J Mater Sci (2010) 45:3331–3335
DOI 10.1007/s10853-010-4352-4

Microwave dielectric properties of BaO–TiO_2–TeO_2 ternary system

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Received: 20 November 2009 / Accepted: 24 February 2010 / Published online: 11 March 2010

Abstract Besides the applications as optical functional materials, tellurium oxides also have attracted interest as microwave dielectric materials. Most TeO_2-based binary and ternary system have large negative temperature coefficient of resonant frequency (τ_f), which is not compatible for the low-temperature cofired ceramic. To compensate τ_f close to zero, two single-phase predecessors of $BaTe_4O_9$ and $TiTe_3O_8$ are synthesized in air at 530–560 and 620–680 °C, respectively. The two predecessors show exceptional dielectric properties and their τ_f are opposite. The BaO–TiO_2–TeO_2 ternary system compounds are investigated by adjusting the ratio of $BaTe_4O_9$ and $TiTe_3O_8$ and sintered at 520–580 °C to develop the microwave properties and compensate the τ_f. After sintered at 560 °C, the ceramic sample with the composition of $0.47BaTe_4O_9$–$0.53TiTe_3O_8$ exhibits a dielectric permittivity of 28, a $Q \times f$-value of 12,200 GHz, and a τ_f of 4.0 ppm/°C measured at 10 GHz.

Introduction

Recently, tellurium oxides have been continuously studied as microwave dielectric materials because most of TeO_2-based binary and ternary system compounds can be sintered in air at temperatures ranging from 500 to 850 °C, which can be applied to the low-temperature cofired ceramic (LTCC) technology. The temperature of materials used for LTCC technology must be lower than the melting point of the metal electrode, which in the case of silver is 875–920 °C, because the LTCC technology requires the cofiring of ceramic layers and the inner circuit [1]. Other requirements for LTCC materials, in terms of their electrical properties, are high relative permittivity (ε_r), high Q-value, and a temperature coefficient of resonant frequency (τ_f) tunable around zero [2]. For the low-temperature sintering of dielectric ceramics, low-melting point glasses, or oxide fluxes (e.g., CuO, B_2O_3, ZnO, V_2O_5) are frequently added so the dielectrics can be cofired with conductor layers such as silver. However, these approaches often result in degradation of dielectric properties of the main formulations caused by the formation of secondary phases and lossy amorphous phases in the grain boundaries. For this reason, exploring low-melting single-phase dielectrics is preferred rather than the addition of sintering aids in the dielectric material development for LTCC application [2–5].

Pure TeO_2 does not become a glass under usual quenching rates and the addition of other elements is needed to form TeO_2-based bulk glasses [6]. So many TeO_2-based binary and ternary glasses as microwave dielectric ceramics have been seriously investigated recently. Udovic et al. [1, 2] have reported the phase formations, microwave dielectric properties, and the compatibility melting with Ag electrode of several Te-based binary compounds such as Bi_2O_3–TeO_2, TiO_2–TeO_2, and the CaO–TeO_2 binary systems. Kwon et al. [5, 7] investigated the BaO–TeO_2 binary systems and further they researched the BaO–TiO_2–TeO_2 ternary system in which they indicated the synthesis and dielectric properties of $BaTiTe_3O_9$. Through their investigations, some of the TeO_2-based dielectrics are potentially candidates to LTCC technology for their low-sintering temperature and excellent dielectric properties. However, whether positive or negative most of these TeO_2-based binary and ternary systems showed large values of τ_f and

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they do not match with the LTCC technology for the temperature dependence up to a maximum of a few tens of ppm/°C.

In the present article, we select two TeO_2-based binary dielectrics $BaTe_4O_9$ and $TiTe_3O_8$ for study because the two dielectrics can be synthesized in air with stable thermomechanical properties and they have opposite τ_f. Yamanaka and Miyake reported that only one compound $TiTe_3O_8$ has a thermodynamically stable single phase in air with the tellurium in the Te^{4+} valence state in the Ti–TeO_2 binary system [8]. Do-Kyun et al. [5] produced single-phase $BaTe_4O_9$ crystallizing with a monoclinic crystal structure at 500 °C. During our experiments, we synthesized pure $BaTe_4O_9$ and $TiTe_3O_8$ and then we attempted to compensate τ_f close to zero by changing the proportions of the two dielectrics and to determine the relative permittivity and $Q \times f$-value of the system.

Experimental procedure

A solid-state reaction method was used to synthesize the compounds from the BaO–TiO_2–TeO_2 system. Reagent grade powders of $BaCO_3$, TiO_2, and TeO_2 were separately stoichiometrically weighed in accordance with the elemental composition of $BaTe_4O_9$ and $TiTe_3O_8$. After that raw materials of $BaTe_4O_9$ and $TiTe_3O_8$ were mixed in alcohol media and ball-milled with 5 mm stabilized zirconia balls for 24 h, and subsequently calcined in air at 530–560 and 620–680 °C for 5 h, respectively. After calcinations, the phase compositions of $x BaTe_4O_9$–$(1 - x)TiTe_3O_8$ ($x = 0.47, 0.50, 0.53, 0.57$) were admixed with the two precursors of $BaTe_4O_9$ calcined at 550 °C and $TiTe_3O_8$ calcined at 640 °C. After the compound powders were ball-milled, they were isostatically pressed into disks 10 mm in diameter and 1–2 mm in thickness. The disks then were sintered at various temperatures from 520 to 580 °C in air, depending on their compositions. The crystalline phases were identified by means of X-ray powder diffraction (XRD, Philips X'Pert) through CuKα radiation over the range of $2\theta = 10°–80°$ (steps of 0.06° and counting time of 1 s). The amount of the component in the system was determined from XRD patterns using the MDI Jade software. Thermochemical properties like glass transition (T_g) and meting temperature (T_m) were determined by differential scanning calorimetry and thermal gravimetry analysis (DTA-TG, STA 449 C, NETZSCH) at a heating rate of 10 K/min. Scanning electron microscopy (SEM, S-530 Hitachi) was used for the microstructural analysis.

The complex dielectric permittivity and dielectric loss were determined at 1 MHz by using a HP4284A LCR meter. The dielectric constant and the quality values Q at microwave frequencies were measured with a network analyzer (Model Agilent E8363A) by using Hakki-Coleman dielectric resonator method [9]. The resonant frequencies at temperatures 20 °C (f_{20}) and 80 °C (f_{80}) were measured. The temperature coefficient of resonant frequency (τ_f) was calculated from the formula: $\tau_f = (f_{80} - f_{20})/(60 \times f_{20}) \times 10^6$ (ppm/°C).

Results and discussion

Formation and dielectric properties of $BaTe_4O_9$ and $TiTe_3O_8$

The stoichiometrically mixed $BaCO_3$ and TeO_2 raw materials calcined at 530–560 °C for 5 h yielded a single-phase of $BaTe_4O_9$, while the pure $TiTe_3O_8$ compound was synthesized by TiO_2 and TeO_2 raw materials calcined at 620–680 °C for 5 h. Figure 1 shows the XRD patterns of calcined $BaTe_4O_9$ and $TiTe_3O_8$ powders. All the peaks were well indexed as those of the $BaTe_4O_9$ (PDF # 36-0887) and $TiTe_3O_8$ (PDF # 24-1348).

Grain morphology was analyzed by using SEM. Figure 2 shows the surface microstructures of $BaTe_4O_9$ specimen sintered at 570 °C and $TiTe_3O_8$ specimen sintered at 760 °C for 2 h, respectively.

The grain shape of the $BaTe_4O_9$ ceramic is very particular and obviously like strip. The ceramics exhibit ~5% porosity and a grain size of 3–6 μm. Microwave dielectric properties of these ceramics, measured at 5.5 GHz, are a $Q \times f$-value of 23,400 GHz, relative permittivity of 15.8, and a τ_f of −115 ppm/°C.

Different from the $BaTe_4O_9$ ceramic, the grain shape of the $TiTe_3O_8$ is granulated. The ceramic of $TiTe_3O_8$ with an estimated porosity of less than 3% and a small grain size ranging from submicrometer to 5 μm were obtained. The microwave dielectric properties of sintered $TiTe_3O_8$ ceramics are determined with a relative permittivity of 49.7 and a $Q \times f$-value of 11,800 GHz at 5 GHz. The τ_f is 125 ppm/°C.

Sintering and dielectric properties of BaO–TiO_2–TeO_2 compounds

Figure 3 shows the thermal behaviors of $x BaTe_4O_9$–$(1 - x)$ $TiTe_3O_8$ ($x = 0.47$, 0.50, 0.53, and 0.57) mixed powders measured by DSC and TG analysis. It is considered if the atmosphere has any affection to the mixtures so we have sintered the $0.47BaTe_4O_9$–$0.53TiTe_3O_8$ mixture under air flow and other three mixtures under N_2 flow. All the four DSC curves reveal that there are three main endothermic reactions during the formation and their positions are roughly the same in each curve. The first endothermic peak is at about 510 °C, which is the glass transition (T_g)

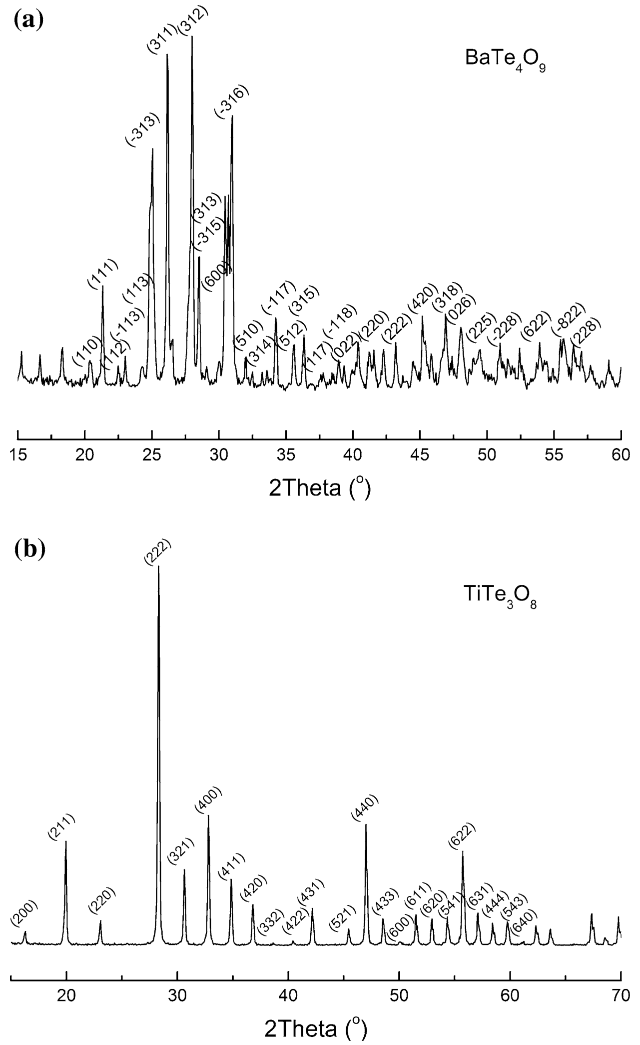

Fig. 1 X-ray diffraction patterns of **a** $BaTe_4O_9$ calcined at 550 °C and **b** $TiTe_3O_8$ calcined at 640 °C for 5 h

temperature of the mixtures. The second and third endothermic peaks corresponding to the temperature of 545 and 575 °C can be considered as the melting points of $BaTe_4O_9$ (T_{m1}) and $TiTe_3O_8$ (T_{m2}), respectively. There is a small exothermic peak around 360 °C in the DSC curve a of the $0.47BaTe_4O_9$–$0.53TiTe_3O_8$ mixture, and this peak corresponds to the weight loss step of curve a in the TG analysis. However, it is still hard to explain the kinetics of this thermal behavior. The weight loss of $0.50BaTe_4O_9$–$0.50TiTe_3O_8$, $0.53BaTe_4O_9$–$0.47TiTe_3O_8$, and $0.57BaTe_4O_9$–$0.43TiTe_3O_8$ mixtures before 460 °C is due to the evaporation of water and organic matter. From 460 °C to the finishing measurement point 645 °C, there is an approximate 0.05% weight increment. It is unclear which factor causes this weight increment, one speculation is that a little bit of flowing gas of N_2 has dissolved in the melting mixtures and possibly reacted with them. Different from the other three mixtures sintered under N_2 flow, $0.47BaTe_4O_9$–$0.53TiTe_3O_8$ mixture sintered under air flow loses weight continuously from the beginning to the end. The weight loss between 360 and 645 °C can be considered as the decomposition and evaporation of ternary tellurium oxides. The total weight loss of each mixture does not exceed 1.7%. Totally, the difference of the mixtures sintered under different atmosphere is not obvious for determining the thermal behaviors.

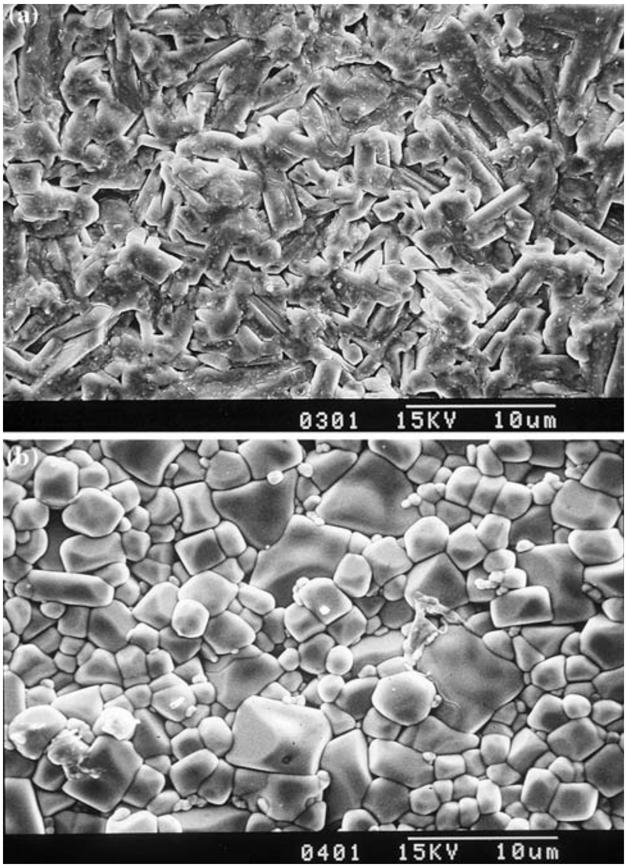

Fig. 2 SEM images of $BaTe_4O_9$ (**a**) sintered at 570 °C and $TiTe_3O_8$ (**b**) sintered at 760 °C for 2 h

Figure 4 shows the XRD patterns of $xBaTe_4O_9$–$(1 - x)TiTe_3O_8$ ($x = 0.47, 0.50, 0.53$, and 0.57) powders sintered at 560 °C for 2 h. Most of the peaks were indexed as those of $BaTe_4O_9$ and $TiTe_3O_8$. The BaO–TiO_2–TeO_2 secondary phases were not found in the system. However, some small peaks of low intensity were indexed as $BaTeO_3$, and it can be identified as the evaporation of TeO_2, which came from the decomposition of a little $BaTe_4O_9$ sintered at 560 °C. In Fig. 3, we have studied that the melting point of $BaTe_4O_9$ is at 545 °C, so some $BaTe_4O_9$ may decompose to $BaTeO_3$ and TeO_2 at 560 °C. The peaks of $BaTeO_3$ are a little higher in curve d than curve a because more $BaTe_4O_9$ compound decomposes for curve d. It is calculated that the mount of $BaTeO_3$ is about 1.5 mol% in curve d by analyzing the XRD result using MDI Jade software. And to get a single composition of $0.53BaTe_4O_9$–$0.47TiTe_3O_8$, more

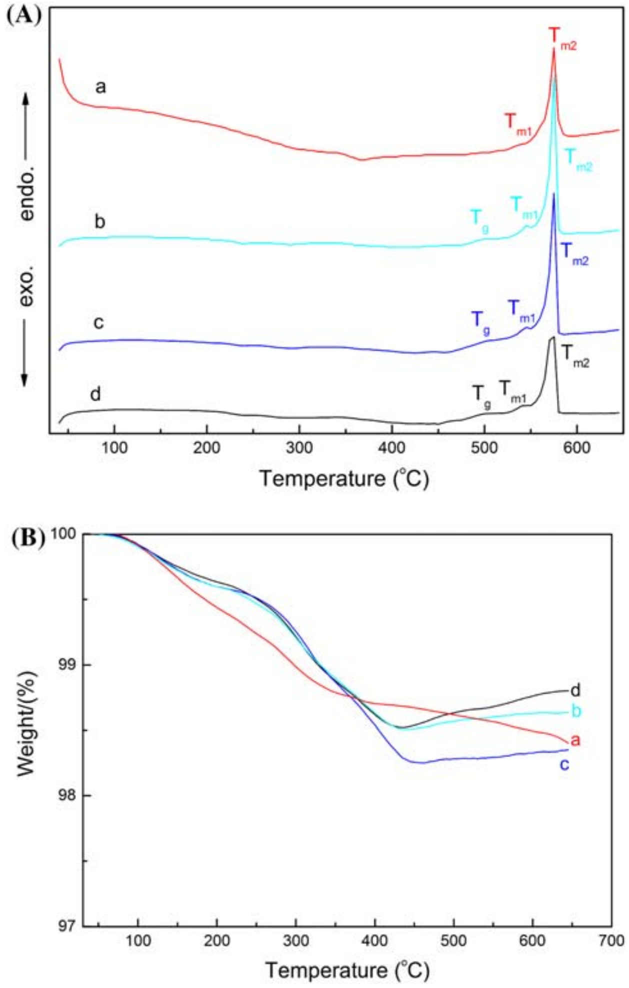

Fig. 3 DSC (**A**) and TG (**B**) traces of xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ mixed powders with x = 0.47, 0.50, 0.53, and 0.57 corresponding to the curves of *a*, *b*, *c*, and *d*, respectively; the 0.47BaTe$_4$O$_9$–0.53TiTe$_3$O$_8$ mixture was sintered under air flow while other three were under N$_2$ flow

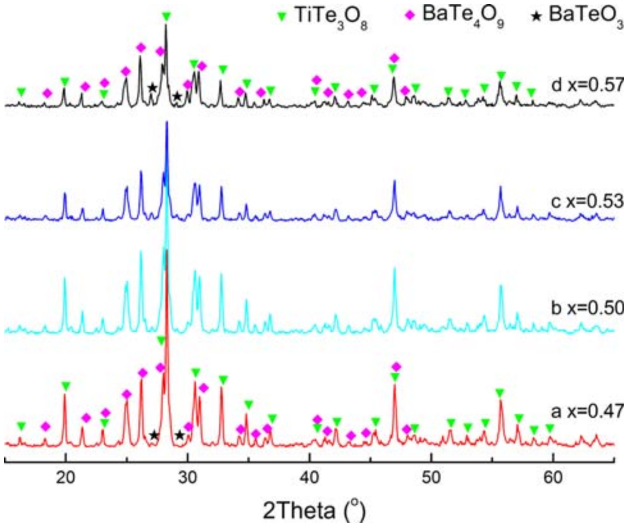

Fig. 4 XRD patterns of xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ mixtures sintered at 560 °C for 2 h with *a* $x = 0.47$; *b* $x = 0.50$; *c* $x = 0.53$; *d* $x = 0.57$

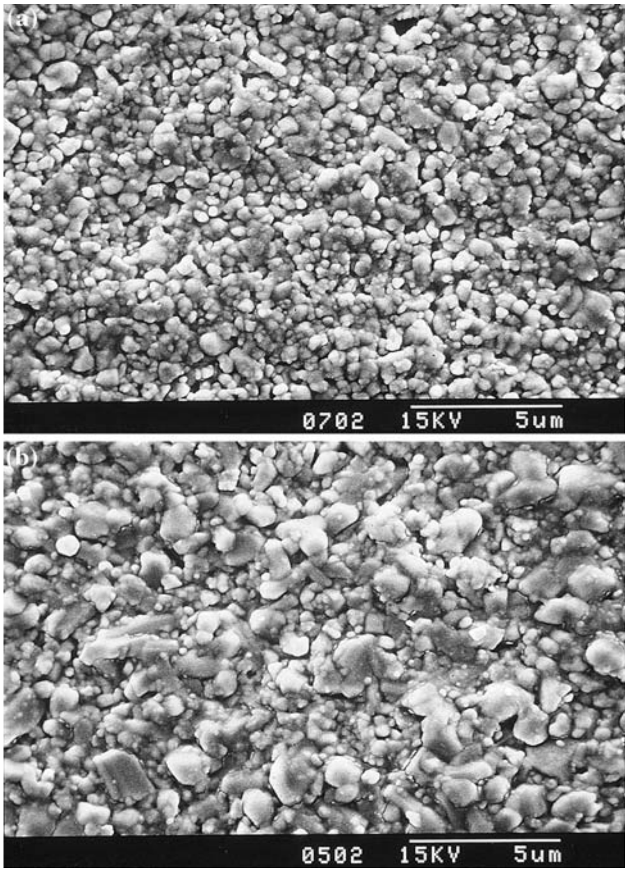

Fig. 5 SEM images of xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ (x = 0.47 (**a**), 0.57 (**b**)) ceramic specimens sintered at 560 °C

about 4.5 mol% TeO$_2$ should be added into the system to make up the loss during sintering.

Grain morphology was analyzed by using SEM. Figure 5 shows surfaces of xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ (x = 0.47 and 0.57) specimens sintered at 560 °C. The 0.47BaTe$_4$O$_9$–0.53TiTe$_3$O$_8$ ceramic has an estimated porosity <3% and exhibits grains that have an average size of 0.71 μm. Comparing with 0.47BaTe$_4$O$_9$–0.53TiTe$_3$O$_8$ ceramic, the grains of 0.57BaTe$_4$O$_9$–0.43TiTe$_3$O$_8$ ceramic integrate more closely with a porosity of less than 2%. However, the particle size of 0.57BaTe$_4$O$_9$–0.43TiTe$_3$O$_8$ ceramic has an uneven distribution and the grain growth is not well-developed like plate morphology. Some glass phases can be obviously seen between the grain boundaries. The average grain size of xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ ceramics sintered at 560 °C with x from 0.47 to 0.57 is corresponding to 0.71, 0.79, 0.86, and 1.08 μm, respectively. Partial melting was observed for all the xBaTe$_4$O$_9$–(1 − x)TiTe$_3$O$_8$ mixtures when they were sintered at 600 °C.

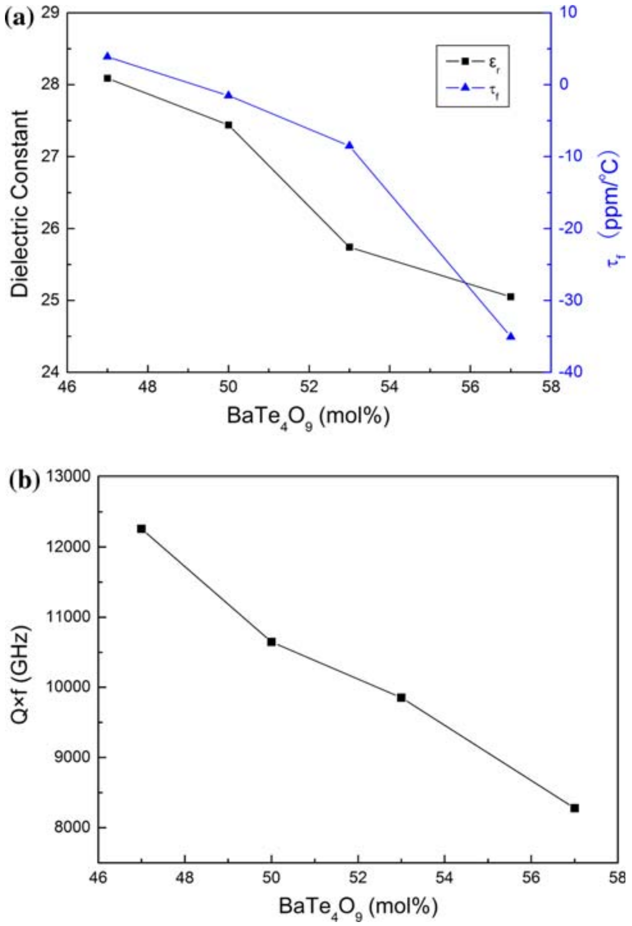

Fig. 6 Microwave dielectric properties of xBaTe$_4$O$_9$–(1 − x) TiTe$_3$O$_8$ ($x = 0.47$, 0.50, 0.53, and 0.57) ceramic specimens sintered at 560 °C (measured at 10 GHz)

Microwave dielectric characteristics of xBaTe$_4$O$_9$–(1 − x) TiTe$_3$O$_8$ compositions sintered at 560 °C are shown in Fig. 6. The relative dielectric permittivity and the temperature coefficient of resonant frequency (τ_f) decrease with the increment of BaTe$_4$O$_9$ because BaTe$_4$O$_9$ has a smaller dielectric permittivity and negative τ_f compared with TiTe$_3$O$_8$. The relative dielectric permittivity reduces from 28 to 25 and the τ_f reduces from 4 to −35 ppm/°C with the increment of BaTe$_4$O$_9$ from 47 to 57 mol%. The τ_f is almost fully suppressed in the 0.5BaTe$_4$O$_9$–0.5TiTe$_3$O$_8$ ceramic and expresses a negative value of −1.5 ppm/°C. The $Q \times f$-value decreases constantly with the content of BaTe$_4$O$_9$ in the system from 47 to 57 mol% because the increment of BaTe$_4$O$_9$ can diminish the uniformity of grain sizes and increase the amount of glass phases in the ceramic. Besides, the evaporation of TeO$_2$ and small contents of BaTeO$_3$ brought out by the decomposition of BaTe$_4$O$_9$ may reduce the $Q \times f$-value slightly. The ceramic sample with the composition of 0.47BaTe$_4$O$_9$–0.53TiTe$_3$O$_8$ exhibits a relative permittivity of 28, a $Q \times f$-value of 12,200 GHz, and a τ_f of 4.0 ppm/°C measured at 10 GHz.

Conclusions

A dielectric composition in the BaO–TiO$_2$–TeO$_2$ ternary system synthesized by the precursor method was investigated in order to evaluate the potential in LTCC application. Single phase of BaTe$_4$O$_9$ and TiTe$_3$O$_8$ was synthesized as the precursors at 550 and 640 °C, respectively. The dielectric compositions of xBaTe4O$_9$–(1 − x)TiTe$_3$O$_8$ ($x = 0.47$, 0.50, 0.53, 0.57) sintered at 560 °C contain the main phases of BaTe$_4$O$_9$ and TiTe$_3$O$_8$, and also a little bit of BaTeO$_3$ phase. Heat characteristic shows the melting points of BaTe$_4$O$_9$ and TiTe$_3$O$_8$ are 545 and 575 °C respectively. The ceramics become a little denser but the grains keep growing in uneven shapes and the glass phases increase with the increment of BaTe$_4$O$_9$. The microwave dielectric properties of sintered 0.47BaTe$_4$O$_9$–0.53TiTe$_3$O$_8$ ceramic are determined with a relative permittivity of 28 and a $Q \times f$-value of 12,200 GHz at 10 GHz. The τ_f is 4.0 ppm/°C. The low-dielectric loss, low-dielectric permittivity, and changeable near zero τ_f make the BaO–TiO$_2$–TeO$_2$ ternary system promising candidates for the application of LTCC. However, sintering mechanisms and compatibility of sintering with silver and aluminum electrode need to be studied to make it more actual for the LTCC application.

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