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TEM observation of liquid phase sintering in V_2O_5 modified $Zr_{0.8}Sn_{0.2}TiO_4$ microwave ceramics

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Abstract

The phenomena of liquid phase sintering in the V_2O_5 modified $(Zr_{0.8}, Sn_{0.2})TiO_4$ (ZST) microwave ceramics has been investigated by using transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDS). The amounts of second phase were too low to be detected by X-ray diffraction (XRD), but could be observed by TEM bright field image. However, the presence of grain boundary phases did not degrade the microwave properties of V_2O_5 modified ZST ceramics. The ε_r value of 37.2, $Q \times f$ value of 51,000 (at 7 GHz) and τ_f value of -2.1 ppm/°C were obtained for ZST ceramics with 1 wt% V_2O_5 addition sintered at 1300 °C.
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Keywords: C. Dielectric properties; TEM; Liquid phase; $(Zr_{0.8},Sn_{0.2})TiO_4$

1. Introduction

The commercial wireless technologies, such as cellular phones and global positioning systems, have been making rapid progress due to the improved performance of dielectric resonators at microwave frequencies [1,2]. Requirements for these dielectric resonators must combine with a high dielectric constant ($\varepsilon_r > 25$) for possible size miniaturization (size of a dielectric resonator $\sim 1/\sqrt{\varepsilon_r}$), a high dielectric quality factor ($Q \times f > 5000$) for low loss devices and a near-zero temperature coefficient of resonant frequency (τ_f) for temperature stable circuits [3].

$ZrTiO_4$ ceramics exhibits the α-PbO orthohombic structure [4]. $ZrTiO_4$ ceramic replaced 20 mol% Zr by Sn ions causes the order–disorder transformation and has been proved to be one of the most popular dielectric resonator material for microwave devices [5,6]. However, the microwave dielectric properties of $(Zr_{0.8},Sn_{0.2})TiO_4$ (ZST) ceramics are very much dependent upon the raw materials, the additives, and the microstructure [7–9]. It is difficult to fully dense the ZST ceramics without any sintering aid. With 1 wt% ZnO addition, ZST ceramics could obtain $\varepsilon_r \sim 37.8$, $Q \times f \sim 45000$ and $\tau_f \sim 0$ ppm/°C. However, its sintering temperature still remained as high as 1400 °C. In past, many researchers made effort in studying the microstructures and the microwave dielectric properties of ZST ceramics by adding small additives such as Fe, La, Ni, Cd and Zn [8–10]. Similar to ZnO, some metal oxides have the ability to form eutectic liquids with TiO_2 at temperatures at or below ~1400 °C. Liquid phase fluxes such as Bi_2O_3, B_2O_3 and CuO have being used to lower the sintering temperature of ceramics. With 1 wt% CuO addition, ZST ceramics sintered at 1260 °C was reported to exhibit the dielectric properties of $\varepsilon_r \sim 38$, $Q \times f$ value ~50,000 (at 7 GHz) and τ_f value ~3 ppm/°C [11]. Since V_2O_5 (melting temperature = 650 °C) is one of the flux formers, it was added to lower the sintering temperature of ZST ceramics in a previous paper [12]. However, the mechanism in lowering the sintering temperature was not discussed in detail.

In this paper, the effect of sintering behavior on the grain morphology of V_2O_5 modified ZST was carefully observed by using the transmission electron microscopy (TEM) coupled with energy dispersive X-ray (EDS). Moreover, the liquid phase effect on the microwave dielectric properties and microstructures were also investigated.

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2. Experimental procedure

Samples of ZST were synthesized by conventional solid-state methods from individual high-purity oxide powders (>99.9%): ZrO_2 (SHOWA Chemicals Inc.), SnO_2 (Hayashi Pure Chemical Industrius Lot, Japan), TiO_2 (Janssen Chemica) and ZnO (Hayashi Pure Chemical Industrius Lot, Japan). The starting materials were mixed according to desired stoichiometry ZST ceramics with 1 wt% addition of ZnO as a sintering aid. The powders were ground in distilled water for 6 h in a ball mill with agent balls. All mixtures were dried and calcined at 1100 °C for 3 h. Then, the calcined powders added further with 1 wt% V_2O_5 were milled again for 5 h with polyvinyl acetate (PVA) solution as a binder. Pellets with 11 mm diameter and 5 mm thick were pressed by uniaxial pressing. After debinding, these pellets were sintered at temperatures of 1260–1340 °C for 3 h. The heating rate and the cooling rate were both set to be 10 °C/min.

The microstructure observation of the sintered ceramics surface was performed by means of scanning electron microscopy (SEM, JEOL JSM 6400, Japan). The crystalline phases of sintered ceramics were identified by X-ray diffraction pattern (XRD, D5000 Diffratometer, Seimens, Germany). The distribution of the V_2O_5 in the specimens and the grain boundary phase were analyzed and observed via TEM (JEOL, AEM3010, Tokyo, Japan) coupled with EDS spectroscopy (Link System, Oxford Instruments, Oxford, UK). The bulk densities of the sintered pellets were measured by the Archimedes method.

The dielectric constant (ε_r) and the dielectric quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method as modified and improved by Courtney [13,14]. A system combined with a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. The temperature coefficient of resonant frequency (τ_f) at microwave frequency was measured in the temperature range from 25 to 80 °C. It can be obtained by measuring $TE_{01\delta}$ resonant frequency at 20 °C (f_{20}) and 80 °C (f_{80}) and then applied to Eq. (1).

$$\tau_f = \frac{(f_{80} - f_{20})}{(60 \times f_{20}) \times 10^6} (\text{ppm}/^\circ\text{C}) \quad (1)$$

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of 1 wt% V_2O_5 modified ZST ceramics at various sintering temperatures for 3 h. It showed that ZST had an orthorhombic type crystal structure and developed slightly at 950 °C, considerably at

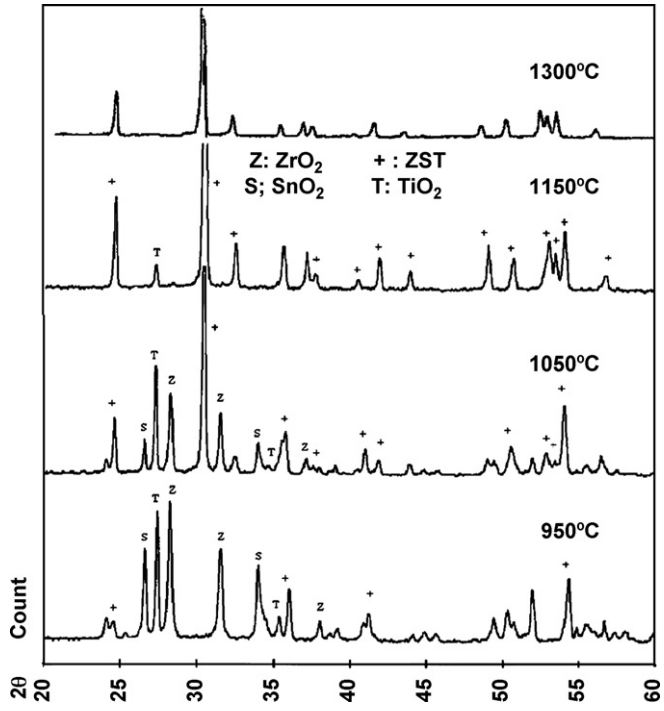

Fig. 1. X-ray diffraction patterns of ZST ceramics sintered at various sintering temperatures for 3 h with 1 wt% V_2O_5 addition.

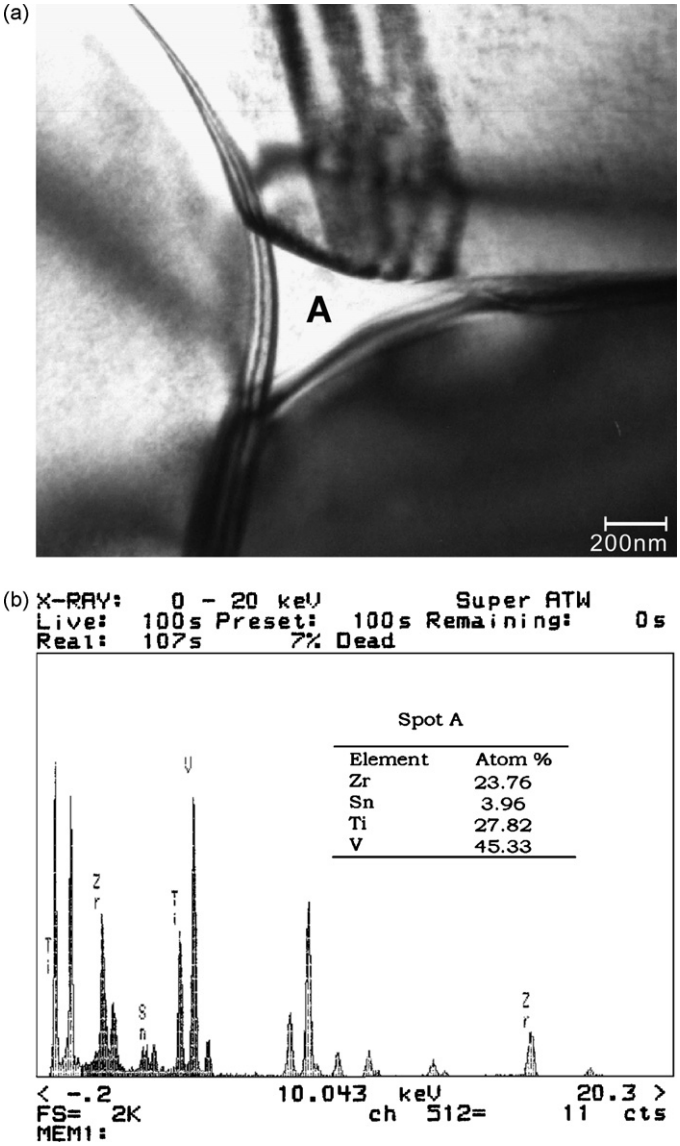

Fig. 2. (a) BF image of ZST grains (sintered at 1300 °C) with rounded grain boundary and (b) EDS analysis of the glassy liquid in the point A.

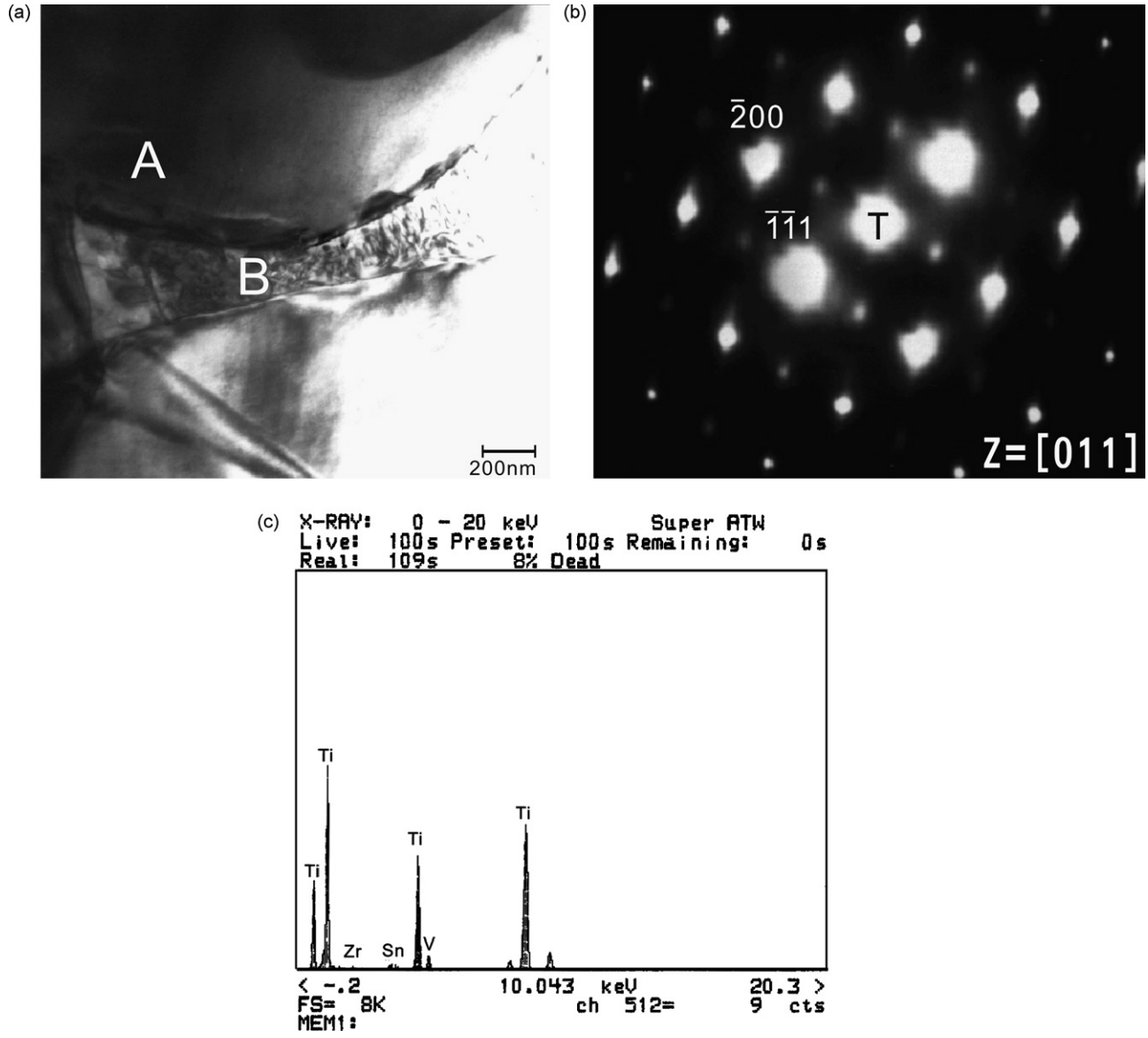

Fig. 3. (a) BF image in the vicinity of a ZST grain with rounded grain boundary sintered at 1260 °C, (b) SADP of ZST grain in region A, and (c) EDS analysis of second phase in the region B.

1150 °C, and fully at 1300 °C. The secondary phase TiO_2 could also be detected while the specimens sintered at 1150 °C but were disappeared in that sintered at 1300 °C owing to the limit of detection of a minor phase by X-ray measurement.

Fig. 2(a) shows the bright field (BF) image of ZST grains with rounded grain boundary. It was clearly observed a glassy liquid was formed in the triple junction region. In addition, according to the EDS analysis, as showed in Fig. 2(b), the glassy liquid had a great amount of vanadium. The result might be that ZrO_2 and V_2O_5 formed eutectic liquid as referring to the phase diagram in the ZrO_2–V_2O_5 system [15] as the heating temperature was up to 700 °C. It is plausible that the ZrO_2–V_2O_5 eutectic liquid promoted the formation of ZST as the heating temperature up to 950 °C, as shown in Fig. 1, considerably lower than that (∼1130 °C) of the ZST powder prepared by a mixed-oxide method [16].

Fig. 3(a) shows BF image of the second phase in the vicinity of a ZST grain with rounded grain boundary sintered at 1260 °C. The ZST grain identified by the selected area diffraction pattern (SADP) is given in Fig. 3(b), indicating a well crystallization of ZST phase. The rounded grain boundary also indicated that liquid phase appeared during the sintering. As identified by EDS analysis of second phase in the region B (found in Fig. 3(c)), it is believed that the formed ZrO_2–V_2O_5 eutectic liquid caused the excess Ti to form a Ti rich compound, such as TiO_2, which was precipitated in the grain boundary during solid state reaction at low temperature of 1150 °C. The EDS results were in agreement with XRD results in Fig. 1. However, when the sintering temperature was higher than 1260 °C, the amount of TiO_2 disappeared since higher temperature provides energy for Ti to diffuse and react completely.

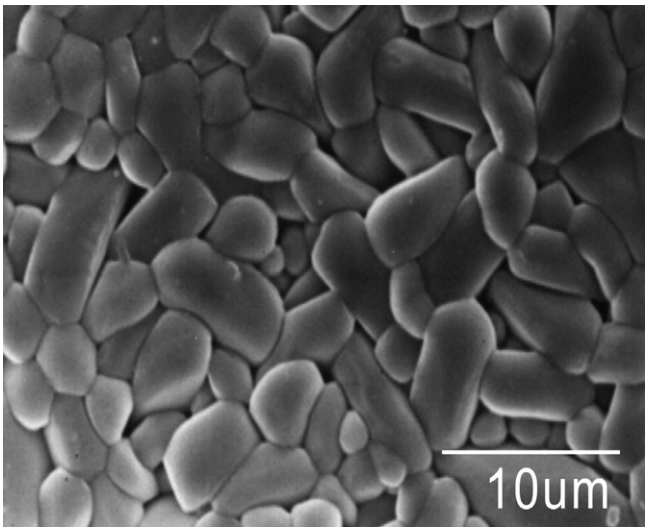

Fig. 4. SEM micrographs of ZST ceramics sintered at 1300 °C for 3 h with 1 wt% V_2O_5 addition.

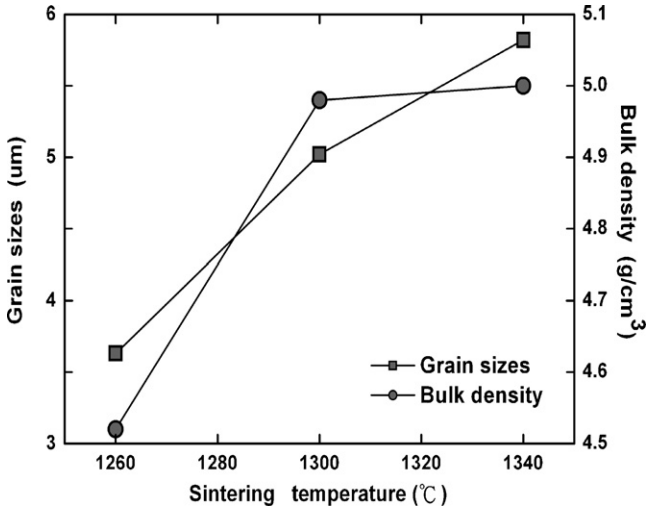

Fig. 5. The grain size and the bulk densities of ZST ceramics with 1 wt% V_2O_5 addition as functions of sintering temperatures.

Fig. 4 illustrates the SEM photographs of 1 wt% V_2O_5 modified ZST ceramics sintered at 1300 °C for 3 h. The ZST ceramics were already dense. However, the grain uniformity showed irregular variation. The liquid phase would be expected to provide a faster transport path for diffusion, thus enhancing the homogenization and densification processes to promote the grain growth. Therefore, the inhomogeneous grain size distribution is believed due to an inhomogeneous liquid phase distribution leading to a heterogeneous microstructure formed during sintering.

Fig. 5 illustrates the grain size and the bulk densities of 1 wt% V_2O_5 modified ZST ceramics as functions of sintering temperatures. The average grain size increased with increasing sintering temperature owing to grain growth. The average grain size of ZST ceramics increased from 3.3 to 5.8 μm with 1 wt% V_2O_5 addition as sintering temperature increased from 1260 to 1300 °C. The grain sizes of these samples were much larger than that of the samples with no liquid [8]. Several possible mechanisms are reported to show how the liquid phase could homogenize the microstructure [17]. The first possibility is that the liquid phase assists rearrangement of the matrix particles at the inclusion/matrix interface into a more efficient packing configuration. The second possibility is that the liquid phase goes into the polycrystalline inclusions by capillary action to break them up and homogenize the microstructure. It is reasonably possible that a combination of penetration and rearrangement is taking place because some penetration of the liquid phase would be necessary to promote efficient particle packing at the interface. Although the liquid phase sintering promotes the densification of ceramics, grain growth in the presence of a liquid phase decreases the kinetics of densification processes considerably relative to solid-state sintering. Therefore, the grain growth rate between 1300 and 1340 °C was slightly lower than that between 1260 and 1300 °C.

The plots of bulk densities of 1 wt% V_2O_5 modified ZST ceramics versus the sintering temperature are also shown in Fig. 5. The apparent density and its corresponding relative theoretical density (TD) increased from 4.55 g/cm^3 (87.5% TD) to 5.04 g/cm^3 (96.9% TD) as the sintering temperature increased from 1260 to 1300 °C. The density of ZST ceramics increased quickly with increasing sintering temperature and seemed to saturate at 1300 °C. The liquid would disappear or be resident in the final stage of liquid phase sintering. In this study, the liquid was resident in the final stage of liquid phase sintering to form in the triple junction region, as shown in Fig. 2(a), and led to the density of specimens saturated at sintering temperature of 1300 °C as showed in Fig. 5. Therefore, the fast densification rate at the sintering temperature between 1260 and 1300 °C is believed due to the liquid phase formed during the sintering process.

Table 1 summaries the dielectric constant (ε_r), dielectric quality factor ($Q \times f$), and temperature coefficient of resonant frequency (τ_f) of ZST ceramics with 1 wt% V_2O_5 addition at different sintering temperatures. The relationship between ε_r values and sintering temperatures revealed the same trend with that between densities and sintering temperatures since higher

Table 1
Dielectric constant (ε_r), dielectric quality factor ($Q \times f$), and temperature coefficient of resonant frequency (τ_f) of ZST ceramics with 1 wt% V_2O_5 addition at different sintering temperatures

Sintering temperature (°C)	Dielectric constant ε_r	Quality factor $Q \times f$ (at 7 GHz)	Temperature coefficient of resonant frequency τ_f (ppm/°C)
1260	30.5	32,000	3.6
1300	37.2	51,000	−2.1
1340	37.4	46,720	−2.0

density means lower pore ($\varepsilon_r = 1$). The dielectric constant increased from 30.5 to 37.4 as the sintering temperature increased from 1260 to 1340 °C. The decrease of ε_r value could be explained owing to lower densities as well as liquid phase effect. In addition, $Q \times f$ value did not reveal the same trend with the density. It was reported that the microwave dielectric loss was mainly caused not only by the lattice vibration modes, but also by the pores and the secondary phases [18,19]. Due to liquid phase sintering, inhomogeneous grain size distribution could happen. Therefore, the $Q \times f$ was arrived maximum at sintering temperature of 1300 °C and then decreased. The difference in grain size distribution was large as the sintering temperature increased to 1340 °C which revealed an increase in lattice imperfection and dielectric quality was then reduced [19]. The τ_f value is well known related to the composition and the secondary phase of the material. Although V_2O_5 additions cause some TiO_2 secondary phase to precipitate in grain boundary at low sintering temperature of 1150 °C, the amount of such secondary phase was less likely to be detected as sintering temperature increased up to 1300 °C. Therefore, the τ_f values did not change much in this experiment, indicating the V_2O_5 modified ZST ceramic is temperature stable. At the level of 1 wt% V_2O_5 addition, ZST ceramic sintered at 1300 °C gave the excellent microwave dielectric properties: ε_r value of 37.2, $Q \times f$ value of 51,000 (at 7 GHz) and τ_f value of −2.1 ppm/°C.

4. Conclusion

In this paper, the evidence of the liquid phase sintering in the V_2O_5 modified ZST microwave ceramics has been observed by using the transmission electron microscopy (TEM) and energy dispersive X-ray analysis (EDS). It was found that liquid phase resulted from the eutectic liquid in the ZrO_2–V_2O_5 system at the temperature higher than 700 °C. Additionally, the ZrO_2–V_2O_5 eutectic liquid caused the excess Ti to form a Ti rich compound, which was precipitated in the grain boundary during solid state reaction. The $Q \times f$ value of ZST ceramics can be promoted to be as high as 51,000 (at 7 GHz) at low sintering temperature of 1300 °C. However, the trace amount of TiO_2 did not affect the temperature coefficient of resonant frequency (τ_f).

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