Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 35 (2009) 1813–1817

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of SiO_2 addition on the microstructure and microwave dielectric properties of ultra-low fire $TiTe_3O_8$ ceramics

Sea-Fue Wang *, Shea-Jue Wang, Yuh-Ruey Wang, Yung-Fu Hsu, Liang-Yo Chen, Jung-Shiung Tsai

Department of Materials and Mineral Resources Engineering, National Taipei University of Technology, Taipei, Taiwan, ROC

Received 20 August 2008; received in revised form 6 September 2008; accepted 4 October 2008

Abstract

In this study, calcined $TiTe_3O_8$ powder mixed with different amounts of SiO_2 was sintered at various temperatures. The effect of SiO_2 addition on the densification, microstructural evolution and dielectric properties of $TiTe_3O_8$ was investigated. Results indicate that SiO_2 addition inhibited the grain growth of $TiTe_3O_8$ and reduced the evaporation of TeO_2. $TiTe_3O_8$ ceramics with 1 wt% SiO_2 addition and sintered at 750 °C possesses the best dielectric properties: ε_r value of 47.6, $Q \times f$ value of 48,800, and τ_f value of +152 ppm/°C. Excess SiO_2 addition results in the poor densification and the existence of secondary phase (SiO_2) dissolved in a small amount of TeO_2. They degrade the dielectric properties and trade off the benefit from the SiO_2 addition.

Keywords: Microwave properties; Densification; Microstructural evolution; $TiTe_3O_8$

1. Introduction

The recent rapid expansion of telecommunication systems has a great demand for dielectric resonators (DRs) as basic components in designing filters and oscillators. Now, dielectric ceramics for use in resonators at microwave frequency have been paid increasing attention due to the fast growth of mobile communication systems such as cellular phone, global positioning systems and personal communication system. For the applications in microwave devices, a high dielectric constant ($\varepsilon > 20$), a high dielectric loss quality ($Q > 2000$), and a near zero temperature coefficient of resonant frequency (0–10 ppm/°C) are required. High dielectric constant makes possible to reduce the size of the material by a factor of $1/\varepsilon_r^{1/2}$ so that the size of circuit can be reduced considerably. The high Q value enables low insertion loss and low bandwidth of the resonance frequency, which are required for achieving high frequency selectivity and stability in the microwave transmitter components.

Recently, dielectric materials are often required to be co-fired with high conductivity electrodes such as Ag and Cu in order to minimize the microwave absorption loss or to form a multilayer structure to increase the volume efficiency, and the process is called as low temperature co-firable ceramic (LTCC) technology. However, the sintering temperatures of common dielectric ceramics are in the range between 1200 and 1500 °C, which is much higher than the melting temperature of Ag (961 °C) or Cu (1064 °C). For instance, the sintering temperatures of $BaO–Nd_2O_3–TiO_2–Nb_2O_5$, $Ba_{6-x}Ln_{8+2x/3}Ti_{18}O_{54}$ and (Zr, Sn)TiO_4 systems are around 1325, 1350 and 1400 °C, respectively [1–3]. There is considerable interest in the development of new materials with low sintering temperatures. One way involved is the investigation of the glass-forming additives on the properties of established microwave materials. For instance, the $BaO–La_2O_3–4.7TiO_2$ ceramic with the addition of 20 wt% $PbO–B_2O_3–SiO_2$ aid can reduce the sintering temperature down to 900 °C, but the microwave properties were degraded [4]. Another way is the use of new material systems with lower sintering temperatures, including Bi_2O_3 and TeO_2-based compounds [5]. The sintering temperature of $Bi_{12}MO_{20-\delta}$

---

* Corresponding author. Present address: National Taipei University of Technology, Department of Materials and Mineral Resources Engineering, 1, Sec. 3, Chung-Hsiao E. Rd., Taipei 106, Taiwan, ROC.
Tel.: +886 2 2771 2171x2735.
E-mail address: seafuewang@yahoo.com (S.-F. Wang).

0272-8842/$34.00 © 2008 Published by Elsevier Ltd and Techna Group S.r.l.
doi:10.1016/j.ceramint.2008.10.012

(M = Si, Ge, Ti, Pb, Mn and $B_{1/2}P_{1/2}$), TiO_2–TeO_2, and Bi_2O_3–ZnO–Nb_2O_5 are around 680–850, 720, and 950 °C, respectively [6–8].

TeO_2, with a melting point of 733 °C, is well known as a network-glass-former in the glass industry, since tellurite glasses have high refractive index, high IR transmission and low dispersion [9]. TeO_2 with ≈20% porosity was shown to display a relative permittivity of 19.3, a $Q \times f$ value of 30,000 GHz and a temperature coefficient of −119 ppm/°C. Recently, researchers have shown that TeO_2-based ceramics possess very low sintering temperatures ranging from 650 to 800 °C and excellent microwave dielectric characteristics, including TiO_2–TeO_2, Bi_2O_3–TeO_2, CaO–TeO_2, BaO–TeO_2, ZnO–TeO_2, and Bi_2O_3–TiO_2–TeO_2 systems [7,10–17]. Single phase $TiTe_3O_8$ sintered at 720 °C to ≈95% of theoretical density exhibits a relative permittivity of 50, a $Q \times f$ value of 30,600 GHz and a temperature coefficient of +133 ppm/°C. A ceramic with nearly zero temperature coefficient of resonant frequency can be obtained from the $TiTe_3O_8$–TeO_2 composite. The permittivity of the Bi_2O_3–TeO_2 compounds varies from 30 to 54, the $Q \times f$ value from 1100 to 41,000 GHz, and the temperature coefficient of resonant frequency from −43 to −144 ppm/°C. On the other hand, the dielectric properties of BaO–TeO_2 compounds at microwave frequencies were ε_r = 10–21, $Q \times f$ = 34,000–55,000 GHz, and τ_f = −51 to −124 ppm/°C.

Though a number of excellent dielectric ceramic compositions with low sintering temperatures are reported in TeO_2-based ceramics, they generally encountered process difficulties such as chemical inhomogeneity and residue porosity in the sintered body, due to the volatile nature of TeO_2. In this study, pre-calcined $TiTe_3O_8$ ceramic powders mixed with different amounts of SiO_2 were sintered at various temperatures. The effects of SiO_2 additive on the densification, microstructural evolution and dielectric properties of $TiTe_3O_8$ are discussed, through X-ray diffraction (XRD), scanning electron microscopy (SEM), thermal analysis, and dielectric characterization.

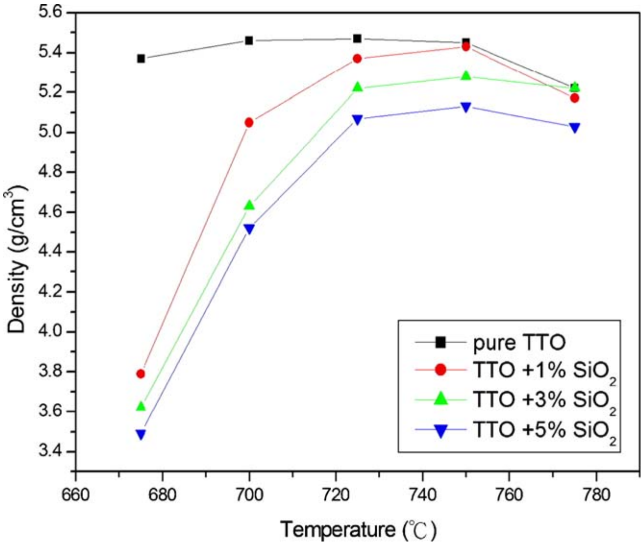

Fig. 1. Sintered density of the $TiTe_3O_8$ ceramics with various amounts of SiO_2 sintered at different temperatures.

2. Experimental procedure

A host material, $TiTe_3O_8$ powder, was prepared using the solid-state reaction technique. Highly pure (>99.9% purity) TiO_2 and TeO_2 (all Merck, Reagent grade) were used as raw materials. Oxides based on the composition of $TiTe_3O_8$ were mixed and milled in methyl alcohol solution using polyethylene jars and zirconia balls for 8 h and then dried at 80 °C in an oven for overnight. After drying, the powders were calcined at 700 °C for 10 h, and then re-milled in methyl alcohol for 8 h. The powders have a particle size of 1.22 μm measured by laser scattering particle size distribution analyzer (Horiba, LA-950). Phase identification on the calcined powders was performed using X-ray diffraction (XRD, Rigaku DMX-2200). The powder was added with a 5 wt% of 15%-PVA solution and pressed into disc-shaped compacts using uniaxial pressure of 1 tons/cm^2. The samples were then heat treated at 550 °C for 2 h to eliminate the PVA, followed by sintering at 650–750 °C for 10 h (heating rate = 10 °C/min). Bulk densities of the sintered samples were measured using the Archimedes method with de-ionized water. Phase identification on the calcined powders as well as the sintered bulk ceramics was performed

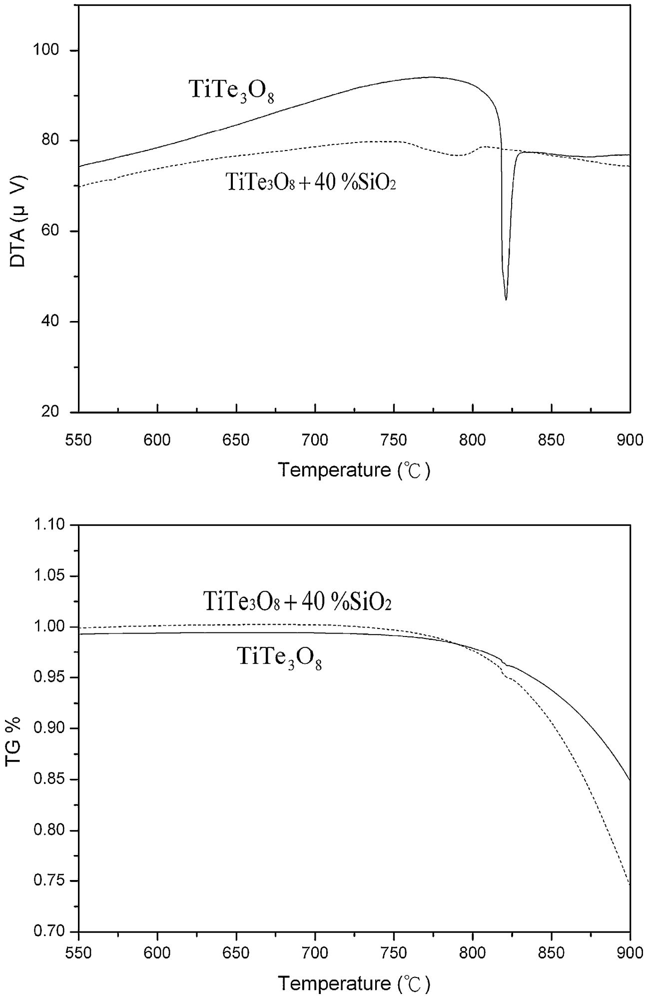

Fig. 2. DTA/TGA results of $TiTe_3O_8$ powder and $TiTe_3O_8$ powder containing 40 wt% SiO_2.

using X-ray diffraction (XRD, Simens D5000). Differential thermal analysis (DTA) was performed in a Pt crucible with heating rate of 10 °C/min using a PerkinElmer Calorimeter, Series 1700 DTA, on mixtures to evaluate the melting reactions. The microstructures of the sintered samples were observed using scanning electron microscopy (SEM, JEOL 6500F) with and energy-dispersive spectroscopy (EDS). The grain size was determined from SEM micrographs by linear intercept method. The sintered samples were further inspected by transmission electron microscopy (Model HRTEM, JEOL-2010), to understand the distribution of various species. The densified cylindrical samples were polished to have an exact thickness of 5 mm for the measurements of microwave properties. The dielectric constant (ε_r) and quality factor ($Q \times f$) were evaluated, based on the cylindrical cavity method (cavity 1005CIRC and software CAVITY, Damaskos, Inc.), using a HP 8722D network analyzer. Detailed measurement procedures have been described elsewhere [18]. The temperature coefficient of resonant frequency (τ_f) was measured within the range from 25 to 80 °C. The τ_f was defined by $(f_t - f_{25})/f_{25}(T - 25\,^\circ C)$ in Damaskos cavity.

3. Results and discussion

Fig. 1 shows the sintered density of the $TiTe_3O_8$ ceramic with various amounts of SiO_2 after sintering at different temperatures. Pure $TiTe_3O_8$ ceramic reaches maximum theoretical density of 96.8% at 725 °C and then slightly decreases with sintering temperature, due to the trapped porosity. Over 98% sintered density was not obtained because of its volatile nature. A theoretical density of 95% can be achieved at the temperature as low as 675 °C which is slightly lower than that reported by Udovic et al. (725 °C) [7]. It has probably resulted from the difference in the particle size of calcined $TiTe_3O_8$ and the sintering profile adopted such as heating and cooling rates. With the addition of SiO_2, it appears that the maximum sintered density is achieved at the temperature of 750 °C. The sintered density reduces with the extent of SiO_2, which is partly contributed from the difference in densities of $TiTe_3O_8$ (5.64 g/cm^3) and SiO_2 (2.65 g/cm^3) and the residual porosities. It is evident that the addition of SiO_2 slightly retards the densification of $TiTe_3O_8$.

Fig. 2 shows the DTA/TGA results of $TiTe_3O_8$ powder and $TiTe_3O_8$ powder with 40 wt% SiO_2. Pure $TiTe_3O_8$ powder encounters an endothermic melting reaction at 821 °C which is much higher than that of TeO_2 powder (733 °C) [9]. With 40 wt% SiO_2 addition, the melting temperature slightly reduces to 789 °C, which may be due to the eutectic reaction between $TiTe_3O_8$ and SiO_2. There is no other reaction as the mixture was heated up to the temperature of 900 °C. TGA results indicate that there is no weight loss associated with the melting reaction. The decrease in weight with temperature is primarily due to the evaporation of the volatile species, which is noticeable at temperatures higher than 800 °C.

SEM microstructures for the as-fired surfaces of ceramics prepared from $TiTe_3O_8$ powders with various amounts of SiO_2 sintered at 750 °C for 10 h are shown in Fig. 3. It seems that the microstructures are closely correlated to the SiO_2 content. A wide grain size distribution was observed for all cases, with the grain sizes in the range of 2–5 μm. For pure $TiTe_3O_8$ ceramic, Fig. 3(a) shows a mixture of elongated, columnar grains along with angular grains. EDS results reveal that the columnar grains and the angular grains are TiO_2 and $TiTe_3O_8$ phases, respectively. The evaporation of TeO_2 from $TiTe_3O_8$ phase during the sintering process leads to the formation of the columnar TiO_2 grains. There is no possibility for the formation

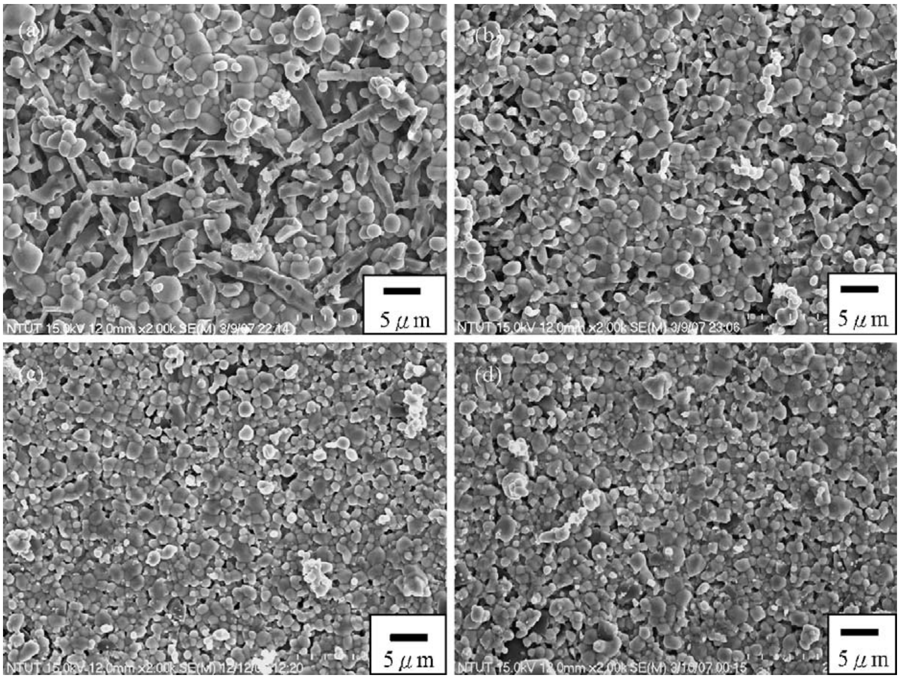

Fig. 3. SEM micrographs of $TiTe_3O_8$ ceramics containing (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, and (d) 5 wt% SiO_2 sintered at 750 °C for 10 h.

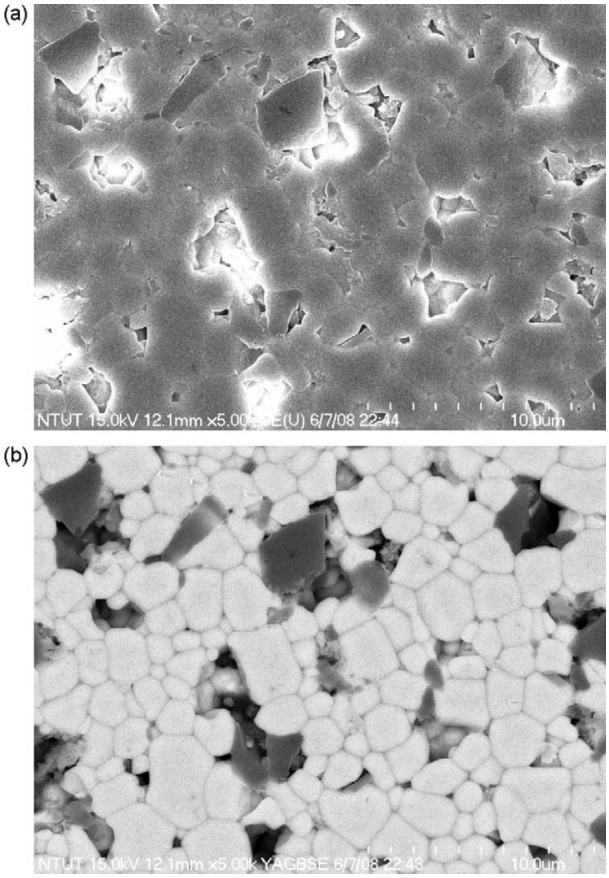

Fig. 4. SEM (a) and back scattering electron image (BEI) of $TiTe_3O_8$ ceramics containing 5 wt% SiO_2 sintered at 750 °C for 10 h (b).

of other phases, because only one compound $TiTe_3O_8$ was reported as a thermodynamically stable single phase in the TiO_2–TeO_2 binary system [19]. Generally, $TiTe_3O_8$ ceramics with SiO_2 addition were porous when sintered below 750 °C. As the sintering temperature reached 750 °C, maximum density was achieved and the residual porosity increases with SiO_2 content (Fig. 1). For $TiTe_3O_8$ ceramics with additions of SiO_2, Fig. 3(b)–(d) exhibit only angular grains in the microstructures. Grain sizes become slightly smaller with SiO_2 addition. It is evident that SiO_2 can inhibit the grain growth of $TiTe_3O_8$ and the evaporation of TeO_2. In order to reveal the detailed information of the structure, $TiTe_3O_8$ ceramic with 5 wt% SiO_2 carefully examined by SEM image is shown in Fig. 4(a) and the corresponding backscattering electron image (BEI) is shown in Fig. 4(b). The lighter color grains in the BEI image were recognized as pure $TiTe_3O_8$ and darker grains were identified as SiO_2 phase dissolved in a small amount of Te, according to the EDS results. Based on above observation, it is evident that the SiO_2 phase can react with the vaporized TeO_2 and form solid solution. Fig. 5 shows the XRD patterns of $TiTe_3O_8$ ceramics with various SiO_2 contents sintered at 750 °C for 10 h. There is no detectable second phase in pure $TiTe_3O_8$ ceramic and $TiTe_3O_8$ ceramics with additions of 1 and 3 wt% SiO_2 after sintering. As the SiO_2 content increased to 5 wt%, a crystalline unknown phase is visible in the XRD pattern, which is expected to be solid solution of SiO_2 and a small amount of TeO_2, combined with the EDS results. Apparently, solubility of SiO_2

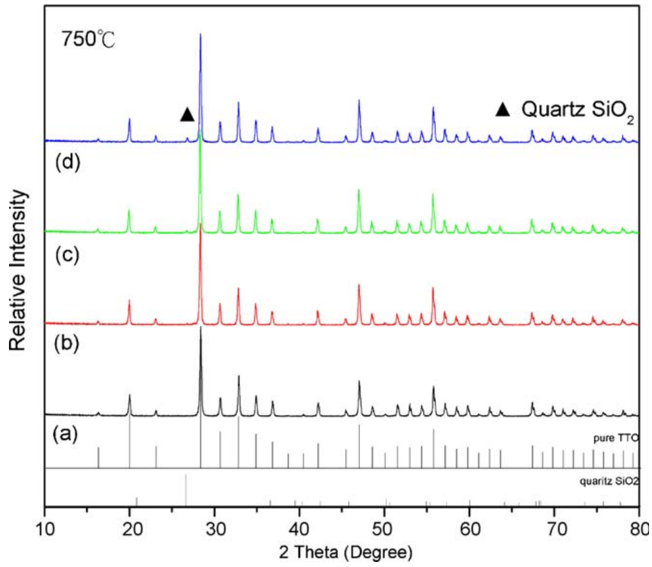

Fig. 5. XRD patterns of $TiTe_3O_8$ ceramics containing (a) 0 wt%, (b) 1 wt%, (c) 3 wt%, and (d) 5 wt% SiO_2 sintered at 750 °C for 10 h.

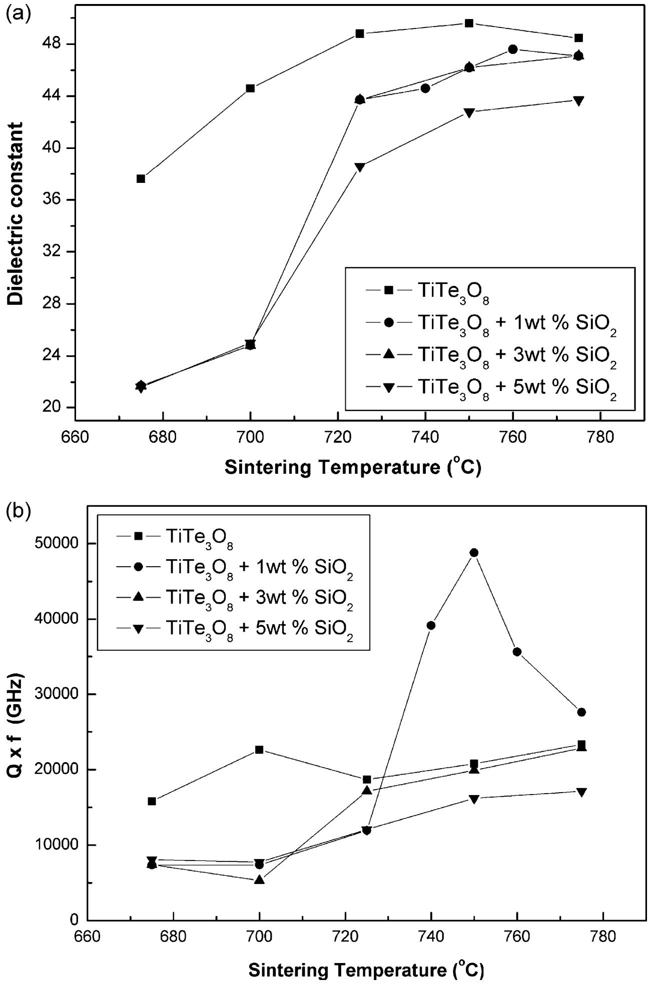

Fig. 6. (a) Dielectric constants and (b) quality factors of $TiTe_3O_8$ ceramics containing (i) 0 wt%, (ii) 1 wt%, (iii) 3 wt%, and (iv) 5 wt% SiO_2 vs. sintering temperature.

Table 1
Part of microwave dielectric properties of the $TiTe_3O_8$ ceramics with various amounts of SiO_2 sintered at different temperatures.

Composition	Sintering temp. (°C)	ε_r	$Q \times f$ (7 GHz)	τ_f (ppm/°C)
$TiTe_3O_8$	725	48.8	18,700	142
$TiTe_3O_8$	750	49.6	20,800	141
$TiTe_3O_8$ + 1%SiO_2	750	47.6	48,800	152
$TiTe_3O_8$ + 1%SiO_2	775	48.7	27,600	153
$TiTe_3O_8$ + 3%SiO_2	750	46.2	19,900	165
$TiTe_3O_8$ + 3%SiO_2	775	47.1	22,900	160
$TiTe_3O_8$ + 5%SiO_2	750	42.8	16,200	133
$TiTe_3O_8$ + 5%SiO_2	775	43.7	17,100	144

in $TiTe_3O_8$ ceramics is limited. Excess SiO_2 would result in poor densification.

Fig. 6(a)–(b) shows the microwave dielectric properties of the $TiTe_3O_8$ ceramics with various amounts of SiO_2 sintered at different temperatures, and Table 1 lists part of the results. They exhibit the same trend in density, which increases with the sintering temperatures. The dielectric constants of dense $TiTe_3O_8$ ceramics are ranging from 37.6 to 49.6. As SiO_2 addition increases, the dielectric constant was degraded by the increasing volume fraction of trapped porosity. The $Q \times f$ values of $TiTe_3O_8$ ceramics are ranging from 15,800 to 23,000, which generally increase with sintering temperature. The $Q \times f$ value is slightly lowered by the addition of SiO_2, with the exception of 1 wt% SiO_2. Fig. 6(b) indicates that the $TiTe_3O_8$ ceramics with 1 wt% SiO_2 addition and sintered at the temperature of 750 °C possesses the best dielectric properties: ε_r value of 47.6, $Q \times f$ value of 48,800, and τ_f value of +152 ppm/°C. As the SiO_2 continues to increase, poor densification and secondary phase formation poison the dielectric properties, particularly for the $Q \times f$ value. They degrade the dielectric properties and trade off the benefit from the SiO_2 addition.

4. Conclusion

Pure $TiTe_3O_8$ ceramic reaches 96.8% of theoretical density at 725 °C and then slightly decrease with sintering temperature, due to the trapped porosity. Grain sizes of $TiTe_3O_8$ ceramics become slightly smaller with SiO_2 addition. Results indicated that SiO_2 can inhibit the grain growth of $TiTe_3O_8$ and the evaporation of TeO_2. EDS results show that solubility of SiO_2 in $TiTe_3O_8$ ceramics is limited. Excess SiO_2 would results in poor densification and secondary phase formation, that are detrimental to the dielectric properties. Best dielectric properties were obtained for $TiTe_3O_8$ ceramic with 1 wt% SiO_2 addition. They include ε_r value of 47.6, $Q \times f$ value of 48,800, and τ_f value of +152 ppm/°C, at the temperature of 750 °C.

References

[1] X.H. Zheng, X.M. Chen, Dielectric ceramics with tungsten–bronze structure in the $BaO–Nd_2O_3–TiO_2–Nb_2O_5$ system, J. Mater. Res. 17 (7) (2002) 1664..

[2] Y. Xu, Y. He, Polymeric precursor synthesis of $Ba_{6-3x}Sm_{8+2x}Ti_{18}O_{54}$ ceramic powder, Ceram. Int. 28 (1) (2002) 75..

[3] G. Wolfram, H.E. Gobel, Existence range, structural and dielectric properties of $Zr_xTi_ySn_zO_4$ ceramics ($x + y + z = 2$), Mater. Res. Bull. 16 (1952) 1455.

[4] C.C. Lee, P. Lin, Effect of glass addition on microwave properties of $BaO{\cdot}La_2O_3{\cdot}4.7TiO_2$, Jpn. J. Appl. Phys. 37 (1998) 6048.

[5] A. Borisevich, P.K. Davies, Microwave dielectric properties of $Li_{1+x-y}M_{1-x-3y}Ti_{x+4y}O_3$ (M = Nb^{5+}, Ta^{5+}) solid solutions, J. Eur. Ceram. Soc. 21 (2001) 1719.

[6] M. Valant, D. Suvorov, Processing and dielectric properties of sillenite compounds $Bi_{12}MO_{20\delta}$ (M = Si, Ge, Ti, Pb, Mn, $B_{1/2}P_{1/2}$), J. Am. Ceram. Soc. 12 (2001) 2900.

[7] M. Udovic, M. Valant, D. Suvorov, Dielectric characterization of ceramics from the $TiO_2–TeO_2$ system, J. Eur. Ceram. Soc. 21 (2001) 1735–1738.

[8] H. Wang, X. Yao, Structure and dielectric properties of pyrochlore-fluorite biphase ceramics in the $Bi_2O_3–ZnO–Nb_2O_5$ System, J. Mater. Res. 16 (1) (2001) 83.

[9] G. Turky, M. Dawy, Spectral and electrical properties of ternary ($TeO_2–V_2O_5–Sm_2O_3$) glasses, Mater. Chem. Phys. 77 (2002) 48–59.

[10] D.K. Kwon, M.T. Lanagan, T.R. Shrout, Synthesis of $BaTiTe_3O_9$ ceramics for LTCC application and its dielectric properties, J. Ceram. Soc. Jpn. 113 (3) (2005) 216–219.

[11] D.K. Kwon, M.T. Lanagan, T.R. Shrout, Microwave dielectric properties of $BaO–TeO_2$ binary compounds, Mater. Lett. 61 (2007) 1827–1831.

[12] M. Udovic, M. Valant, D. Suvorov, Phase formation and dielectric characterization of the $Bi_3O_3–TeO_2$ system prepared in an oxygen atmosphere, J. Am. Ceram. Soc. 87 (4) (2004) 591–597.

[13] M. Valant, D. Suvorov, Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates'', J. Eur. Ceram. Soc. 24 (6) (2004) 1715–1719.

[14] M. Udovic, M. Valant, D. Suvorov, Formation and decomposition of Bi_2TeO_6 compound, J. Eur. Am. Ceram. Soc. 24 (2004) 953–958.

[15] M. Udovic, M. Valant, D. Suvorov, Formation and crystal-structure determination in the $Bi_2O_3–TiO_2–TeO_2$ system prepared in an oxygen atmosphere, J. Am. Ceram. Soc. 89 (11) (2006) 2462–2469.

[16] M. Udovic, D. Suvorov, Sintering and dielectric characterization of pseudoternary compounds from the $Bi_2O_3–TiO_2–TeO_2$ system, J. Am. Ceram. Soc. 90 (8) (2007) 2404–2408.

[17] G. Subodh, M.T. Sebastian, Glass-free $Zn_2Te_3O_8$ microwave ceramic for LTCC applications, J. Am. Ceram. Soc. 90 (7) (2007) 2266–2268.

[18] N.J. Damaskos, B.J. Kelsall, Measuring dielectric constants of low loss materials using a broadband cavity technique, Microwave J. 38 (1995) 140.

[19] S. Yamanaka, M. Miyaka, Study of the ternary Ti–Te–O system, J. Less-Common Met. 159 (1990) 179–189.