# Novel low loss, low permittivity $(1-x)SiO_2-xTiO_2 + y$wt% $H_3BO_3$ microwave dielectric ceramics for LTCC applications

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# [1]Novel Low Loss, Low Permittivity (1-x) $SiO_2$-x$TiO_2$+ywt%$H_3BO_3$ Microwave Dielectric Ceramics for LTCC Applications

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## Abstract

Novel microwave dielectric material of (1-x) $SiO_2$-x$TiO_2$ for low-temperature cofired ceramic (LTCC) application was investigated in this paper. $TiO_2$ coated $SiO_2$ powder prepared by a sol-gel method under solvothermal conditions (SGS) revealed an adsorption of fine $TiO_2$ particles on the $SiO_2$ surface. $TiO_2$ coated $SiO_2$ improved the microwave properties of $SiO_2$ ceramics. As the $TiO_2$ content x increased in the $(1-x)SiO_2–xTiO_2$ （$0.1 \leqq x \leqq 0.3$） system, dielectric constant ($\varepsilon_r$) and temperature coefficient of resonance frequency ($\tau_f$) of the material were increased due to the mixing effect of $TiO_2$ phase. The $0.85SiO_2–0.15TiO_2$ and $0.9SiO_2–0.1TiO_2$ceramics sintered at 1200 ℃ showed $\varepsilon_r = 5.4$ and 4.6, quality factor ($Q \cdot f$) = 40500 and 36300 GHz, and $\tau_f$ =2.5 and -0.5 ppm/℃. The sintering temperature of $0.9SiO_2–0.1TiO_2$ ceramic is lowered from 1200℃/3h to 950℃/6h by the addition of $H_3BO_3$. $0.9SiO_2–0.1TiO_2$ ceramics with 10 wt% $H_3BO_3$ sintered at 950℃/6h possesses excellent microwave dielectric properties of $\varepsilon_r$~4.67, $Q \cdot f$ ~78000 GHz and $\tau_f$ ~-0.7

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ppm/℃. From the X-ray diffraction and EDS analysis of cofired ceramics, the $H_3BO_3$ added $0.9SiO_2$–$0.1TiO_2$ ceramic does not react with Ag at 950 ℃. The attractive advantages such as low dielectric constant, low sintering temperature, high-performing microwave dielectric properties, chemical compatibility with Ag metal electrodes, no toxicity, and abundant raw materials source and low cost constituents make the $SiO_2$ ceramic as potential candidates for substrate and LTCC devices.

## 1. Introduction

The search for microwave dielectric materials with a high quality factor ($Q{\cdot}f$), a low dielectric constant ($\varepsilon_r$), and a near-zero temperature coefficient of resonant frequency ($\tau_f$) is essential in microwave dielectric material research. $SiO_2$ ceramics has been considered to be an important material for missile radome, high-frequency microwave devices, and microwave substrates applications because of its excellent chemical, mechanical, and microwave dielectric properties [1-3]. In our previous work, the $SiO_2$ ceramic sintered at 1550 ℃ possessed good microwave dielectric properties of $\varepsilon_r$~3.52, $Q{\cdot}f$ ~92400 GHz and $\tau_f$ ~-14.5 ppm/℃ [4]. However, its sintering temperature is too high for being applied as low temperature co-fired ceramic materials. Moreover, the non near zero negative temperature coefficient of resonance frequency $\tau_f$ value of $SiO_2$ ceramics prohibits its use in practical applications. Addition of other phase with opposite $\tau_f$ value and low sintering temperature to form composite ceramics is an effective way to compensate the $\tau_f$ value and reduce the sintering temperature simultaneously. Thus, we can expect that a dielectric composite material with a near zero $\tau_f$ value and low temperature could be obtained by combining $SiO_2$ with $TiO_2$ ( $\tau_f$ =450 ppm/℃). A uniform distribution of additives in the $SiO_2$ matrix is very essential. Ceramic powders are normally prepared by physical mixture which is inherently non-uniform because each component of the mixtures has difference in particle size distribution, particle morphology and surface properties. Thus, numerous chemical coating techniques have been employed to obtain a uniform distribution of additives [5-10].

There is a great deal of interest to create $SiO_2$-$TiO_2$ core-shell composite microspheres, which may exhibit novel properties not found in the single oxide one [11-13]. $SiO_2$-$TiO_2$ composite microspheres have been prepared by many methods including impregnation, grafting, precipitation, reverse suspension, sol–gel, Electrostatic attraction technology and so on [14–21]. However, the composite microspheres prepared by the above methods showed low surface areas and inhomogeneous and poor microwave dielectric properties of ceramics using these powders. In contrast, the solvothermal process is one of the commonly used methods for preparing nanoscaled powders because of its low synthesis temperature, low equipment cost, simple synthesis procedures, and uniform components. Hence, a process for fabricating the core-shell $TiO_2$-wrapped-$SiO_2$ ($SiO_2$-$TiO_2$) powders was developed in this work. Nanoscaled $SiO_2$ powders were used as the core materials and the core-shell structure was formed by a chemical solution method, by adding tetrbutyl titanate solution into the $SiO_2$ dispersed base solution by an ultrasonic process under the solvothermal conditions. The (1-x)$SiO_2$-x$TiO_2$ ($0.1 \leqq x \leqq 0.3$)

composite ceramics were prepared using the core-shell structured powders and their microstructure，sintering behavior, and microwave dielectric properties have been investigated in detail. The experimental data were compared with those predicted by the dielectric rules of mixture.

## 2. Experimental

All chemicals were analytical-grade reagents and used as received without further purification. All experiments were conducted in air. To prepare the $SiO_2$-$TiO_2$ core-shell particles, 2.0 g $SiO_2$ [4] as core particles were dispersed in a mixture solution of 25 ml ethanol and 0.5 ml tetrbutyl titanate (TBOT) by ultrasonicator in reactor. A mixture solution of 25 ml ethanol, 10 ml deionized water and 0.25 ml nitric acid was stirred for 12 h and sealed in autoclaves for 24 h at 180 ℃ to complete the sol-gel process. The product was filtered out and washed with deionized water for six times and calcined at 550℃ for 1 h with a heating rate of 5 ℃/min. The prepared microspheres with polyvinyl alcohol water solution were pressed into cylindrical compacts with the diameter of 13.5 mm under a uniaxial pressure of 125 MPa. The compacts were placed in an alumina crucible and heated to the sintering temperatures varying from room temperature to 1350 ℃ with a rate of 1.5 ℃/min. After sintered for 3 h in air atmosphere, the compacts were cooled to 1000 ℃ with a rate of 2 ℃/min, and then freely cooled down to room temperature inside the furnace. The $HBO_3$ doped (1-x) $SiO_{2\text{-}x}TiO_2$+ywt%$H_3BO_3$ ceramics were sintered at 900-1150 ℃ for 3 -6h.

The XRD patterns obtained on D/max-2550V/PC X-ray diffractomater (Rigaku, Japan) using Cu k$\alpha$ radiation at a scan rate $2\theta = 0.02\ s^{-1}$ were used to determine the identity of crystalline phases. The morphology of the prepared core-shell structured $SiO_2$-$TiO_2$ powder was characterized by high-resolution transmission electron microscopy (JEM-2100, Japan). The X-ray Photoelectron Spectroscopy (XPS) measurements were performed on an AXIS ULTRA spectrometer (Kratos Analytical Ltd, Japan) with a monochromatic Al. The Raman spectra were obtained on ALMEGA Dispersive Raman spectrometer (ALMEGA-TM, Thermo Nicolet, USA).

The bulk densities of the sintered pellets were measured by the Archimedes method using distilled water as medium. The phase evolution of the $SiO_2$ ceramics was performed by XRD. The microstructures were observed on the as-sintered ceramic surfaces of samples by a scanning electron microscopy (SEM, FEI-quanta 200, USA). Cylindrical samples with the diameter of about 10 mm and thickness of about 5 mm were used for evaluating the microwave dielectric properties. Dielectric behaviors at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method with a vector network analyzer (ZVB20, Rohde & Schwarz, Germany). The temperature coefficient of resonant frequency ($\tau_f$) was calculated with the following equation

$$\tau_f = \frac{f_{80} - f_{25}}{f_{25} \times (80 - 25)}, \qquad (1)$$

Where $f_{80}$ and $f_{25}$ were the $TE_{01\delta}$ resonant frequency measured at 80 ℃ and 25 ℃, respectively.

## 3. Results and discussion

Fig.1 shows the characterization of the pure $SiO_2$ and $SiO_2$ @ $TiO_2$ core shell structural microspheres, respectively. As monodispersed amorphous $SiO_2$

nanospheres (Fig. 1(a)) were coated with a layer $TiO_2$, some sharp anatase diffraction peaks could be observed from Fig. 1(b). The TEM images (Fig. 1(c), (d)) and the Electron diffraction patterns (Fig. 1(e), (f)) are more intuitive to show that the $SiO_2$ @ $TiO_2$ core shell structural microspheres were obtained in this work. The $TiO_2$ shell has a smaller particle size about 10 nm, a narrower particle size distribution and a more uniform morphology compared to the present literatures [22-24]. XPS measurements results (Fig. 1(g)) further confirmed the existence of $TiO_2$ coating on the surface of $SiO_2$ nanospheres. It can be seen from Fig. 1(g) that the sample contains Ti, Si, O and C elements. The photoelectron peak for Ti $_{2p}$ appears clearly at a binding energy $E_b$=458eV, Si $_{2p}$ is at $E_b$ = 104 eV, O $_{1s}$ at $E_b$ = 531 eV and $C_{1s}$ at $E_b$ = 284 eV. The carbon peak is attributed to the residual carbon from precursor solution and adventitious hydrocarbon (i.e. from the XPS instrument itself). The Ti peak comes from the $TiO_2$ coating. Results indicated that core-shell structural $SiO_2$-$TiO_2$ composite nanospheres were successfully synthesized by SGS with more homogeneous coating and well dispersion in this work.

Fig. 2 shows that the XRD patterns and the Raman spectra of the (1-x) $SiO_2$-x$TiO_2$ （$0.1 \leqslant x \leqslant 0.3$) ceramics sintered at 1200 ℃ for 3 h. All the main peaks in Fig.2 (A) could be indexed in terms of cristobalite low ($SiO_2$, PDF#76-0940) ,quartz ($SiO_2$, PDF#03-0419) and rutile, syn($TiO_2$, PDF#89-4202), and no trace of the impurity phase existed. This suggests that no chemical reaction between $SiO_2$ and $TiO_2$ has occurred. It should be emphasized that the relative content of quartz in the sample is so small that can be negligible in some discussions. The crystal structure of

Cristobalite low is tetragonal P41212 (92), and Rutile, syn is tetragonal P42/mnm(136). The difference in crystal structure and good stability of both phases limited the reaction between $SiO_2$ and $TiO_2$. As shown in Figure 2(B) the Raman spectra exhibit phonon modes at 148, 240, 450 and 612 $cm^{-1}$ for samples. The bands at 148, 450, 612 $cm^{-1}$ can be assigned as $B_{1g}$, $E_g$ and $A_{1g}$ modes, respectively. A broad band observed at about 240 $cm^{-1}$ was considered as a fundamental mode. All of these lines in our spectra are in good agreement with the spectra of $TiO_2$ rutile phase. In addition, as seen from the inset in Fig 2(B). the bands at 230 and 420 $cm^{-1}$ can be assigned as A1 and B1 modes, respectively, which are in good agreement with the spectra of $SiO_2$.

Fig. 3 shows the variation of bulk density ( $\rho$ ), dielectric constant ($\varepsilon_r$) , $\tau_f$ and $Q{\cdot}f$ value of (1-x)$SiO_2$-x$TiO_2$ ($0.1 \leqq x \leqq 0.3$) ceramics with x sintered at various temperature. As $TiO_2$ content x increased, the $\rho$ values increased, which, for the fixed composition, depended on sintering temperatures. And the optimized bulk density about 2.35g/$cm^3$ (relative density of 92.7%) was obtained at 1200℃ for x=0.15.

It’s clearly found in Fig. 3 (A) that the $\varepsilon_r$ values increased with an increase of $TiO_2$ which has much higher dielectric constant ($\varepsilon_r$~104) compared with that of $SiO_2$ ($\varepsilon_r$~3.82). The variation of $\varepsilon_r$ in this case is obviously governed by the mechanical mixture law and closely follows the changes observed in their Raman patterns.

The $\tau_f$ values changed (Fig. 3(B)) from negative to positive with an increase of $TiO_2$ phase content x and near zero $\tau_f$ values of -1.9~2.5 ppm/℃ could be obtained at x=0.15.

Comparing measured values with calculated values of density, dielectric constant, $Q\cdot f$ and $\tau_f$ defined as ideals without second phases, the effect of the second phases on the microwave dielectric properties of (1-x) $SiO_2$ -x$TiO_2$ system can be understood.

The density ($\rho_{mixture}$) of two-phase mixture can be computed using the following formula（Eq.(2)）[25-26]

$$\rho_{mixture} = V_1\rho_1 + V_2\rho_2 \, , \qquad (2)$$

Where $V_i$ and $\rho_i$ （i=1, 2）are the volume fraction and density of the two components, respectively. The $\varepsilon_r$ of the mixture is obtained as follows (Eq.(3))[25-26]

$$\ln\varepsilon_{r,mixture} = V_1 \ln\varepsilon_{r1} + V_2 \ln\varepsilon_{r2} \, , \qquad (3)$$

Where $\varepsilon_{ri}$（i=1, 2） is the dielectric constant of the two components.

The variations of density and $\varepsilon_r$ with x for (1-x) $SiO_2$ -x$TiO_2$ ceramics sintered at 1200 ℃ are shown in inset of Fig. 3(A) (full symbols), which were corrected, marked as half symbols, based on the flowing equation (Eq.(4) ) [27]

$$\varepsilon_r = \varepsilon^{obs}(1+p) \, , \; p = 1 - \frac{\rho}{\rho_{th}} \, , \qquad (4)$$

where p is porosity. The open symbol values were calculated based on the mixture rule. The overall trend for experimental values of density showed good agreement with calculated ones by the mixture rule, except for the former having lower values. In Fig.3(A), the densities increased with increasing x content, which could be ascribed to the fact that the density of $TiO_2$ (4.253 g/cm3) is greater than that of $SiO_2$ (2.317g/cm3). And the experimental $\varepsilon_r$ values generally agrees with those of the calculated results, despite the existing little difference between them due to the random distribution of $SiO_2$ and $TiO_2$ phases in composite ceramics.

The variation of $Q{\cdot}f$ and $\tau_f$ values of (1-x) $SiO_2$ -x$TiO_2$ composite ceramics sintered at 1200 ℃ with x content is plotted in inset of Fig. 3(B). The $Q{\cdot}f$ value of $SiO_2$ and $TiO_2$ is 94,000 and 19,500 GHz, respectively, whereas their $\tau_f$ value is -14.5 and 450 ppm/℃, respectively. With x increasing from 0.1 to 0.3, the $Q{\cdot}f$ value decreases from 40,500 to 27,500GHz, and $\tau_f$ value increases from -0.5 to 64 ppm/℃. A near-zero $\tau_f$ value occurs at x=0.15 in 0.85$SiO_2$-0.15$TiO_2$ ceramic, which can reach a $Q{\cdot}f$ value of 40,500GHz. In addition, the $\tau_f$ and $Q{\cdot}f$ values of a mixture were calculated by following formulas (Eq.(5), Eq.(6))[26]

$$\tau_{f\cdot mixture} = V_1\tau_{f1} + V_2\tau_{f2}\,, \tag{5}$$

$$Q^{-1}_{mixture} = V_1Q^{-1} + V_2Q^{-1}\,, \tag{6}$$

Where $\tau_f$ and $Q$ are the temperature coefficient of resonant frequency and quality factor of the two components, respectively. The $Q$ values in the equation can be replaced by the $Q{\cdot}f$ values. It is obvious that the variation of $\tau_f$ values of mixed phases varied around the straight line corresponding to the rule of mixtures. The calculated and observed $\tau_f$ and $Q$ values showed good agreement. At the same time, one can see the apparently random variation in $Q{\cdot}f$ and $\tau_f$ with x content in the samples. This maybe mentioned here that the above equation for porosity correction is not applied to the value of quality factor and $\tau_f$. It must be noted that $Q{\cdot}f$ values, which depends greatly on the preparation conditions, porosity, grain morphology etc. , does not show any specific relationship with the rule of mixtures. The product $Q{\cdot}f$ is maximum (40,500GHz) around x=0.15 in (1-x) $SiO_2$ -x$TiO_2$ composite ceramics where the $\tau_f$ takes a near-zero value ($\tau_f$=2.5ppm/℃). It is worthwhile to note that the intermediate phases show better quality factors compared to the end phase components, which is very rare in dielectric mixtures. From Figure 3(B), it is clear that the drop in quality factor is more for the $TiO_2$ rich compositions. It is well known that the phase transition from anatase to rutile around 760 ℃ was a major source of concern in its dielectric loss quality, since it involves collapse of the relatively open anatase structure. This collapse takes place by a distortion of the oxygen framework and shifting of the majority of $Ti^{4+}$ ions, by rupturing two out of the six Ti-O bonds to form new bonds. Many studies have pointed out that doping with aliovalent additives or sintering in reduced atmosphere can accelerate oxygen vacancy formation and expedite the anatase to rutile transformation [27].

As shown in Fig 3(B), the $Q{\cdot}f$ values increased with an increase of the sintering temperature up to 1200 ℃ and then slightly decreased with the further increase of sintering temperature. The optimized $Q{\cdot}f$ value 40500 GHz was obtained at 1200 ℃ and further increase in sintering temperature remarkably decreased the $Q{\cdot}f$ values. It is well know that $\varepsilon_r$ is dependent on the density, polarizabilities, phase composition, and structural characteristics, while the $Q{\cdot}f$ values is affected by not only these factors but also the crystal vibration mode, secondary phase, densification and crystal defect [25-27]. In this work, the observed change trend in $\varepsilon_r$ and $Q{\cdot}f$ values of 0.85$SiO_2$-0.15$TiO_2$ is attributed primarily to variations in bulk density (see Fig. 3 (A)). The $\tau_f$ value of $SiO_2$ ceramics is strongly depended on the phase composition and phase content. As the sintering temperature increases, the quartz phase(PDF#03-0419) of $SiO_2$ is gradually transformed into cristobalite low phase(PDF#76-0940)[4]. In this work, the slight decrease of $\tau_f$ values of $0.9SiO_2$-$0.1TiO_2$ ceramics with increased sintering temperature can be ascribed to the reduction of quartz phase which has a higher $\tau_f$ value of 28.7 ppm/℃ than cristobalite phase(-14.7 ppm/℃).

In order to decrease the sintering temperature of $SiO_2$-$TiO_2$ composite ceramics for LTCC applications, $H_3BO_3$ was added into $0.9SiO_2$-$0.1TiO_2$ matrix. Fig. 4 shows the effects of the $H_3BO_3$ content and the sintering temperature on the microwave dielectric properties of $0.9SiO_2$-$0.1TiO_2$ ceramics. As the y composition changes from 0 to 12.5, there was no remarkable change in the dielectric constant ($\varepsilon_r$) of the specimens. An obviously improved $Q{\cdot}f$ value on $H_3BO_3$ addition was also observed. In addition, the $\tau_f$ values could be modified with the additive of $H_3BO_3$. At y=10, the specimen shows the optimum dielectric properties: $\varepsilon_r$=4.67, $Q{\cdot}f$ =78000 GHz, and $\tau_f$=-0.7 ppm/℃. Based on above results, it was believed that 10 wt% $H_3BO_3$ was effective in reducing the sintering temperature of $0.9SiO_2$-$0.1TiO_2$ ceramics from 1200 to 950 ℃ without degradation of dielectric properties. This good result is related to the enhancement of the densification of $0.9SiO_2$-$0.1TiO_2$+ywt %$H_3BO_3$ ceramics at the low temperatures obtained by a liquid sintering process.

The XRD pattern and SEM image of the 10 wt% $H_3BO_3$-doped $0.9SiO_2$-$0.1TiO_2$ cofired with Ag at 950 ℃/6h are shown in Fig.5 indicated that the silver does not react with the glass–ceramic composite and is distributed randomly. It is unexpectedly observed that the gold ring （marked as B ）appeared at the boundary between Ag (marked as C) and the ceramic substrate (marked as A).

For an ideal microwave substrate material the $\tau_f$ should be close to zero. Alumina, Forsterite and $Zn_2SiO_4$ are three good candidates for substrate applications but high negative $\tau_f$ and high processing temperature put constraints on their use in temperature stable microwave devices such as oscillators [28-29]. A recently developed ceramics $Li_2MoO_4$, $Li_2WO_4$ and $CaWO_4$+1wt$MnSO_4$, in spite of their low processing temperature, their $\tau_f$ is too far away from zero [29-31]. Very recently, X.C. Wang reported the (1-x)(0.75$ZnAl_2O_4$)-0.25$TiO_2$)-x$SrAl_2SiO_8$(x=0.3) ceramics possess a good microwave dielectric properties of $\varepsilon_r$ =5.4, $Q{\cdot}f$=40500 GHz and a $\tau_f$ of 2.5 ppm/℃, but its sintering temperature is too high (1550 ℃). K.T. Wu et al reported that The $ZrTi_2O_6$ filled PTFE composite exhibits a dielectric constant of 7.42 with a loss tangent of 0.0022 (10 GHz) at an optimum filler loading of 46 vol% [33]. Nijesh K. et al reported the PTFE/$BaWO_4$ and $ZrTi_2O_6$/PTFE can be prepared at ultra low temperatures, which having a dielectric constant of 4.3 and 6.7, together with a loss tangent of 0.004 and 0.003, respectively[34-35]. A comparison between the literature work and the current work was made, as shown in Table 1. By comparison with those data, the new 0.9$SiO_2$-0.1$TiO_2$-10wt%$H_3BO_3$ ceramic is advantageous over these materials in respect to low dielectric constant, low dielectric loss and temperature compensation which is a necessary requirement for microwave dielectric substrate and LTCC applications [36，37].

## 4. Conclusions

Using nanoscaled $SiO_2$ powders as the starting material, core-shell structured microsphere was formed by wrapping $SiO_2$ with $TiO_2$ derived from a sol–gel process under solvothermal conditions with process temperature at 180 ℃. Microstructure, sintering behavior and microwave dielectric properties of the $SiO_2$-$TiO_2$ composite ceramics were investigated. The (1-x)$SiO_2$-x$TiO_2$ (0.1≤x≤0.3) composite ceramics were well sintered at temperatures from 1150 to 1350 ℃. The dielectric constant was increased with the molar ratio of $TiO_2$ in (1-x) $SiO_2$-x$TiO_2$ composite ceramics. The analysis of the crystal structure based on XRD and Raman spectra suggested that no additional phase was formed in the entire range of composition formation. The 0.85$SiO_2$-0.15$TiO_2$ ceramics have low dielectric constant, high quality factor and near zero $\tau_f$ value. This thermally stable dielectric property is an important requirement for fabricating temperature stable oscillators and filters in microwave circuits. The microwave dielectric properties were further improved obviously when the 0.9$SiO_2$-0.1$TiO_2$ ceramics were sintered at low temperatures with small addition of $H_3BO_3$. Furthermore, from the X-ray diffraction and EDS analysis of cofired ceramics, the $H_3BO_3$-added 0.9$SiO_2$–0.1$TiO_2$ ceramic does not react with Ag at 950 ℃. The 0.9$SiO_2$-0.1$TiO_2$-10wt%$H_3BO_3$ dielectrics with $\varepsilon_r$ =4.7, excellent quality factor and temperature stability is proposed as a suitable microwave substrate and LTCC material.

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## Figure and tables caption

**Fig. 1** Characterization of the pure $SiO_2$ and $SiO_2$ @ $TiO_2$ core shell structural microspheres: XRD patterns of $SiO_2$ (a) and $SiO_2$ @ $TiO_2$ core shell structural microspheres (b), TEM images of $SiO_2$ (c) and $SiO_2$ @ $TiO_2$ core shell structural microspheres (d) ,electric diffraction pattern of $SiO_2$ (e) and $SiO_2$ @ $TiO_2$ core shell structural microspheres (f) , and XPS pattern of $SiO_2$ @ $TiO_2$ core shell structural microspheres (g).

**Fig. 2** (A) XRD patterns and (B) Raman spectra of the (1-x) $SiO_2$-x$TiO_2$ （0. 1≤x≤0. 3) sintered at 1200 ℃ for 3 h. The inset picture in Fig. 2 (A) is the XRD patterns of the 0.85$SiO_2$- 0.15$TiO_2$ ceramics sintered at different temperatures for 3 h. The inset picture in Fig.2(B) is the magnified view of the peak.

**Fig. 3** The variation of (A) bulk Density and dielectric constant $\varepsilon_r$, (B) $Q\cdot f$ and $\tau_f$ value of the (1-x) $SiO_2$-x$TiO_2$（0. 1≤x≤0. 3) sintered at different temperatures for 3 h. Inset shows The variations of experimental (full symbols), corrected experimental (half symbols) and calculated (open symbols) in the Fig 3(A) and the $Q\cdot f$ and $\tau_f$ *value* in Fig 3(B) of (1-x)$SiO_2$- x$TiO_2$ ceramics sintered at 1200 ℃ as a function of x.

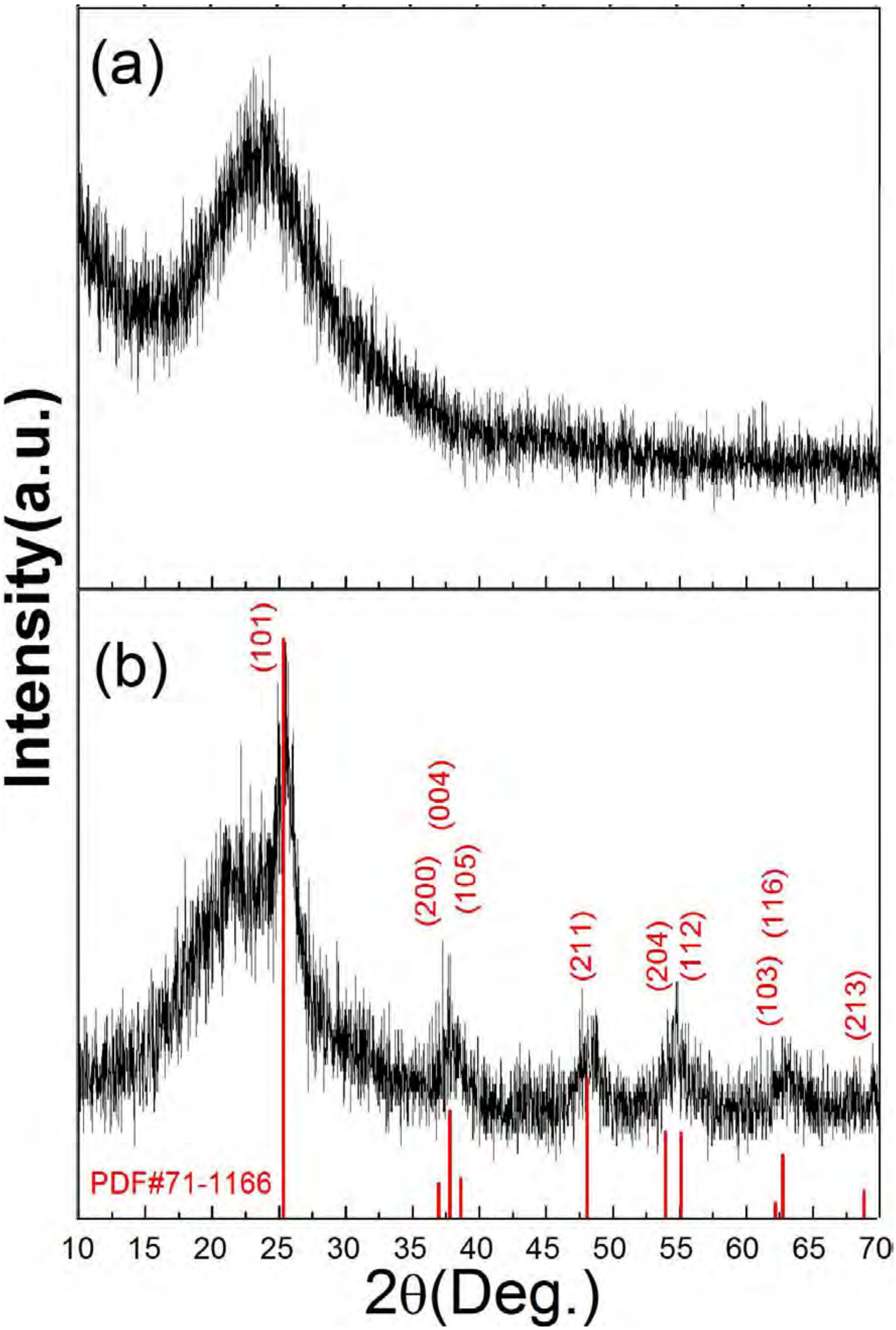
**Fig. 4** The dielectric constant $\varepsilon_{r,}$ quality factor $Q\cdot f$ and temperature coefficient of resonant frequency $\tau_f$ of 0.9$SiO_2$-0.1$TiO_2$ + y$H_3BO_3$ ceramics added with y=0, 5 wt%, 7.5 wt%, 10 wt% and 12.5wt% $H_3BO_3$ as a function of sintering temperature.

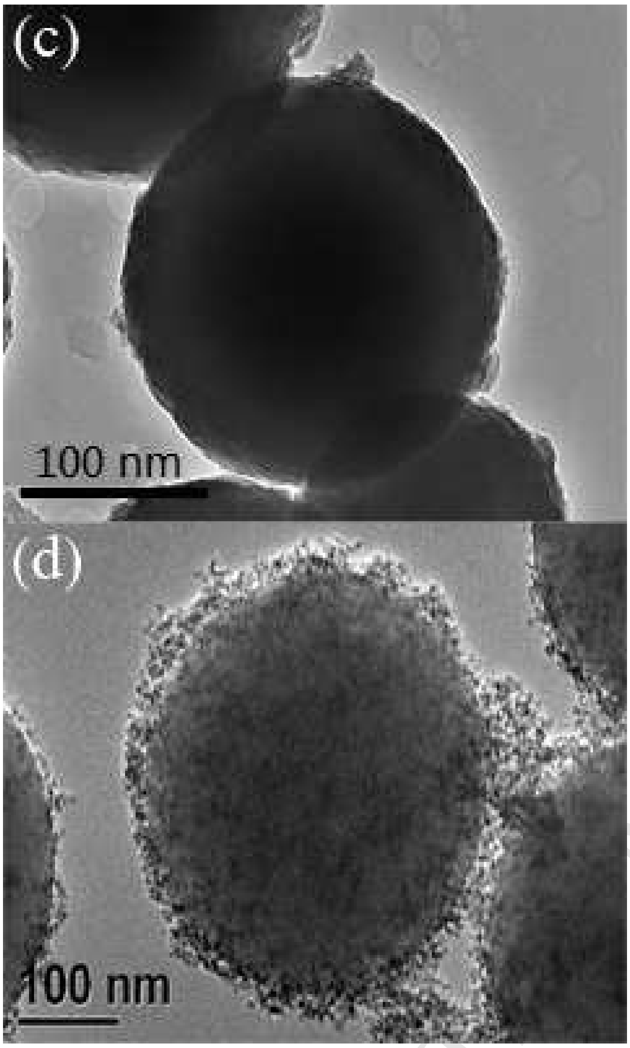
**Fig. 5** XRD pattern, SEM image (inset) of sintered 10wt% $H_3BO_3$ added-0.9$SiO_2$-0.1$TiO_2$+20wt% Ag

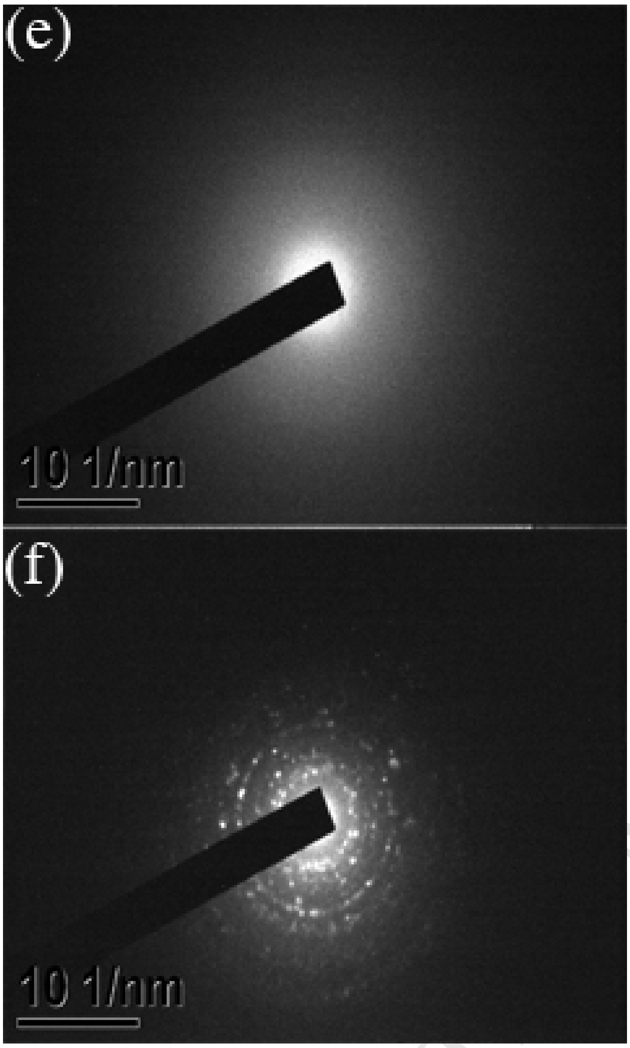
**Table 1** Comparison of Microwave Dielectric Properties of Some Compounds with Microwave Relative Permittivity below 10

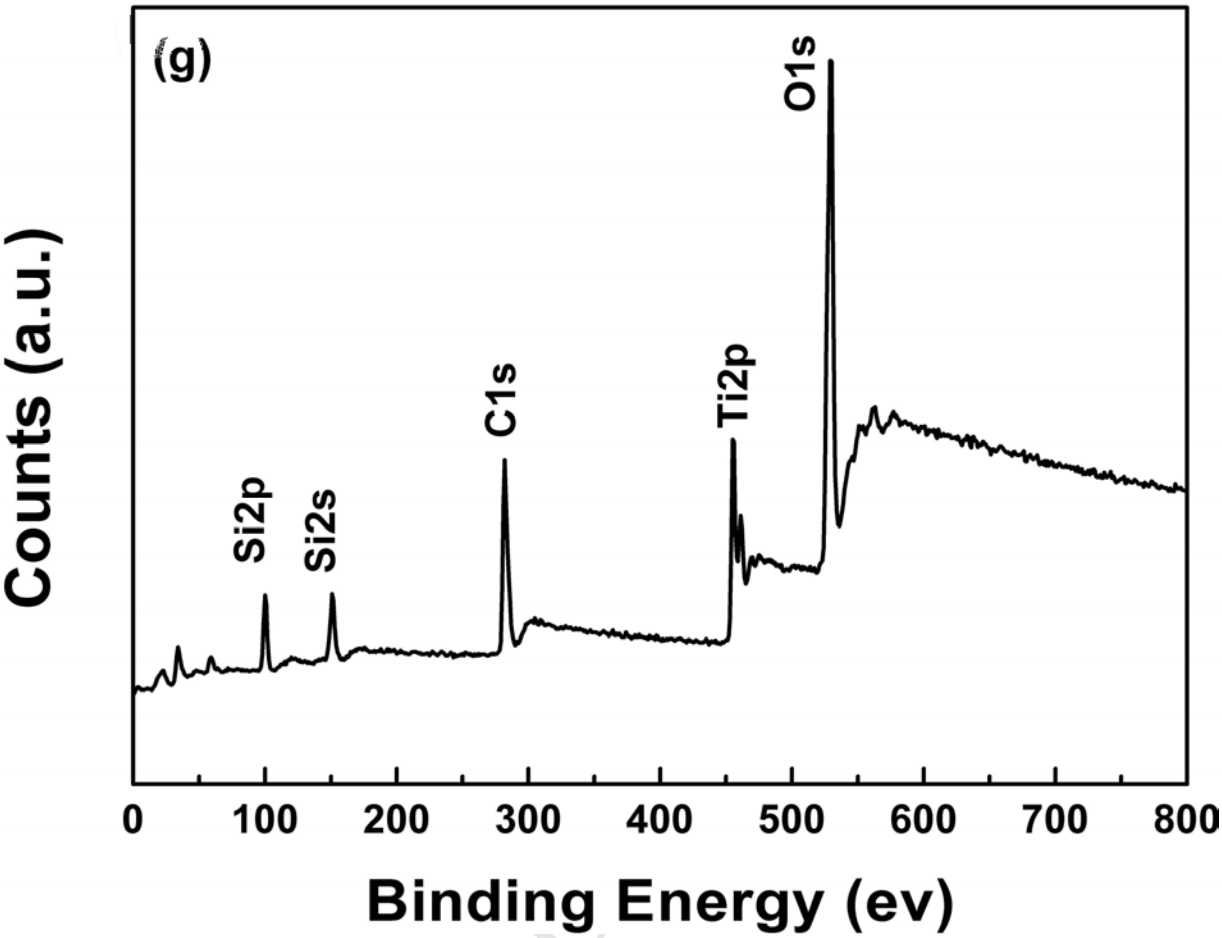
| *No.* | *Composition* | *$S_T$ ($^0C$)* | *Density ($g/cm^3$)* | *$\varepsilon_r$* | *$Q\cdot f$ ($10^3$GHz)* | *$\tau_f$ (ppm/°C)* |
|---|---|---|---|---|---|---|
| 1 | $0.9SiO_2$-$0.1TiO_2$-5wt%$H_3BO_3$ | 1150 | 1.87 | 4.12 | 90.4 | -3.7 |
| 2 | $0.9SiO_2$-$0.1TiO_2$-5wt%$H_3BO_3$ | 1050 | 1.92 | 4.07 | 85.5 | -4.9 |
| 3 | $0.9SiO_2$-$0.1TiO_2$-7.5wt%$H_3BO_3$ | 1050 | 1.95 | 4.03 | 76.9 | -1.5 |
| 4 | $0.9SiO_2$-$0.1TiO_2$-10wt%$H_3BO_3$ | 950 | 1.98 | 4.67 | 78.0 | 0.7 |
| 5★ | $(1-x)\ SiO_2$-$xTiO_2$, $x$=0.10 | 1200 | 2.19 | 4.6 | 36.3 | -0.5 |
| 6★ | $(1-x)\ SiO_2$-$xTiO_2$, $x$=0.15 | 1200 | 2.35 | 5.4 | 40.5 | 2.5 |
| 7★ | $Zn_2SiO_4$ | 1340 | - | 6.6 | 219 | -61 |
| 8★ | $Mg_2SiO_4$ | 1450 | - | 6.8 | 270 | -67 |
| 9★ | $Li_2MoO_4$ | 540 | 2.895 | 5.5 | 46 | -160 |
| 10★ | $Li_2WO_4$ | 650 | - | 5.5 | 62 | -146 |
| 11★ | $CaWO_4$+1wtMnSO$_4$ | 1050 | - | 6.6 | 129.5 | -56 |
| 12★ | $(1-x)(0.75ZnAl_2O_4)$-$0.25TiO_2)$-$xSrAl_2SiO_8$,$x$ =0.3 | 1550 | - | 7.32 | 27.13 | 2.98 |

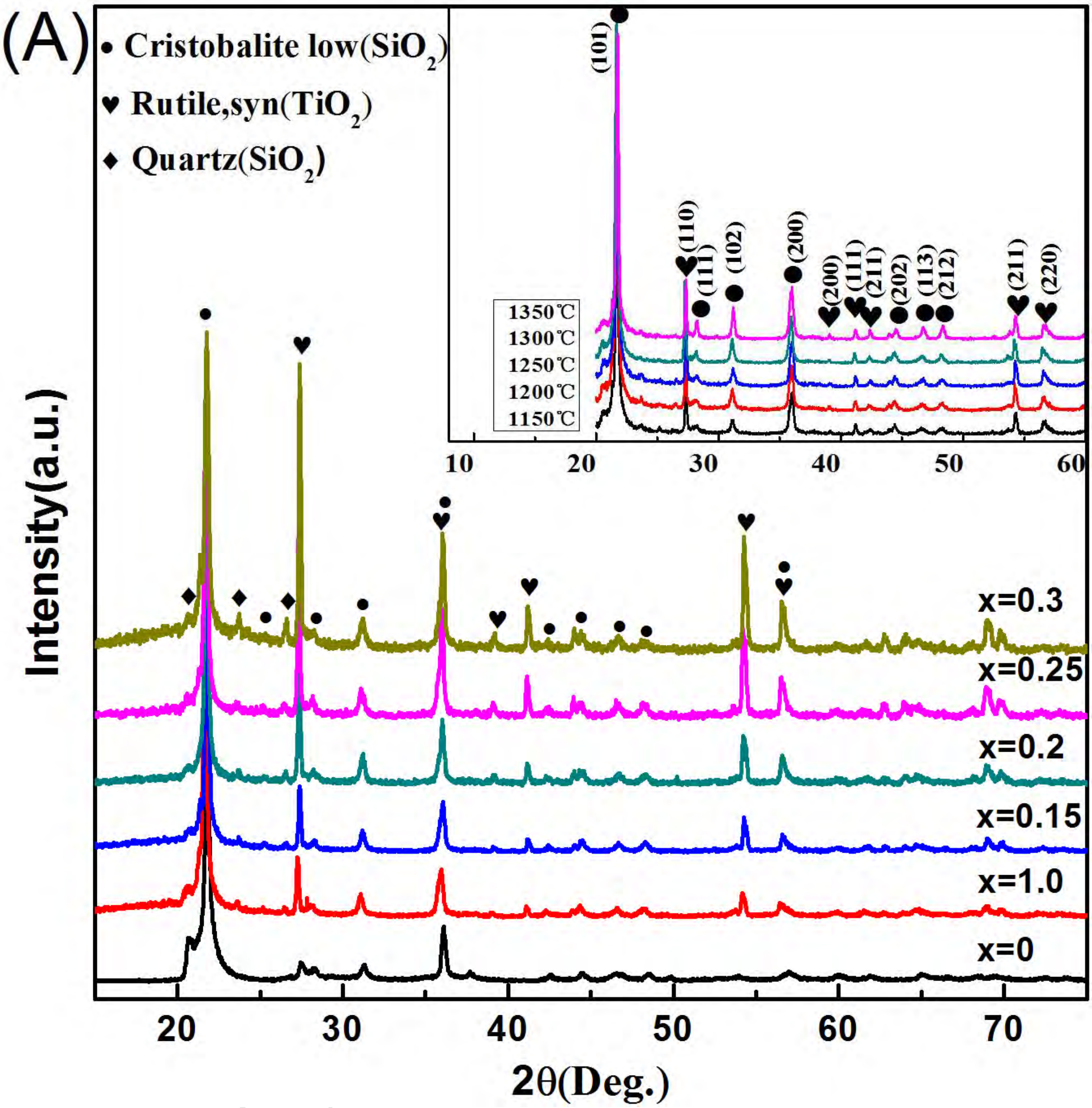
★*Data from reference* [28-35 *;$S_T$, Sintering temperature*

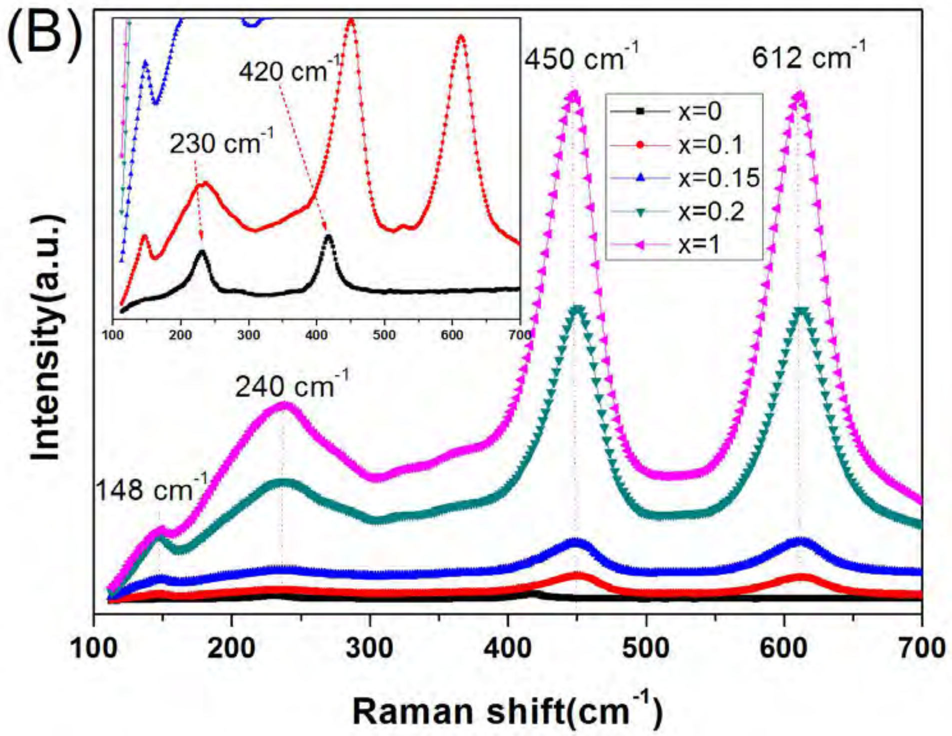

(a)
(b)
Intensity(a.u.)
(101)
(200)
(004)
(105)
(211)
(204)
(112)
(103)
(116)
(213)
PDF#71-1166
10
15
20
25
30
35
40
45
50
55
60
65
70
2θ(Deg.)

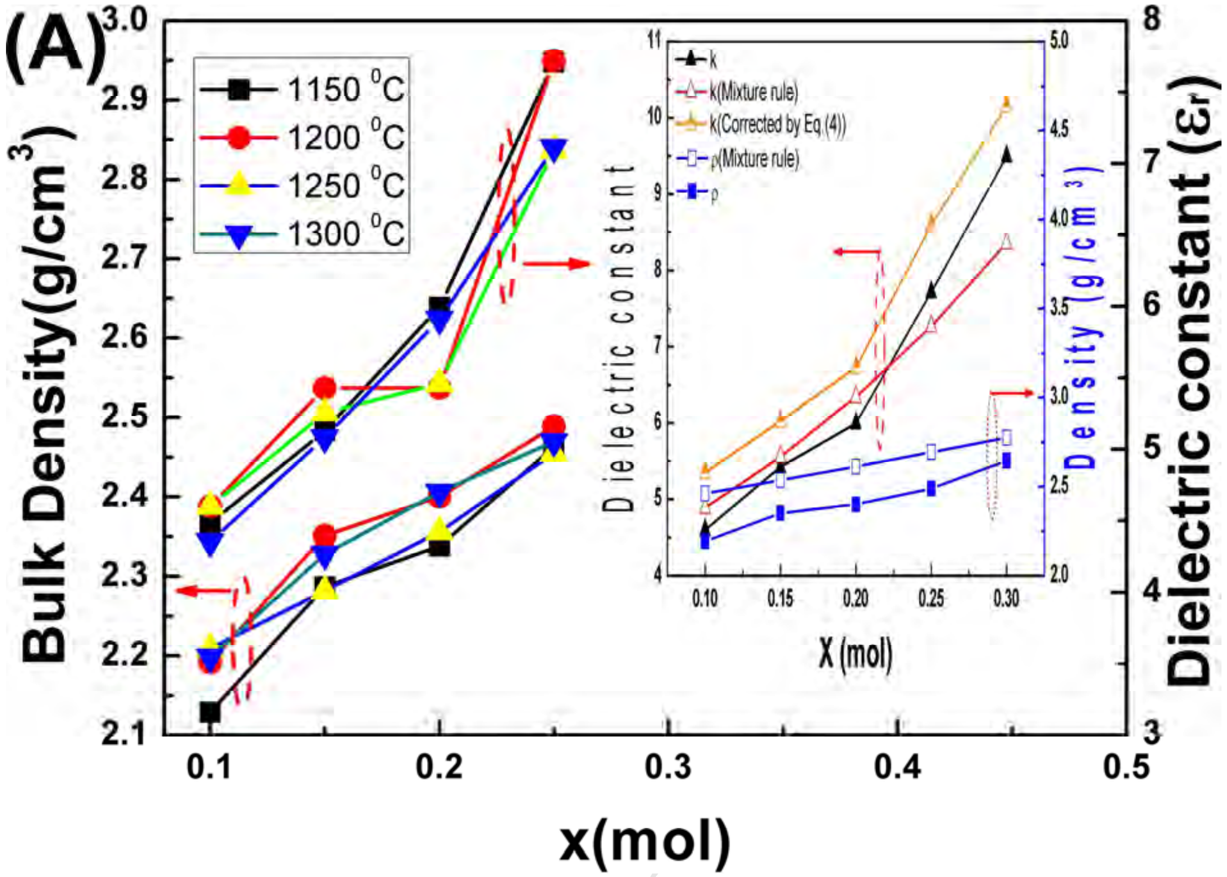

(c)
100 nm
(d)
100 nm

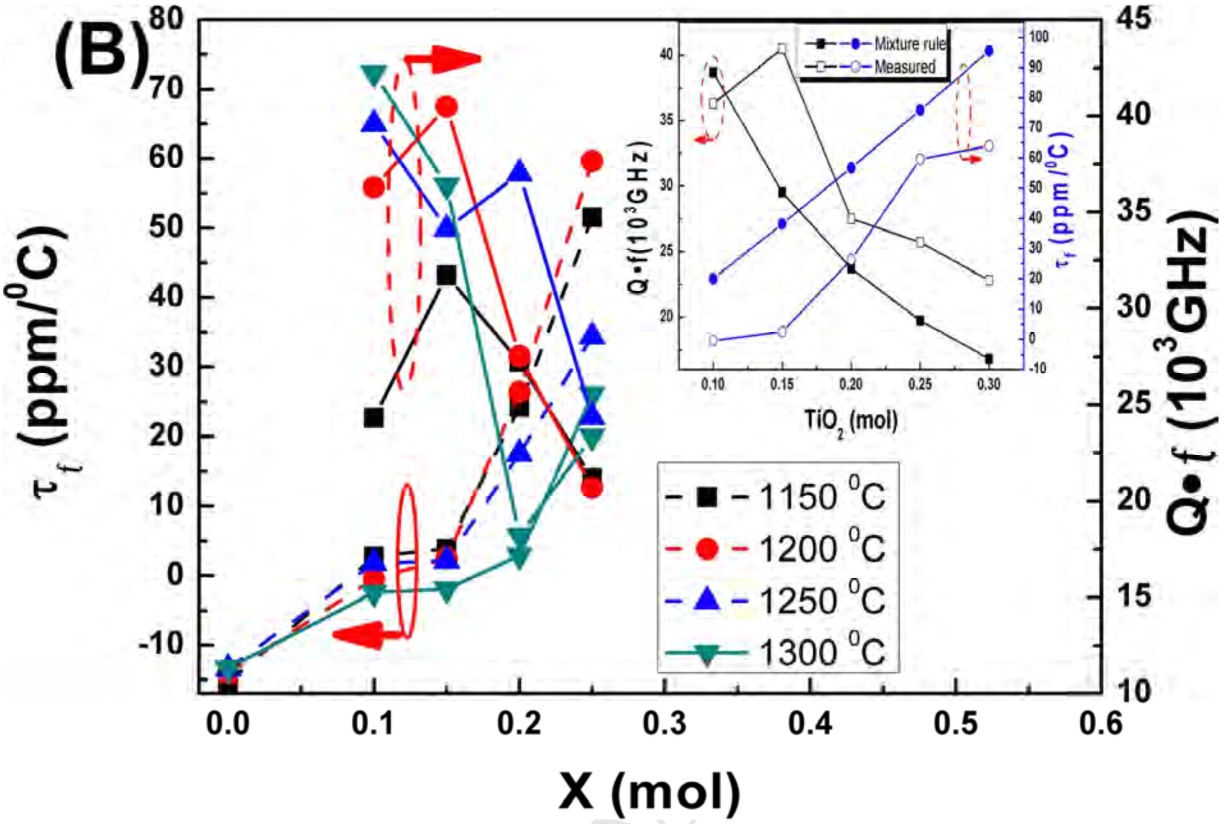

(e)
10 1/nm
(f)
10 1/nm

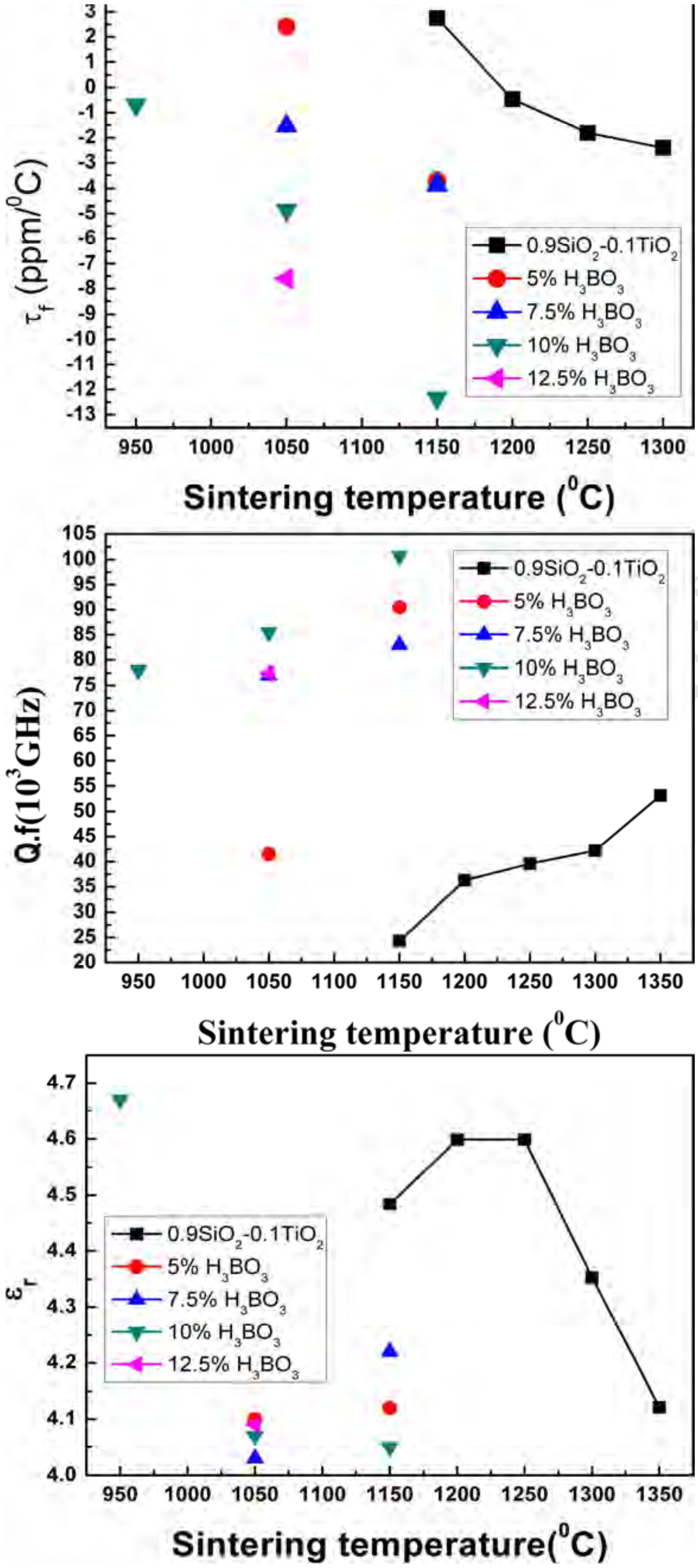

(g)
O1s
Ti2p
C1s
Si2p
Si2s
Counts (a.u.)
0
100
200
300
400
500
600
700
800
Binding Energy (ev)

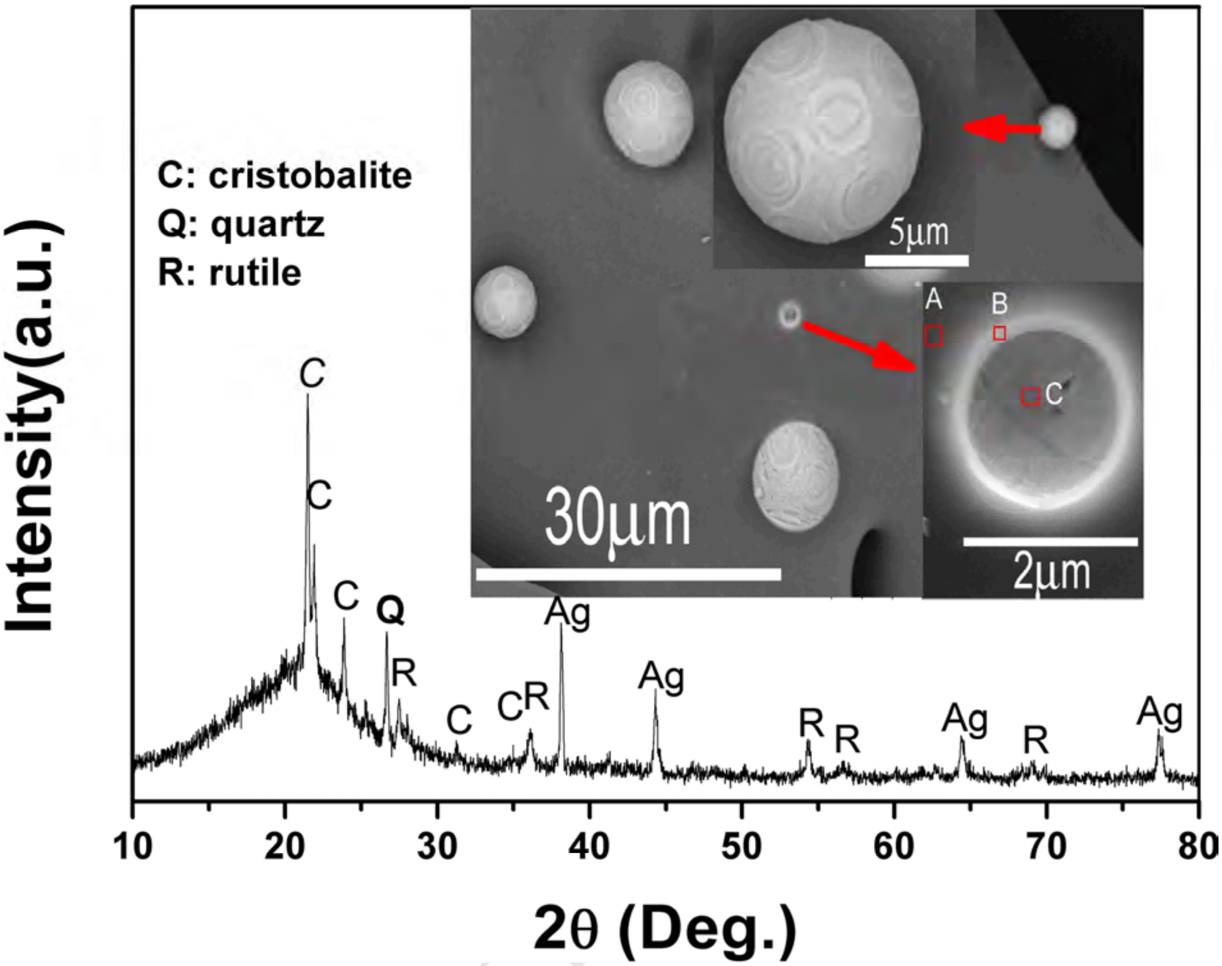

(A)
• Cristobalite low($SiO_2$)
♥ Rutile,syn($TiO_2$)
♦ Quartz($SiO_2$)
Intensity(a.u.)
2θ(Deg.)
20
30
40
50
60
70
x=0.3
x=0.25
x=0.2
x=0.15
x=1.0
x=0
(101)
(110)
(111)
(102)
(200)
(200)
(111)
(211)
(202)
(113)
(212)
(211)
(220)
1350℃
1300℃
1250℃
1200℃
1150℃
10
20
30
40
50
60


(B)
450 cm-1
612 cm-1
420 cm-1
230 cm-1
240 cm-1
148 cm-1
x=0
x=0.1
x=0.15
x=0.2
x=1
Intensity(a.u.)
Raman shift(cm-1)
100
200
300
400
500
600
700


(A)
Bulk Density(g/cm$^3$)
Dielectric constant ($\varepsilon_r$)
x(mol)
3.0
2.9
2.8
2.7
2.6
2.5
2.4
2.3
2.2
2.1
8
7
6
5
4
3
0.1
0.2
0.3
0.4
0.5
1150 °C
1200 °C
1250 °C
1300 °C
k
k(Mixture rule)
k(Corrected by Eq.(4))
ρ(Mixture rule)
ρ
Dielectric constant
Density (g/cm$^3$)
X (mol)
11
10
9
8
7
6
5
4
5.0
4.5
4.0
3.5
3.0
2.5
2.0
0.10
0.15
0.20
0.25
0.30


(B)
τ_f (ppm/⁰C)
80
70
60
50
40
30
20
10
0
-10
Q•f (10³GHz)
45
40
35
30
25
20
15
10
0.0
0.1
0.2
0.3
0.4
0.5
0.6
X (mol)
1150 ⁰C
1200 ⁰C
1250 ⁰C
1300 ⁰C
Mixture rule
Measured
Q•f(10³GHz)
40
35
30
25
20
τ_f (ppm/⁰C)
100
90
80
70
60
50
40
30
20
10
0
-10
0.10
0.15
0.20
0.25
0.30
TiO₂ (mol)


τf (ppm/0C)
3
2
1
0
-1
-2
-3
-4
-5
-6
-7
-8
-9
-10
-11
-12
-13
950
1000
1050
1100
1150
1200
1250
1300
Sintering temperature (0C)
0.9SiO2-0.1TiO2
5% H3BO3
7.5% H3BO3
10% H3BO3
12.5% H3BO3
Q.f(10^3GHz)
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
950
1000
1050
1100
1150
1200
1250
1300
1350
Sintering temperature (0C)
0.9SiO2-0.1TiO2
5% H3BO3
7.5% H3BO3
10% H3BO3
12.5% H3BO3
εr
4.7
4.6
4.5
4.4
4.3
4.2
4.1
4.0
950
1000
1050
1100
1150
1200
1250
1300
1350
Sintering temperature(0C)
0.9SiO2-0.1TiO2
5% H3BO3
7.5% H3BO3
10% H3BO3
12.5% H3BO3


C: cristobalite
Q: quartz
R: rutile
C
C
C
Q
R
C
C
R
Ag
Ag
R
R
Ag
R
Ag
5μm
A
B
C
30μm
2μm
Intensity(a.u.)
2θ (Deg.)
10
20
30
40
50
60
70
80

- The optimum sintering temperature of $0.9SiO_2$–$0.1TiO_2$ ceramics is lowered from 1200 ℃ to 950 ℃ by the addition of $H_3BO_3$.

- $0.9SiO_2$–$0.1TiO_2$ ceramics with 10 wt% $H_3BO_3$ sintered at 950 ℃/6 h possesses excellent microwave dielectric properties of $\varepsilon_r$~4.67, Q•$f$ ~78000 GHz and $\tau_f$ ~-0.7 ppm/℃.

- It was found that the $H_3BO_3$-added $0.9SiO_2$–$0.1TiO_2$ ceramics does not react with Ag at 950 ℃.