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# A novel low-fired, temperature-stable, and low-cost $(1-x)BaCu(B_2O_5)-xTiO_2$ microwave dielectric ceramic

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**Abstract:**

$BaCu(B_2O_5)$ is a typical microwave dielectric ceramic (MDC) with a low sintering temperature, but it exhibits a large negative temperature coefficient of resonant-frequency ($\tau_f$) which makes it difficult to use in wireless communications. We employ $TiO_2$ to improve its temperature-stability of resonant-frequency, and reveal the effects of $TiO_2$ on the densification and the microwave dielectric properties of $BaCu(B_2O_5)$. Here we show that $BaCu(B_2O_5)$ can be well-sintered at 825°C with proper $TiO_2$ additions; we find that the $TiO_2$ grains homogeneously distribute in the boundaries of $BaCu(B_2O_5)$ grains, resulting in the $\tau_f$ compensation of $BaCu(B_2O_5)$. Enhanced temperature-stability of resonant-frequency can be achieved by increasing the content of $TiO_2$ properly. A novel temperature-stable $(1-x)BaCu(B_2O_5)-xTiO_2$ ($x$=0.20) MDC ($\tau_f$ =-0.8±3.0 ppm/°C, $\varepsilon_r$= 8.8±0.36, Q×$f$ = 28612±1170 GHz) is obtained using some low-cost raw materials. Our results provide the underlying insights needed to guide the design of temperature-stable MDCs for wireless communication applications.

**Keywords**: microwave dielectric ceramics; $BaCu(B_2O_5)$; temperature-stable; cost-saving

## 1. Introduction

High performance microwave dielectric ceramics have attracted wide attentions with the rapid development of wireless communications [1-3]. The low temperature co-fired ceramic (LTCC) technology is widely used to fulfill the requirements of miniaturization, integration and multi-function. This technology requires the microwave dielectric ceramics to have low sintering temperatures, near-zero temperature coefficients of resonant frequency and high quality factors [4]. Low-cost and sustainable fabrications have also become the key focuses because of the recent energy and environmental concerns. Over the past decade, $BaCu(B_2O_5)$ has been commonly used as an effective sintering aids, due to its low melting temperature (~850°C) and the good wettability, to lower the sintering temperatures of dielectric ceramics [5-11]. Meanwhile, $BaCu(B_2O_5)$ can be easily fabricated using some simple raw materials: $Ba(OH)_2 \cdot 8H_2O$, CuO and $H_3BO_3$. Furthermore, $BaCu(B_2O_5)$ exhibits a low relative permittivity (7.4) and a high quality factor (50000GHz), which makes it capable to be a potential candidate for microwave applications [5]. However, $BaCu(B_2O_5)$ has a large negative $\tau_f$ value (−32ppm/°C), precluding its use for the practical purposes. Fortunately, one can compensate for the large $\tau_f$ (positive or negative) by adding the compound with a opposite $\tau_f$ value. It's known that $TiO_2$ exhibits a large positive $\tau_f$ value (+460 ppm/°C) [12] and has been successfully used to improve the temperature stabilities of resonant frequency of many microwave dielectric ceramics [13-18]. Nevertheless, there are no reports about adjusting the $\tau_f$ value of $BaCu(B_2O_5)$ with $TiO_2$ additions as far as the literature is concerned. Therefore, we attempt to present a novel temperature-stable and low-cost microwave dielectric ceramic based on the $(1-x)BaCu(B_2O_5)-xTiO_2$ system in this study. The phase composition, microstructure and microwave dielectric properties of $(1-x)BaCu(B_2O_5)-xTiO_2$ ($0.10 \leq x \leq 0.30$) ceramics were also investigated as a function of $TiO_2$ content.

**2. Experimental procedure**

All the raw materials, including $TiO_2$ (98%), $Ba(OH)_2 \cdot 8H_2O$ (99%), CuO (99%) and $H_3BO_3$ (99.5%), were obtained from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The $BaCu(B_2O_5)$ powder was synthesized through a conventional solid-state route. Reagent-grade $Ba(OH)_2 \cdot 8H_2O$, CuO, and $H_3BO_3$ were weighed in stoichiometry, then ball milled with some $ZrO_2$ balls in alcohol for 6h, and subsequently calcined at 800°C for 3h in air. The as-synthesized $BaCu(B_2O_5)$ was crushed, ground, and sieved by a 200 mesh. Then, the $BaCu(B_2O_5)$ powders were mixed with some reagent-grade $TiO_2$ through the ball-milling for 6h according to the formula as follows: $(1-x)BaCu(B_2O_5)-xTiO_2$ ($x$ is equal to 0.10, 0.15, 0.20, 0.25, and 0.30, respectively). The final mixed powders were pressed into the cylinders with 15 mm in diameter and 7 mm in thickness with 5wt% PVA functioning as the binder.

The samples were sintered at 800-850°C in air for 2h after being burnt off at 600°C for 1h to remove the binder.

The bulk densities of the sintered ceramic samples were measured through the Archimedean method and distilled water was used as the medium. The nominal theoretical densities ($\rho_T$) of the (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ multiphase ceramics were calculated using the following formula: $\rho_T = \frac{\sum m_i}{\sum V_i} = \frac{\sum m_i}{\sum m_i/\rho_i} = \frac{m_{BCB}+m_{TiO2}}{m_{BCB}/\rho_{BCB}+m_{TiO2}/\rho_{TiO2}}$, where $m_i$, $v_i$, and $\rho_i$ refer to the mass, volume, and theoretical density of the component *i*, respectively. The phase compositions of the samples were identified according to the X-ray powder diffraction patterns (XRD, Bruke D8 ADVANCE, Germany, Cu $K\alpha_1$, 40 kV and 40 mA). The sintered samples were crushed into powders prior to the examination. The microstructures of the sintered samples were characterized by a scanning electron microscopy (SEM, Jeol, JSM5610LV, Japan). Before visualization, the surfaces of the samples were coated with a thin layer of gold. The quality-factor (Q×*f*) values and the relative dielectric constants ($\varepsilon_r$) at microwave frequency were determined by a network analyzer (Agilent N5230C, USA) at room temperature according to the post-resonant method [19]. The temperature coefficients of resonant frequency ($\tau_f$) were also measured with the same method at the temperatures ranging from 25°C to 85°C, and calculated by the equation ($\tau_f = \frac{f_{85}-f_{25}}{f_{25}\times(85-25)} = \frac{f_{85}-f_{25}}{f_{25}\times 60} \times 10^6 (ppm/°C)$), where $f_{85}$ and $f_{25}$ represent the resonant frequencies at 85°C and 25°C, respectively. The Raman signals were collected at room temperature and detected by a DILOR XY-800 triple-grating Raman spectrometer equipped with a liquid-nitrogen-cooled CCD. The 10 mW output of the 514.5nm line of $Ar^+$ ion laser was used as the excitation source. The obtained Raman spectra exhibited a resolution approximately of 0.5 $cm^{-1}$.

## 3. Results and discussion

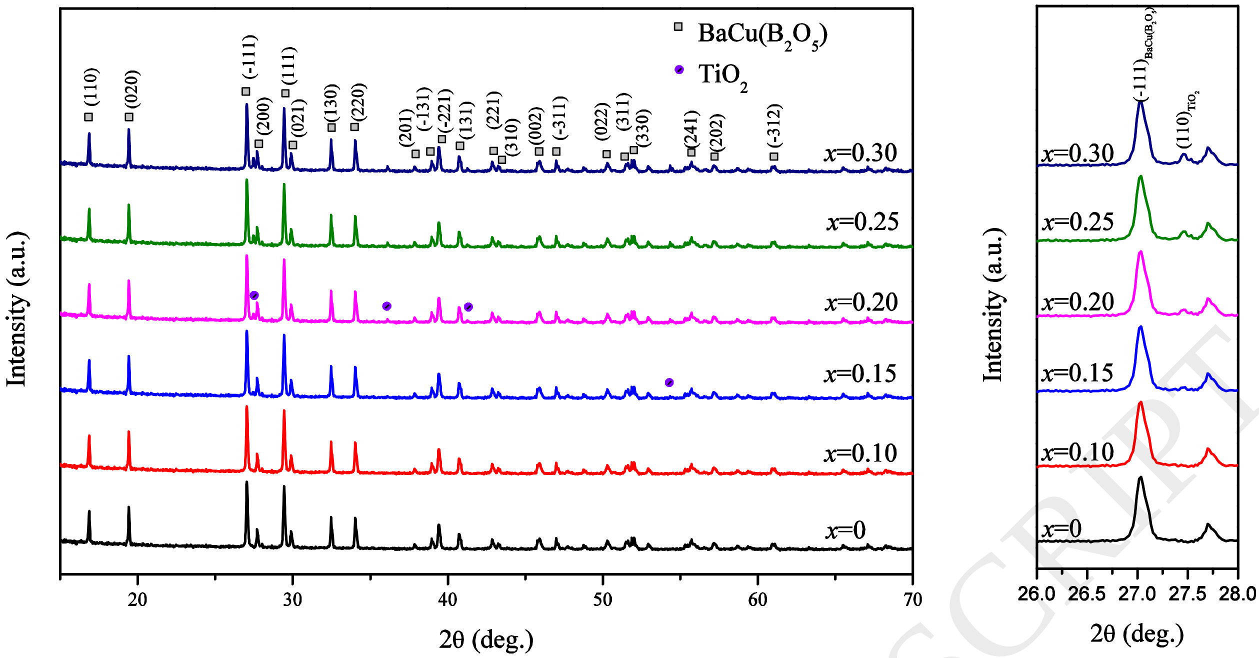


Figure 1 Typical XRD patterns of (1−*x*)BaCu($B_2O_5$)−*x*$TiO_2$ ceramics sintered at 825°C for 2h.

Figure 1 illustrates the XRD patterns of (1−*x*)BaCu($B_2O_5$)−*x*$TiO_2$ ceramics sintered at 825°C for 2h. It is detected no phase except BaCu($B_2O_5$) (JCPDS #88-0386) for *x*=0, indicating that all the raw materials react completely to form BaCu($B_2O_5$) phase. BaCu($B_2O_5$) performs a monoclinic structure and belongs to the space group C2(5) and Z=2 [20]. The lattice parameters are a=6.485Å, b=9.165Å, and c=3.971Å. The $TiO_2$ phase (JCPDS # 21-1276) coexisting with BaCu($B_2O_5$) is detected from *x*=0.15 to 0.30, suggesting that they behave as a mixture. However, no $TiO_2$ phase is detected when *x* is equal to 0.10 probably due to the XRD detection limit. The relative volume fraction of $TiO_2$ phase can be defined as the ratio of the most-intense XRD peak height of $TiO_2$ to the sum of the most-intense peak heights of $TiO_2$ and BaCu($B_2O_5$). The as-calculated proportions of $TiO_2$ phase are 0.042±6, 0.071±3, 0.092±8, and 0.108±8 for *x*=0.15, 0.20, 0.25, and 0.30, respectively. This result is essentially in agreement with the volume fractions estimated by the equation[21] ($v_i = \frac{x_i M_i/\rho_i}{\sum x_i M_i/\rho_i}$ $(i = TiO_2,\ BCB)$, where $x_i$, $\rho_i$ and $M_i$ refer to the mole fraction, density and relative molecular mass of component *i*, respectively).

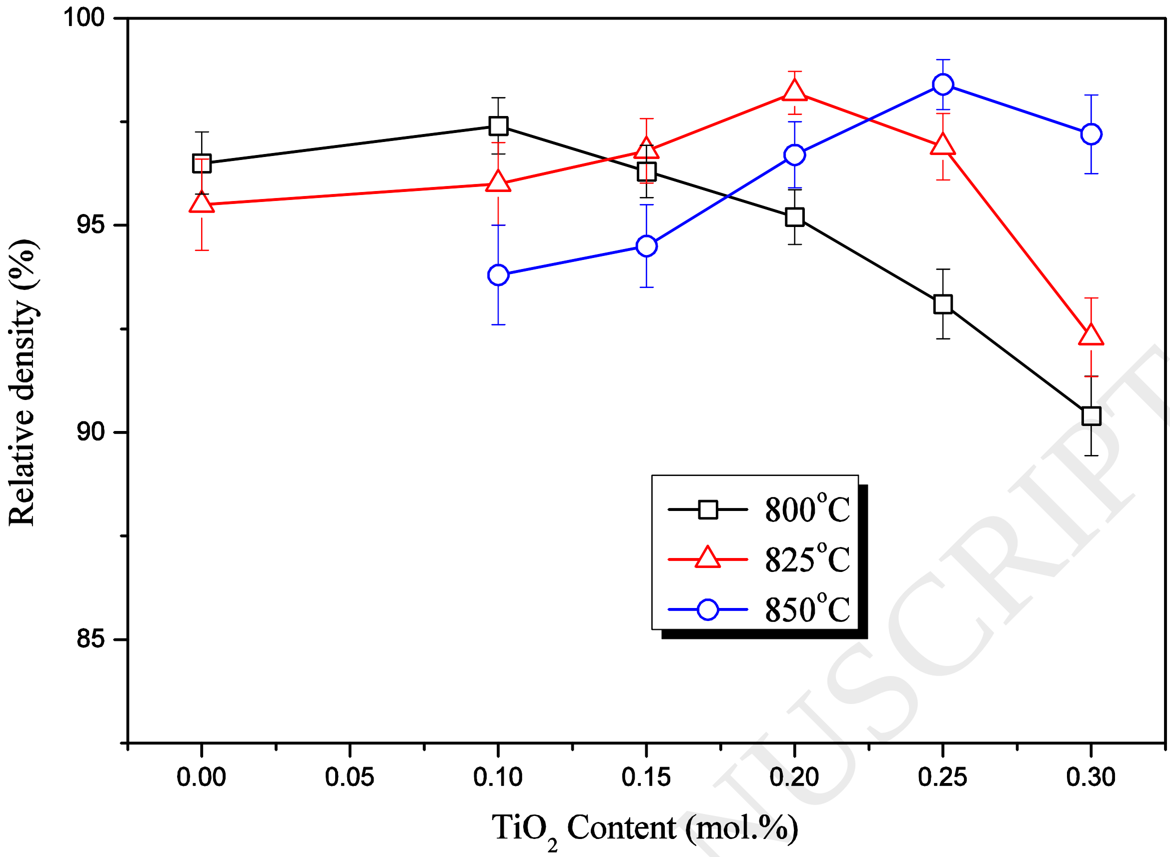


Figure 2 Relative densities of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 800-850°C for 2h.

Figure 2 exhibits the relative densities of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 800-850°C. The variations of the relative densities are similar for all the samples sintered at different temperatures. It means, the relative density increases with the increment of $TiO_2$ content, reaches the saturations and then decreases. This result indicates that a proper amount of $TiO_2$ improves the densification of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramics and (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ (*x* is equal to 0~0.25) can be well sintered at 825°C for 2h.

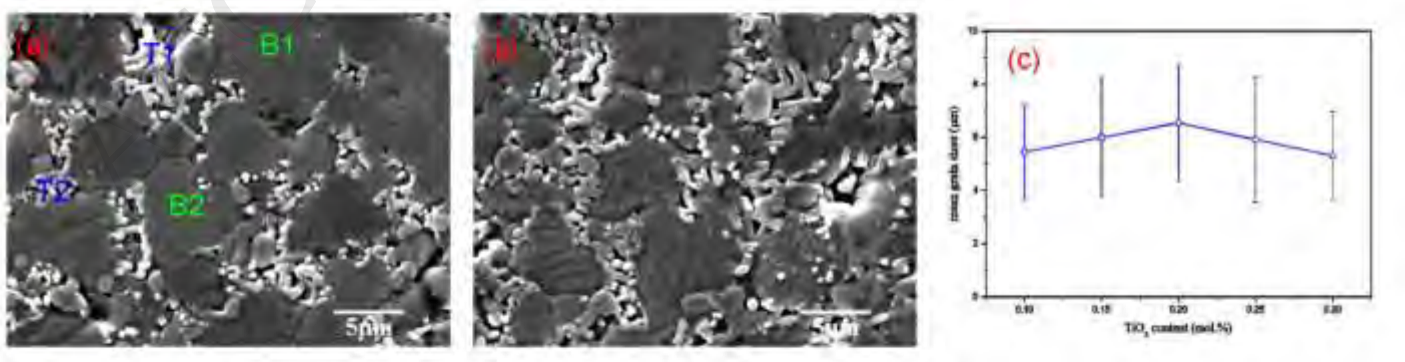


Figure 3 Typical SEM images of the polished and thermal etched surface morphology of the (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 825°C for 2h. (a) *x*=0.20, (b) *x*=0.30, and (c) mean grain sizes of $BaCu(B_2O_5)$ phase.

The polished and thermal etched surface morphology of the (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ceramic samples sintered at 825°C for 2h was characterized. All the (1-$x$)$BaCu(B_2O_5)$-$x$$TiO_2$ ($x$=0.10-0.25) ceramic samples show dense microstructures with the mean grain size (MGZ) of $BaCu(B_2O_5)$ phase about 5.9±2.0 μm, much larger than the MGZ (4μm) of pure $BaCu(B_2O_5)$ sintered at 810°C [5]. This results indicates that (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ($x$=0.10-0.25) can be well sintered at 825°C. The typical SEM images ($x$ is equal to 0. 20, 0.30) are depicted in Figure 3. Two kinds of randomly-distributed grain shapes are observed in all the as-sintered ceramic samples, as shown in Figure 3(a) as spot B1, B2, T1, and T2, respectively. The darker polygonal grains (B1, B2), with Ba and Cu ions detected at a ratio of approximately 1:1 and no Ti ions, are identified as the $BaCu(B_2O_5)$ phase by the EDS analysis and the XRD results (Figure 1), while the rod-shape grains (T1, T2) are identified as the $TiO_2$ phase. Unfortunately, some big pores occur in the 0.70$BaCu(B_2O_5)$−0.30$TiO_2$ sample (Figure3(b)), indicating that too much $TiO_2$ is disadvantageous to the densification of (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ceramics at 825°C. The MGZs of $BaCu(B_2O_5)$ phase in the as-sintered (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ceramic samples were also measured by the tool of Image Pro 6 software (Figure 3(c)). The MGZs of $BaCu(B_2O_5)$ phase in the sintered samples firstly increase when the $TiO_2$ content increases from 0.10 to 0.15, and saturate (6.5±2.2μm) at $x$ is equal to 0.20. This result means that a proper amount of $TiO_2$ is beneficial to the grain growth of $BaCu(B_2O_5)$ phase.

Figure 4 depicts the $\tau_f$ values of the (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ceramic samples sintered at 825°C for 2h. The $\tau_f$ value measured shifts from −32±3.8ppm/°C to 29.4±3.0ppm/°C as the $TiO_2$ content ($x$) increases from 0 to 0.30. For a multiphase ceramic composite with random distributions of the components, the $\tau_f$ can be formulated by the common equation ($\tau_f = \sum v_i \tau_{fi} = (1-v)\tau_{fBCB} + v\tau_{fTiO2}$), where $\tau_{fi}$ and $v_i$ refer to the $\tau_f$ value and the volume fraction of component $i$. The red dash line in Figure 4 presents the curve of $\tau_f$ values simulated by the equation mentioned above. The $\tau_f$ values measured are similar to the general calculated ones, suggesting that $TiO_2$ distributes randomly in the (1−$x$)$BaCu(B_2O_5)$−$x$$TiO_2$ ceramics as shown in Figure 3. Furthermore, a near-zero $\tau_f$ (-0.8±3.0ppm/°C) is obtained in the 0.80$BaCu(B_2O_5)$−0.20$TiO_2$ ($x$ is equal to 0.20) ceramics sintered at 825°C for 2h.

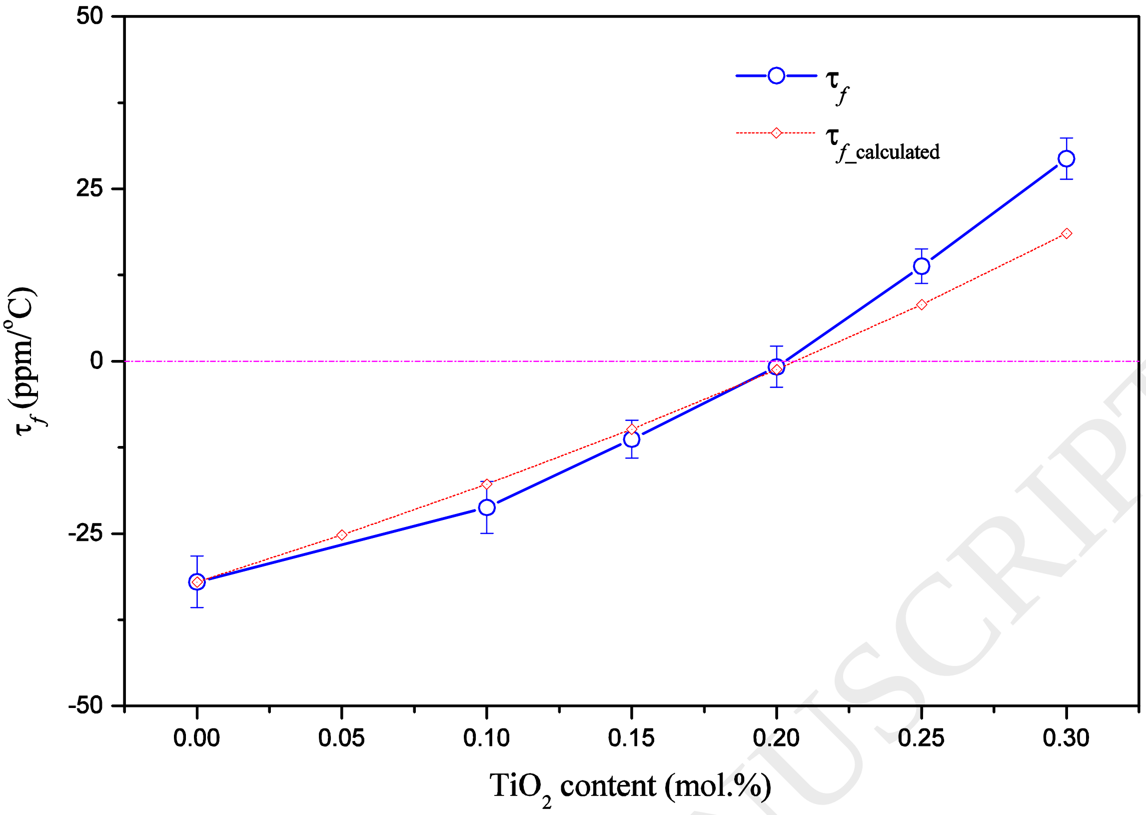


Figure 4 Temperature coefficients of resonant frequency ($\tau_f$) of the (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 825°C for 2h.

Figure 5 illustrates the relative permittivities ($\varepsilon_r$) and Q×*f* of the (1−*x*) $BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 825°C for 2h as a function of $TiO_2$ content (*x*). The $\varepsilon_r$ gradually increases from 7.4±0.30 to 12.6±0.32 when *x* increases from 0 to 0.30. For a multiphase ceramic, the $\varepsilon_r$ value depends on the phase composition, relative density and permittivity of the component. The increment of $\varepsilon_r$ value in this research might attribute to the high permittivity of $TiO_2$ (104) [22]. The magenta dash line in Figure 5 presents the curve simulated by the logarithmic rule model equation for diphase composite ceramics with randomly distributed components. The experimental $\varepsilon_r$ data are close to the relative permittivities simulated when *x* is equal to 0.10, 0.15 and 0.20, respectively. Meanwhile, a deviation from the simulated curve occurs when *x* is higher than 0.20.

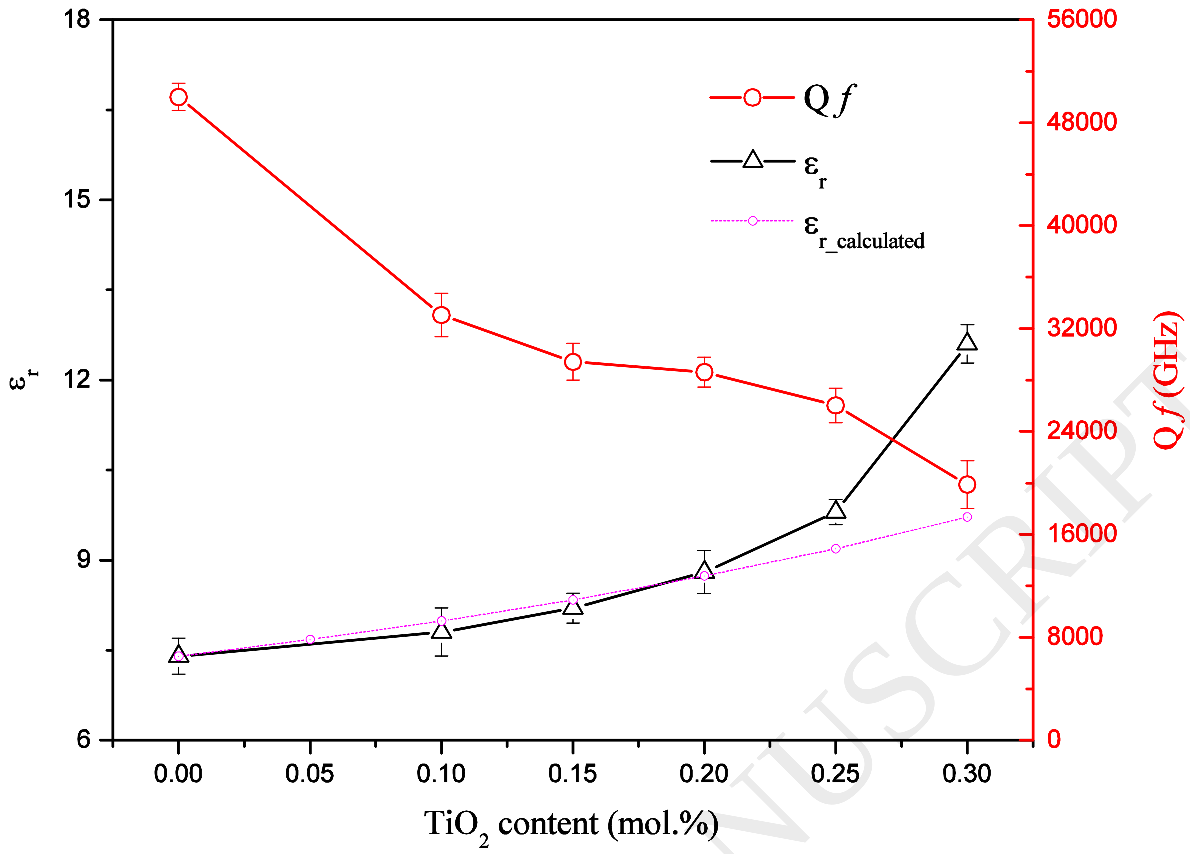


Figure 5 Relative permittivities ($\varepsilon_r$) and Q×*f* of $(1-x)BaCu(B_2O_5)-xTiO_2$ ceramic samples sintered at 825°C for 2h.

It was reported that $TiO_2$ and $BaCu(B_2O_5)$ exhibited high Q×*f* values: 44000GHz [22] and 50000GHz [5], respectively. The Q×*f* value decreases monotonously when the $TiO_2$ content (*x*) increases from 0 to 0.30. The maximum Q×*f* is 50000±1050GHz (*x*=0) and minimum 19875±1860GHz (*x*=0.30). Although no $TiO_2$ phase is detected (Figure 1) in the sintered $(1-x)BaCu(B_2O_5)-xTiO_2$ ceramic samples when *x* is equal to 0.1, a dramatic decrease of the Q×*f* value from 50000±1050 GHz to 33056±1680 GHz occurs, as clearly shown in Figure 5. The Q×*f* value decreases monotonously with the further increment of $TiO_2$ content, and a further rapid decrease of Q×*f* value occurs when *x* is equal to 0.30. Generally, the Q×*f* value is determined by both intrinsic factors, like phase compositions and absorptions of phonon oscillation, and extrinsic factors like porosity, impurity, defect, grain boundary, etc [19]. $BaCu(B_2O_5)$ phase in the as-sintered $(1-x)BaCu(B_2O_5)-xTiO_2$ ceramic samples coexists with the randomly distributed $TiO_2$ phase (Figure 3). The ratio of $TiO_2$ to $BaCu(B_2O_5)$ and the corresponding phase boundaries increase when $TiO_2$ content (*x*) increases. This inevitably leads to the changes of Q×*f* value. In addition, the porosity also plays an important role. The Raman spectra of the corresponding ceramic samples are also carried out to verify that the intrinsic properties such as vibration modes are unchanged or not. It was reported that the Raman peak positions is a function of the particular symmetry mode [23, 24]. The Raman peak shifts provide a context for vibration modes. [25]. The Raman spectra of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples contain both the bands at 143 ($E_g$), 196.5 ($E_g$), 394 ($B_{1g}$), 512 ($A_{1g}$), and 635.5 $cm^{-1}$ ($E_g$) from the $TiO_2$ phase[26] and the bands at 107.5 ($A_g$), 176.5 ($B_g$), 263($A_g$), 329($A_g$), 483, 637.5 ($B_g$) and 671.5 ($A_g$) $cm^{-1}$ from the $BaCu(B_2O_5)$ phase[27-28]. Furthermore, with the increment of the $TiO_2$ phase content, the intensities of the bands identified from $TiO_2$ phase increase, but no obvious shifts of the Raman peak position occurs. This result indicates that the vibration modes of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples are unchanged. According to the XRD results (Figure 1) and Raman data (Figure 6), we suggest that the intrinsic factors of all the (1−*x*)$BaCu(B_2O_5)$-*x*$TiO_2$ ceramic samples are similar, and that the variation of Q×*f* values mainly attributes to the extrinsic factors such as boundaries and porosity. In summary, a temperature-stable $BaCu(B_2O_5)$−$TiO_2$ microwave dielectric ceramic with excellent dielectric properties ($\tau_f$ = -0.8±3.0 ppm/°C, $\varepsilon_r$=8.8±0.36, Q×*f* =28612±1170 GHz) can be obtained when *x* is equal to 0.20.

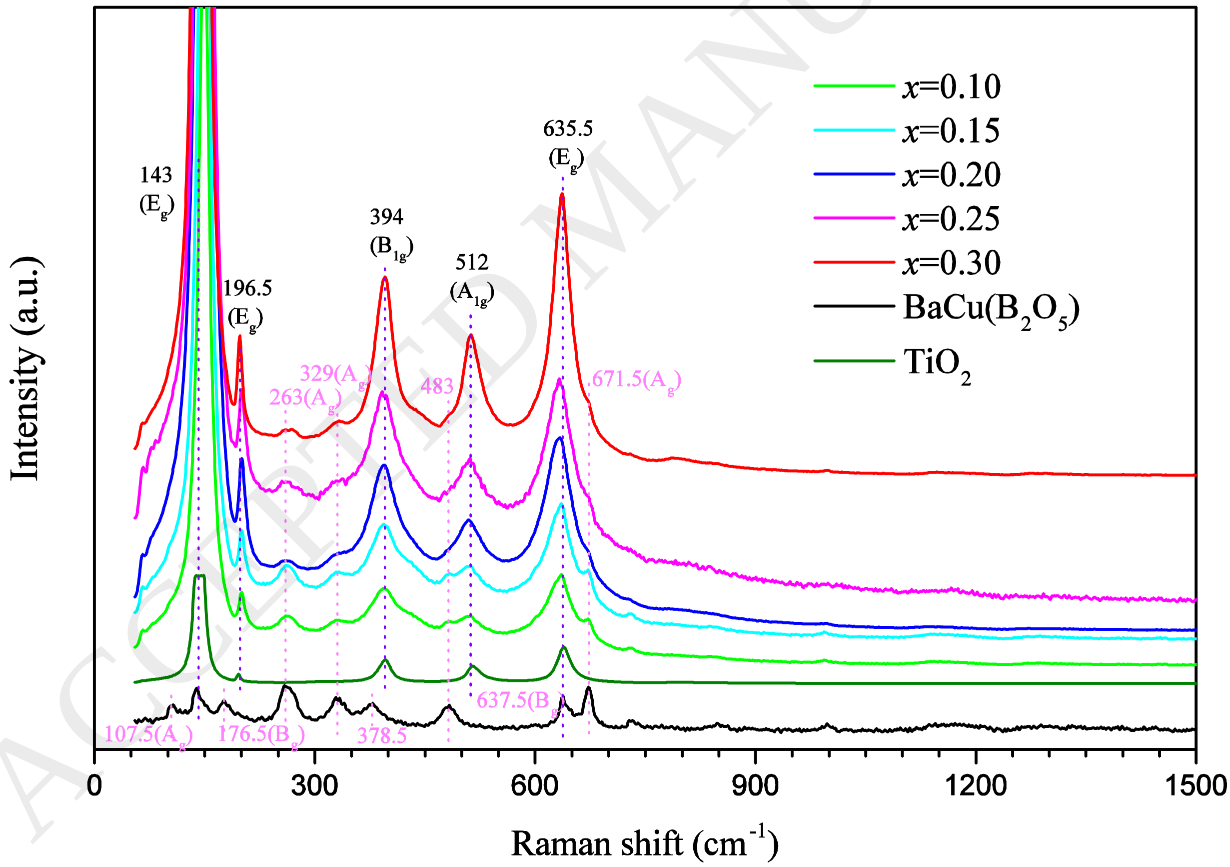


Figure 6 The Raman spectra of (1−*x*)$BaCu(B_2O_5)$−*x*$TiO_2$ ceramic samples sintered at 825°C for 2h.

Low-cost and sustainable fabrications have been becoming the key focuses due to recent energy and environmental concerns. The raw materials used in this research such as $TiO_2$, $Ba(OH)_2 \cdot 8H_2O$ and $H_3BO_3$ were simple and cost-saving. Figure 7 illustrates the comparison of dielectric properties and cost of some typical microwave dielectric ceramics (MDCs) sintered at 825°C. Only the MDCs sintered at 825 °C were chose to eliminate the cost differences caused by processes such as sintering. The prices of materials were also obtained only from the Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) to eliminate price differences of the same materials from different reagent companies. It can be clearly seen that the $0.80BaCu(B_2O_5)$-$0.20TiO_2$ ceramic exhibits the lowest price. Considering that a near zero $\tau_f$ was required, the $0.80BaCu(B_2O_5)$-$xTiO_2$ ceramic is expected to be a promising and competitive candidate for LTCC applications.

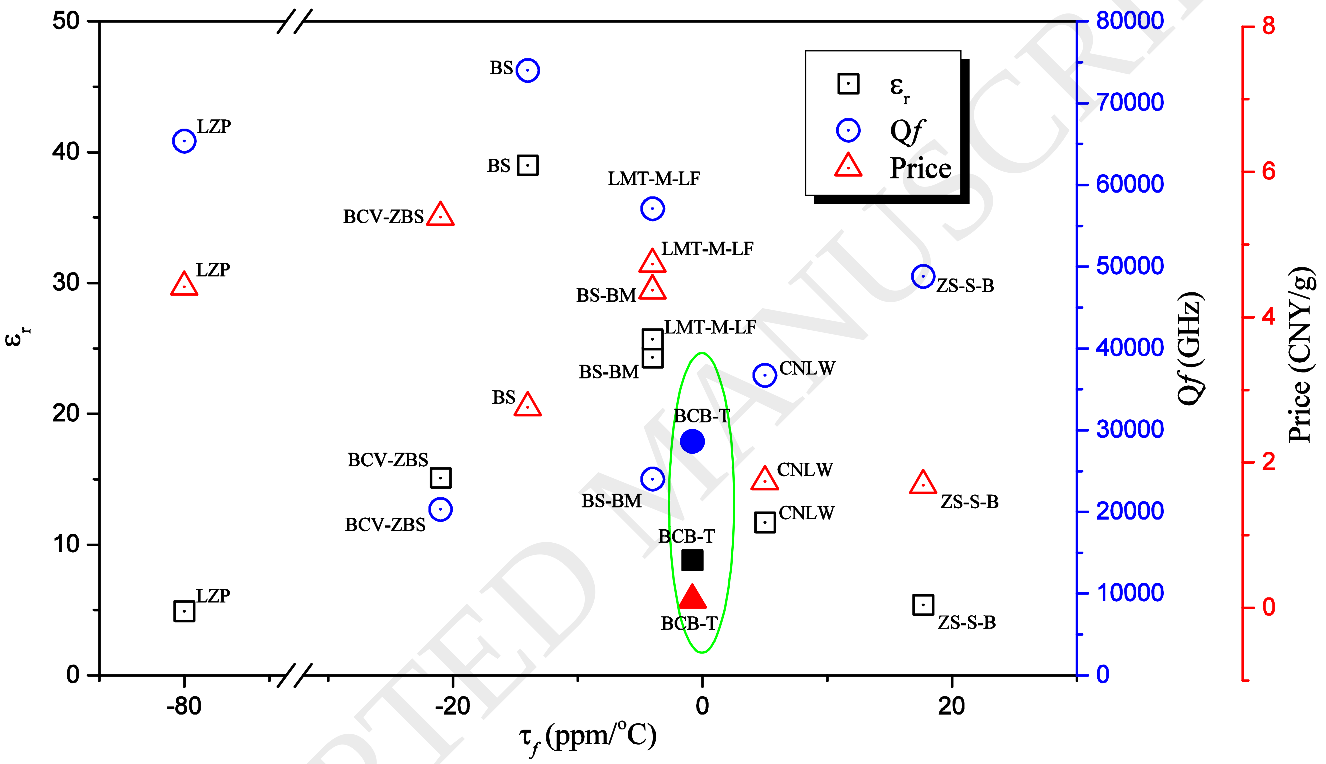


Figure 7 The Comparison of dielectric properties and cost of several typical microwave dielectric ceramics sintered at 825°C. LZP (after Ref. [29]); BCV-ZBS (after Ref. [30]); BS (after Ref. [31]); BS-BM (after Ref. [32]); LMT-M-LF (after Ref. [33]); CNLW (after Ref. [34]); ZS-S-B (after Ref. [35]); BCB-T (represents the as-fabricated $0.80BaCu(B_2O_5)$−$0.20TiO_2$, marked by a green ellipse).

**4. Conclusions**

A novel temperature-stable $(1-x)Ba(B_2O_5)-xTiO_2$ ceramics was fabricated by a solid state reaction method using some low-cost raw materials: $TiO_2$, $Ba(OH)_2{\cdot}8H_2O$, CuO and $H_3BO_3$. The monoclinic $BaCu(B_2O_5)$ phase coexists with $TiO_2$ phase. As the $TiO_2$ content ($x$) increases, the $\varepsilon_r$ value rises up from 7.4±0.30 to 12.6±0.32 and the $\tau_f$ monotonously shifts from negative (-32±3.8

ppm/°C) to positive (29.4 ± 3.0 ppm/°C). Meanwhile, the Q×*f* decreases from 50000 ± 1050 GHz to 19875 ± 1860 GHz. A temperature-stable ($\tau_f$=-0.8 ± 3.0 ppm/°C) 0.80BaCu($B_2O_5$)−0.20$TiO_2$ ceramic with $\varepsilon_r$=8.8 ± 0.36 and Q×*f* =28612 ± 1170 GHz, was obtained at 825°C. Furthermore, the 0.80BaCu($B_2O_5$)−0.20$TiO_2$ ceramic could be a promising and competitive candidate for LTCC applications.

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