterization

The crystal phases of the sintered samples were determined by powder X-ray diffraction (XRD) using Cu Kα radiation (X'Pert PRO of PANalytical B.V.,) after crushing and grinding. The collection conditions were as follows: 40 kV, 40 mA, 2θ range: 10–80°, step scan: 0.0167°, scan type: continuous. The Hitachi S-4800 field emission scanning electron microscopy with energy dispersive analysis system of X-ray (EDS, Horiba EMAX ENERGY EX-350) was used to characterize the microstructure and chemical component elements. The dielectric constant and loss tangent were measured using Agilent 4294A precision impedance analyzer at 100 kHz. The tunability was measured with a LCR meter at biases up to 1000 V d.c. via an external power supply.

3. Results and discussion

Fig. 1 shows the XRD patterns of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO ceramics sintered at 1350 °C for 3 h. Three distinguished crystalline phases, cubic $BaZr_{0.2}Ti_{0.8}O_3$, orthorhombic Mg_2SiO_4, and cubic MgO, were observed but no other phase was detected. With the decrease of MgO content and the increase of Mg_2SiO_4 content, the diffraction peaks from MgO decrease gradually and the diffraction peaks from Mg_2SiO_4 increase. It is apparent that $BaZr_{0.2}Ti_{0.8}O_3$, Mg_2SiO_4 and MgO are distributed as individual phases in the final composite bulk ceramics.

Fig. 2 shows the FESEM images of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO composite ceramics sintered at 1350 °C for 3 h. The FESEM image and element mapping of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO ($x = 48$ and 24) as determined by energy dispersive spectroscopy (EDS) are shown in Fig. 3. Three kind of different grains can be found clearly: dark, nearly round larger grains, platelike grains with sharp corner and light, smaller grains with average grain size of about 0.5 μm. The element mapping of Si Kα1 and Ba Lα1 in Fig. 3 can show the distribution of Mg_2SiO_4 and $BaZr_{0.2}Ti_{0.8}O_3$ grains clearly. Therefore, we can identify that the dark, larger grains are MgO; white, smaller grains are $BaZr_{0.2}Ti_{0.8}O_3$; and the platelike grains are Mg_2SiO_4. With the decrease of MgO content and the increase of Mg_2SiO_4 content, more and more Mg_2SiO_4 grains can be found (Fig. 2). MgO grains become smaller with the decrease of MgO content (Fig. 3b). We can conclude that Mg_2SiO_4 and MgO were randomly dispersed relative to the ferroelectric $BaZr_{0.2}Ti_{0.8}O_3$ phase without any detectable new phase as shown in Fig. 2.

From the XRD and FESEM study, we know that $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composite ceramics are composed of tunable ferroelectric phase $BaZr_{0.2}Ti_{0.8}O_3$ and dielectric phases Mg_2SiO_4 and MgO. Because of the relatively low dielectric constant and loss tangent of Mg_2SiO_4 and MgO, it is expected that $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites have lower dielectric constant and loss tangent. Fig. 4 shows the dielectric constant and loss tangent of $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composite ceramics at 100 kHz. With the increase of sintering temperature from 1300 °C to 1350 °C, the dielectric constant of the composites increase and the loss tangent decrease. Increasing Mg_2SiO_4 content tends to decrease the dielectric constant of composites, which is due to lower dielectric constant of Mg_2SiO_4 than that of MgO. The dielectric constant of composites is much smaller than that of $BaZr_{0.2}Ti_{0.8}O_3$ ($\varepsilon \sim 22{,}000$ at 100 kHz) [12,16]. Low dielectric constant will improve the ability to the impedance match to the device. On the other hand, the loss tangent of composites sintered at 1350 °C is ~0.0012–0.0016, which is comparable to that of $50BaZr_{0.2}Ti_{0.8}O_3$–50MgO [16,17]. Adding Mg_2SiO_4 and MgO into $BaZr_{0.2}Ti_{0.8}O_3$, three phases ($BaZr_{0.2}Ti_{0.8}O_3$, Mg_2SiO_4 and MgO) composites formed and the dielectric constant and loss tangent decreased, just as we expected.

The tunability may be defined as (dielectric constant with no applied voltage) – (dielectric constant with an applied voltage)/(dielectric constant with no applied voltage). For simplicity purposes, tunability can be represented as

$$T = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} = \frac{C(0) - C(E)}{C(0)}$$

where C is the capacitance and E is the applied dc electric field. Fig. 5 shows the effect of applied field on the tunability of the $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites at 100 kHz at room temperature. The tunability of $40BaZr_{0.2}Ti_{0.8}O_3$–$12Mg_2SiO_4$–48MgO under 2 kV/mm is 15.6%. With the increase of Mg_2SiO_4 content, the tunability of $40BaZr_{0.2}Ti_{0.8}O_3$–$30Mg_2SiO_4$–30MgO decreases slightly to 14.2%. Further increasing Mg_2SiO_4 content results in an anomalous increase of tunability: $40BaZr_{0.2}Ti_{0.8}O_3$–$48Mg_2SiO_4$–12MgO composite has lower dielectric constant than $40BaZr_{0.2}Ti_{0.8}O_3$–$12Mg_2SiO_4$–48MgO but slightly higher tunability (17.9%). Compared with binary $50BaZr_{0.2}Ti_{0.8}O_3$–50MgO, $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites have reduced dielectric constant, comparable tunability [17], but lower sintering temperature. Decreasing dielectric constant by ferroelectric–dielectric composite method is usually strongly correlated a decrease in tunability. In order to decrease dielectric constant of composite, it is necessary to increase the dielectrics content. For example [3], increasing MgO content in $Ba_{0.6}Sr_{0.4}TiO_3$–MgO from 30 wt% to 60 wt% results in a decrease

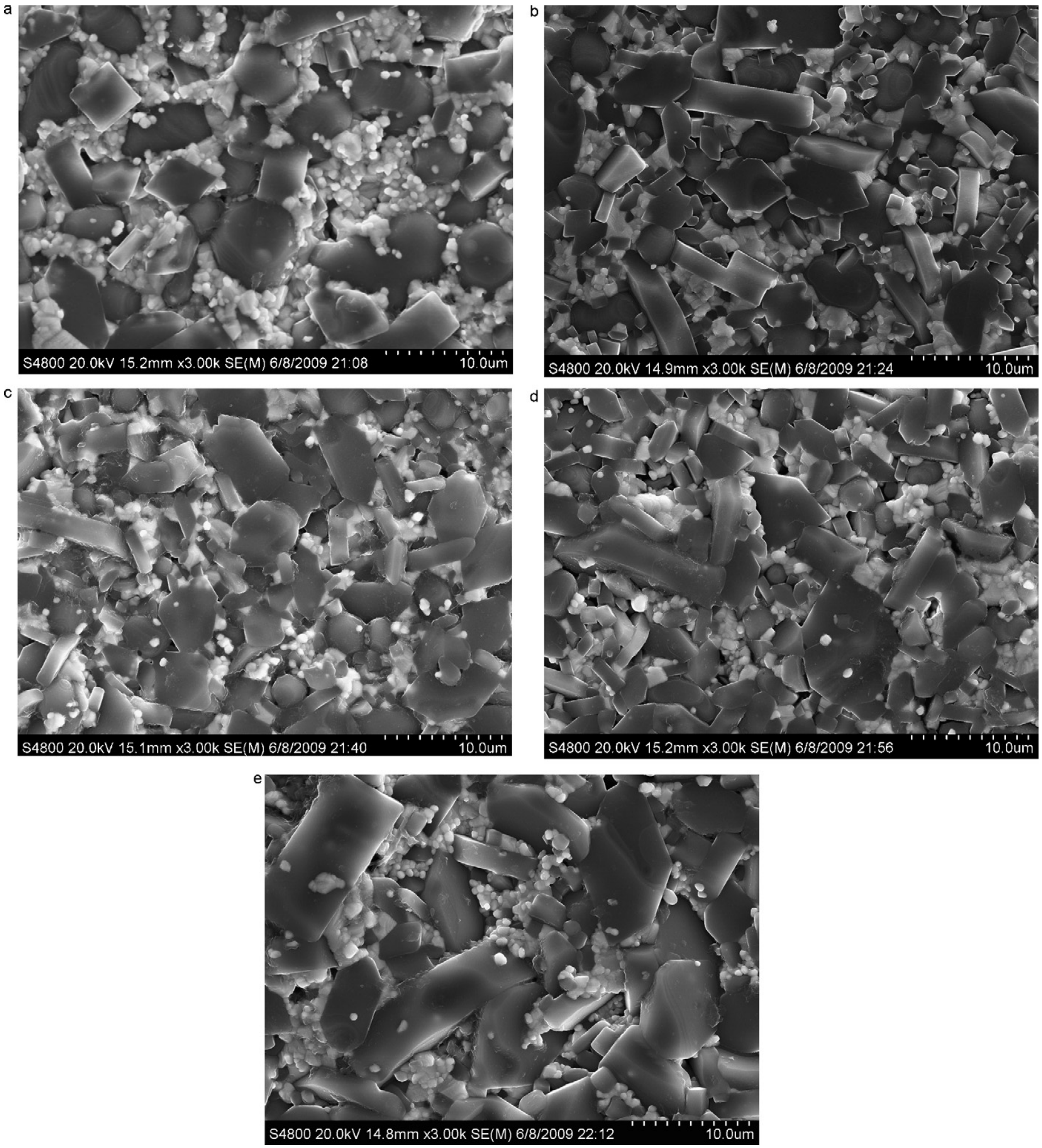

Fig. 2. FESEM images of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO composites ceramics sintered at 1350 °C for 3 h. From (a) to (e), $x = 48$ wt%, 36 wt%, 30 wt%, 24 wt% and 12 wt%, respectively.

of dielectric constant from 636 to 118 and tunability at 2 kV/mm from 15% to 10%. No literatures reported the effect of MgO content on the dielectric constant and tunability of BZT/MgO composite. We can expect the similar results with BST/MgO. Therefore, it is difficult to decrease the dielectric constant of two-phase composites and increase their tunability. In present work, an anomalous relation between dielectric constant and tunability was observed in three-phase $BaZr_{0.2}Ti_{0.8}O_3$–Mg_2SiO_4–MgO composites: with increasing Mg_2SiO_4 content above 30 wt%, the dielectric constant of composite decreases and the tunability increases. It is beneficial to tunable application.

As Tagantsev stated [18], mixing a tunable ferroelectric with a linear dielectric may modify the electrical properties of the material due to mainly two effects: (i) "doping effect" – effect of doping of the ferroelectric lattice via the substitution of the ions of the host material and (ii) "composite effect" – effects of redistribution of the electric field in the material due to the precipitation of the non-ferroelectric phase at the grain boundaries or in the bulk of

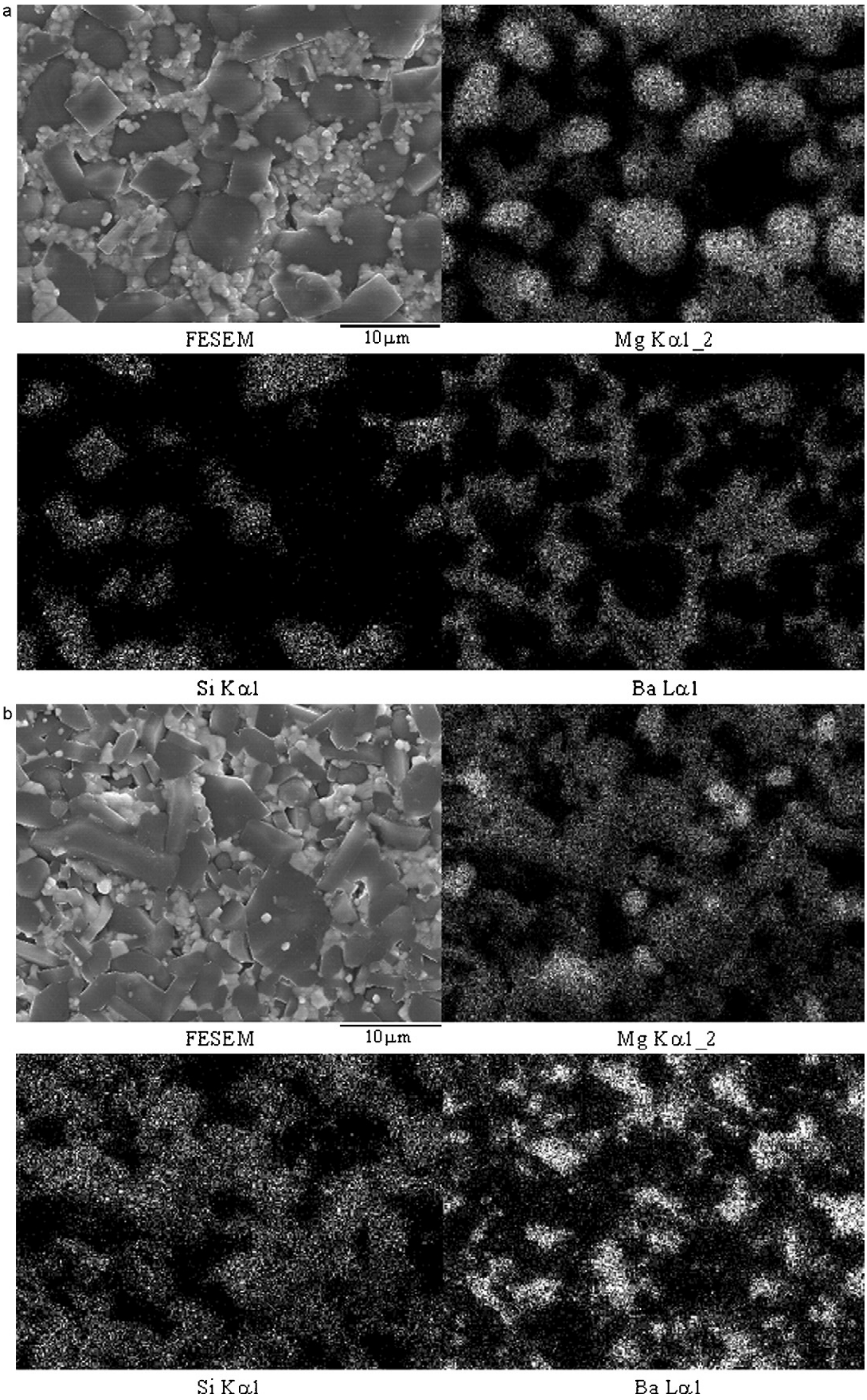

Fig. 3. FESEM image and element mapping of $40BaZr_{0.2}Ti_{0.8}O_3$–$(60-x)Mg_2SiO_4$–xMgO as determined by energy dispersive spectroscopy (EDS). (a) $x = 48$ wt% and (b) $x = 24$ wt%.

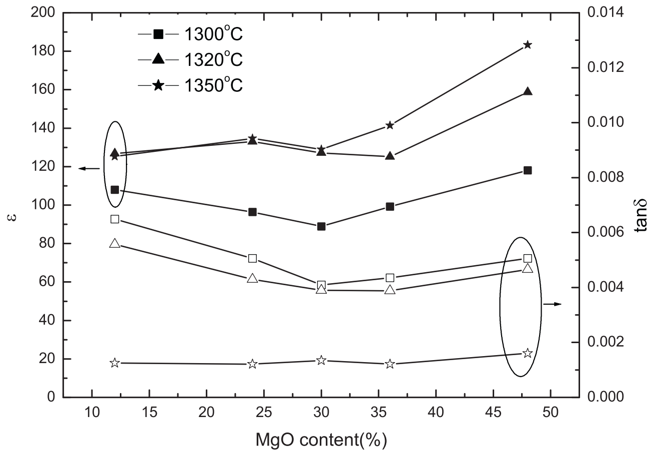

Fig. 4. Dielectric constant (solid) and loss tangent (open) of $40BaZr_{0.2}Ti_{0.8}O_3–(60-x)Mg_2SiO_4–xMgO$ composite ceramics sintered at various temperatures.

the material. For $BaZr_{0.2}Ti_{0.8}O_3–Mg_2SiO_4–MgO$ composite, the first effect can be ignored. The big contrast in the values of dielectric constants of linear dielectrics ($Mg_2SiO_4–MgO$) and the ferroelectric ($BaZr_{0.2}Ti_{0.8}O_3$) affects the redistribution of the electric field around the dielectrics. The dielectric constant of the ferroelectric under applied electric field becomes in-homogeneously distributed over the volume of the ferroelectric. The overall tunability of the composite, thus changes. Two competitive phenomena affect the tunable properties of the ferroelectric when it is diluted with a dielectric [19]. First, the reduction of the volume of ferroelectric, which is responsible for tuning, will cause suppression of the tunability of the material. Second, the redistribution of the electric field surrounding the linear dielectrics will affect the local tuning of the ferroelectric. Depending on the shape of the linear dielectrics and on the dielectric constants of the components, the impact of each of these two effects on the composite tunability is different and the second effect may be stronger [19]. With the increase of Mg_2SiO_4 content and the decrease of MgO content, the volume of ferroelectric $BaZr_{0.2}Ti_{0.8}O_3$ decrease due to smaller density of Mg_2SiO_4 than that of MgO, the tunability of composite will be suppressed. It is the fact as x decreases from 48 wt% to 30 wt%. The anomalous increased tunability in composite with $x < 30$ wt% can be attributed to redistribution of the electric field. Mg_2SiO_4 and MgO have different dielectric constants, they will have different effects on the redistribution of the electric field. The combination of linear dielectrics with different dielectric constants can result in the change of dielectric constant and loss tangent and even increase the tunability by affecting the redistribution of the electric field in the composite. As x decreases from 30 wt% to 12 wt%, the increase of the tunability due to redistribution of the electric field exceeds the decrease of the tunability due to ferroelectric dilution, so the tunability of composite ceramics increases anomalously.

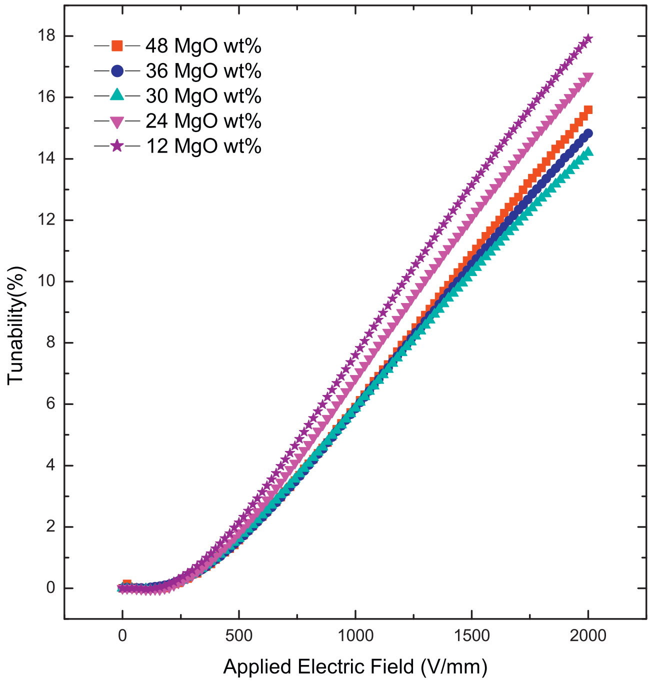

Fig. 5. The tunability of $40BaZr_{0.2}Ti_{0.8}O_3–(60-x)Mg_2SiO_4–xMgO$ composites at 100 kHz at room temperature (sintering temperature: 1350 °C).

4. Conclusions

$BaZr_{0.2}Ti_{0.8}O_3–Mg_2SiO_4–MgO$ composites were prepared by conventional solid-state route and their microstructure and dielectric properties were investigated for tunable microwave applications. XRD patterns showed that ferroelectric ($BaZr_{0.2}Ti_{0.8}O_3$) and dielectric ($Mg_2SiO_4–MgO$) three phase composites were formed. The $BaZr_{0.2}Ti_{0.8}O_3–Mg_2SiO_4–MgO$ composites exhibited relatively high tunability in combination with reduced dielectric permittivity and low loss tangent. An anomalous relation between dielectric constant and tunability was observed. The tunability of $BaZr_{0.2}Ti_{0.8}O_3–Mg_2SiO_4–MgO$ composites was 14.2–17.9% at 100 kHz under 2 kV/mm, indicating that it is a promising candidate material for tunable microwave applications requiring low dielectric constant.

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