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Low temperature processing of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics with improved Q factor

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ABSTRACT

Polycrystalline $(Zr_{0.8}Sn_{0.2})TiO_4$ (ZST) ceramics have been synthesized by solid-sate reaction method. The effect of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ glass addition (0.2–1.0 wt.%) on microwave dielectric properties of ZST ceramics are investigated. The increase in average grain size via growth of large grains and dissolution of small grains is explained by Ostwald ripening phenomena. The highest $Q \times f_0$ values are found to be 61,500, 48,500 and 51,900 GHz for the ZST dielectric resonators added with B_2O_3, $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$ respectively. The effect of liquid phase sintering on microstructure and microwave dielectric properties of ZST ceramics is discussed.

1. Introduction

Microwave ceramics are increasingly used for resonators, filters, duplexers and antenna systems for wireless communications. Especially, multilayer microwave devices are being investigated to let those devices increase volume efficiency. Multilayer chip inductors (MLCI) are one of the key surface mounted devices and have been extensively developed in recent years. These components are fabricated by lamination of ferrite and Ag electrode paste alternately and then co-fired to form a monolithic structure [1]. To keep up with the trend in miniaturization of electronic equipments and related components, particularly with the rapid development of integrated circuits and surface mounting technology, the demand for multilayer ceramic capacitors is increasing drastically [2]. Accordingly, low temperature co fired ceramics (LTCC) technology becomes more important for cost effectiveness. Often LTCC is used as substitute for multi chip modules (MCM). Integration proceeds by combining thick film and LTTC materials [3]. The sintering temperatures of microwave dielectrics such as ZST are too high to use low melting point electrodes. It was imperative to lower the sintering temperature of these microwave ceramics in order to use silver or copper electrodes i.e., the sintering temperature of co firing with high conductivity metals should be lower than the melting temperature of Ag (961 °C) or Cu (1064 °C) [4].

Lowering sintering temperature with glass additions is generally a most effective and least expansive technique. The motivation of this study with glass additions are (a) to reduce the sintering temperature of ZST and thereby the cost of production without any deterioration in the microwave dielectric properties, (b) to probe the relation between microstructure and quality factor, (c) to suppress the secondary phases and (d) to improve the microwave dielectric properties of ZST. The influence of these additives on phase, densification, microstructure and microwave dielectric properties on ZST is discussed. However, no systematic study on the effect of these additives to ZST ceramics has been reported previously.

2. Experimental

2.1. Sample preparation

Samples of $(Zr_{0.8}Sn_{0.2})TiO_4$ were synthesized by conventional solid-state reaction method from individual high-purity oxide powders ZrO_2, SnO_2 and TiO_2 all with 99.9% purity, Sigma Aldrich, USA. The staring materials were mixed according to the desired stoichiometry of $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics, with 1 wt.% addition of ZnO as a sintering aid. A planetary ball mill (Retsch, PM100) was used to prepare these powders. These powders were mixed at the wheel speed of 100 rpm for 1 h using zirconia balls and deionized water as milling media. The powders were dried and calcined at 1300 °C for 1 min. The calcined powders were again ball milled at the wheel speed of 300 rpm for 15 h to reduce the particle size. The particle size of the milled powder was obtained using a particle size analyzer (Zeta Sizer 3000 HSA). The glass additives were weighed stoichiometrically and mixed for 2 h in agate mortar using deionized water as a medium. Then it was melted above their deformation temperature and powdered (450 °C for B_2O_3, 610 °C for $ZnO–B_2O_3$ and 570 °C for $5ZnO–2B_2O_3$). The formation of the glassy phases was confirmed using X-Ray diffraction method. The calcined powders were remilled with different amounts (0.2–1.0 wt.%) of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ additions for 1 h. After remilling with different amounts (0.2–1.0 wt.%) of B_2O_3, $ZnO–B_2O_3$ or $5ZnO–2B_2O_3$ with the calcined powder, the fine powder is compacted in to cylindrical specimens by uniaxial pressing at 110 MPa pressure. The pellets were sintered at temperatures of

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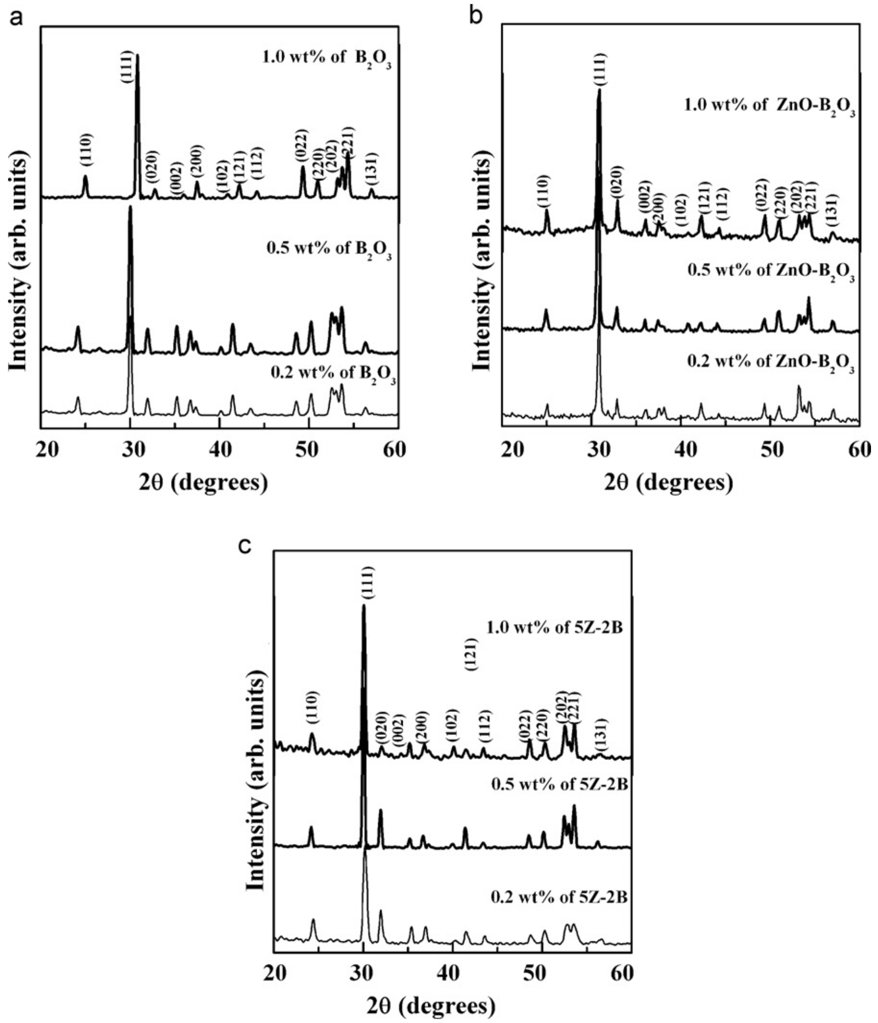

Fig. 1. (a) XRD patterns of the ZST ceramics added with (a) B_2O_3, sintered at 1150 °C for 3 h, (b) ZnO–B_2O_3, sintered at 1200 °C for 3 h, (c) 5ZnO–$2B_2O_3$, sintered at 1250 °C for 3 h.

1100–1250 °C for 3 h. The heating and cooling rates were 15 °C/min and 2 °C/min, respectively.

2.2. Characterization techniques

The crystalline phase of the calcined ZST powders and the sintered ZST ceramics was identified using X-Ray Diffractometer (Philips PW 1830). The microstructure of the sintered ZST ceramics was observed by Scanning Electron Microscopy (Philips XL 30 ESEM).

The theoretical relative bulk density (D) of the ZST–glass ceramics was calculated using the following equation:

$$D = \frac{W_1 + W_2}{\left[W_1/D_1 + W_2/D_2\right]} \tag{1}$$

where W_1 and W_2 are the weight percentage of the ZST matrix and glass with bulk densities D_1 and D_2 in the mixture, respectively [5]. The bulk densities of the ZST ceramics were measured by Archimedes method.

A vector network analyzer (Agilent 8722ES) was used to measure the microwave dielectric properties. Dielectric constant (ε_r) of the ZST dielectric resonators (DRs) was measured by using Hakki–Coleman method [6] as modified and improved by Courtney [7]. The Q factor was measured using reflection method with a cylindrical cavity having dimensions 3.0 times the DR. The rigid coaxial cable was provided at center of the cavity for electromagnetic field coupling and it can be moved in and out for adjusting between weak coupling and strong coupling. The cavity was connected to the network analyzer and rigid coaxial cable was adjusted in such a way that weak coupling exists between the rigid coaxial cable and DR. Weakly coupled condition was used to minimize the coupling losses. The unloaded Q_u value was calculated using the coupling coefficient and loaded Q_l value, using $Q_u = Q_l(1 + k)$, here k is the coupling coefficient, when the DR was in weakly coupled condition [8]. The temperature coefficient of resonance frequency (τ_f) at microwave frequency was measured using an invar cavity by heating the ZST ceramics from +25 °C to +80 °C.

3. Results and discussion

3.1. Crystal structure

The XRD patterns of the ZST ceramics added with B_2O_3, ZnO–B_2O_3 and 5ZnO–$2B_2O_3$ with different concentrations, sintered at 1150, 1200 and 1250 °C, for 3 h are shown in Fig. 1(a–c), respectively. All the samples showed a homogeneous phase with α-PbO orthorhombic structure and the space group of the structure is $D_{2\,h}^{14}$ = pbcn. The average initial particle size of the milled powder is 220 nm. The crystallite sizes of glassy additives added ZST ceramics were calculated from the Williamson-Hall plot (βCos θ vs. Sin θ). The mean crystallite sizes of glassy additives added ZST ceramics ranged between 40 and 65.5 nm. The lattice constants of the glassy additives added ZST ceramics were calculated and it is observed that there is no deviation from the pure ZST ceramics. Secondary phases were not observed up to the 1.0 wt.% level of these additives due to the fact that the detection of minor secondary phases by X-ray diffraction is extremely difficult. Even though no secondary phase is observed there are variations in peak intensities and splitting of the peaks.

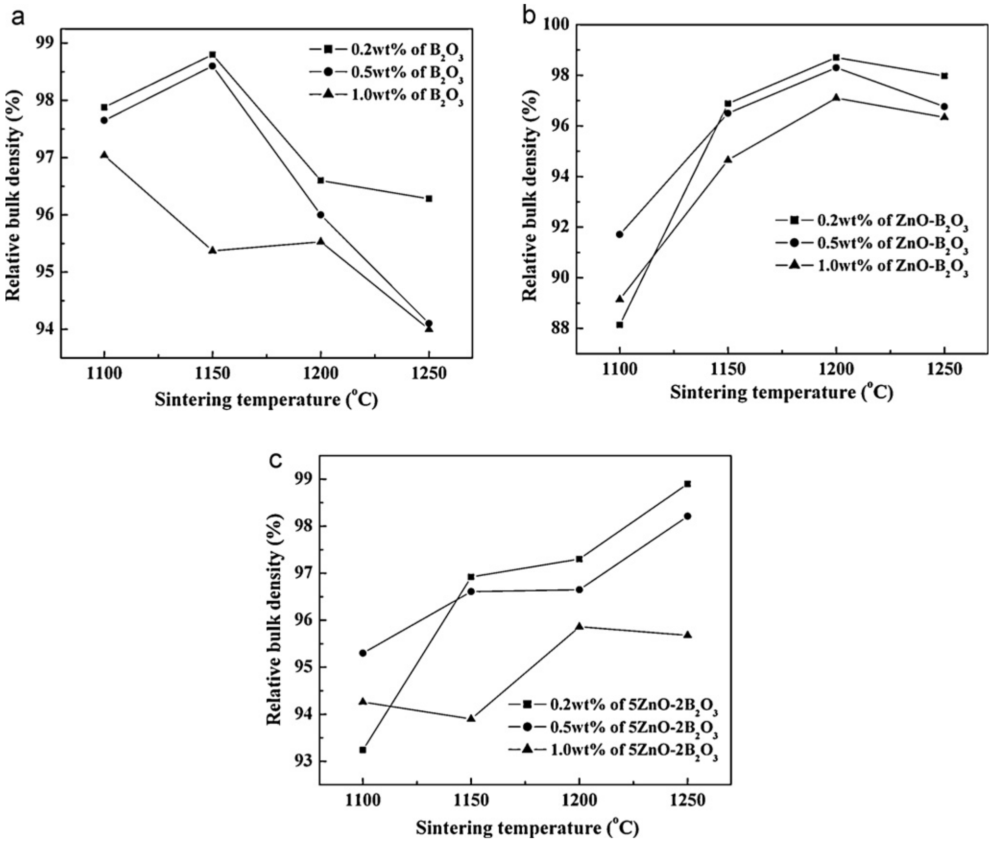

Fig. 2. (a) Variation in relative bulk density as a function of sintering temperature with different wt.% of B_2O_3, (b) variation in relative bulk density as a function of sintering temperature with different wt.% of ZnO–B_2O_3, (c) variation in relative bulk density as a function of sintering temperature with different wt.% of 5ZnO–2B_2O_3.

3.2. *Relative bulk density*

The variation in relative bulk density as a function of sintering temperature with different wt.% of glassy additives B_2O_3, ZnO–B_2O_3 (BZ) and 5ZnO–2B_2O_3 (5Z–2B) up to 1 wt.% is plotted in Fig. 2(a–c), respectively. In the case of ZST ceramics added with B_2O_3, relative bulk density of the samples decreased with increase in sintering temperature. All the samples were sintered in the 1100–1250 °C range for 3 h. In all cases it is found that as the wt.% of the glass additives is increased, the relative bulk density of the ZST ceramics decreased. The samples showed maximum densities of 98.6, 98.2 and 98.7 at 1150, 1200 and 1250 °C for the samples added with B_2O_3, ZnO–B_2O_3 and 5ZnO–2B_2O_3 respectively for 3 h of sintering. The difference in the sintering temperatures could be the consequence of the difference in the melting points of the glass additives used. The decrease in relative bulk density at higher sintering temperatures may be due to the evaporation of additives, non-uniform grain growth and formation of secondary phases. The decrease in sintering temperature is attributed to the flux formation by the glass additives.

The increase in relative bulk density and larger grain sizes obtained in the present study can be explained as follows: In liquid phase sintering, the surrounding particles will bring capillary pressure, and it could promote densification because particles would be realigned to get better packing. In addition, during liquid phase sintering, contact pressure between particles will be improved to promote mass transfer through dissolution and precipitation, as well as plastic deformation and vapor transfer resulting in grain growth. When a powder compact is sintered in the presence of a liquid phase, the relative bulk density of the compact increases and at the same time grains grow. The phenomenon in which the average grain size increases via growth of large grains and dissolution of small grains in a matrix is referred to as Ostwald ripening. Because of the capillary pressure exerted on a particle, its solubility in the matrix increases as the particle size decreases. Therefore, the atoms dissolved in the matrix from small particles and are transported to large particles, resulting in growth of large grains. Moreover fine particles have tremendous surface areas and surface energy. The finer the particle is, the higher is the surface energy [9]. The larger grains and higher densities obtained in the present study can be due to the uniform distribution of the glassy additives.

3.3. *Microstructure*

The microstructures of the ZST ceramics added with different glass additives B_2O_3, ZnO–B_2O_3 and 5ZnO–2B_2O_3 are shown in Figs. 3(a–c), 4(a–c) and 5(a–c), respectively where a, b and c corresponds to 0.2, 0.5 and 1.0 wt.% of the additive concentration. The sintering temperatures of ZST ceramics added with B_2O_3, ZnO–B_2O_3 and 5ZnO–2B_2O_3 were 1150, 1200 and 1250 °C, respectively and the sintering duration is 3 h in all cases. Samples added with 0.2 and 0.5 wt.% of B_2O_3 exhibited an average grain size of 12 and 18 μm respectively but the relative bulk density remained almost the same. In calculating the percentage of densification, the theoretical relative bulk density used was the value calculated using Eq. (1). Microstructure with 1 wt.% ZnO–B_2O_3 (Fig. 4c) is quite different and the relative bulk density is also low. In the case of other two glass additives, lower concentration of the additives gave the highest relative bulk density with uniform microstructure and the largest average grain size. With higher concentration of the additive, either the grain growth became non-uniform or grows in to smaller grains. It can be seen that the lower sintering temperatures are favoring densification with glassy additives. Compared to similar studies [4], the microstructure obtained in this study is

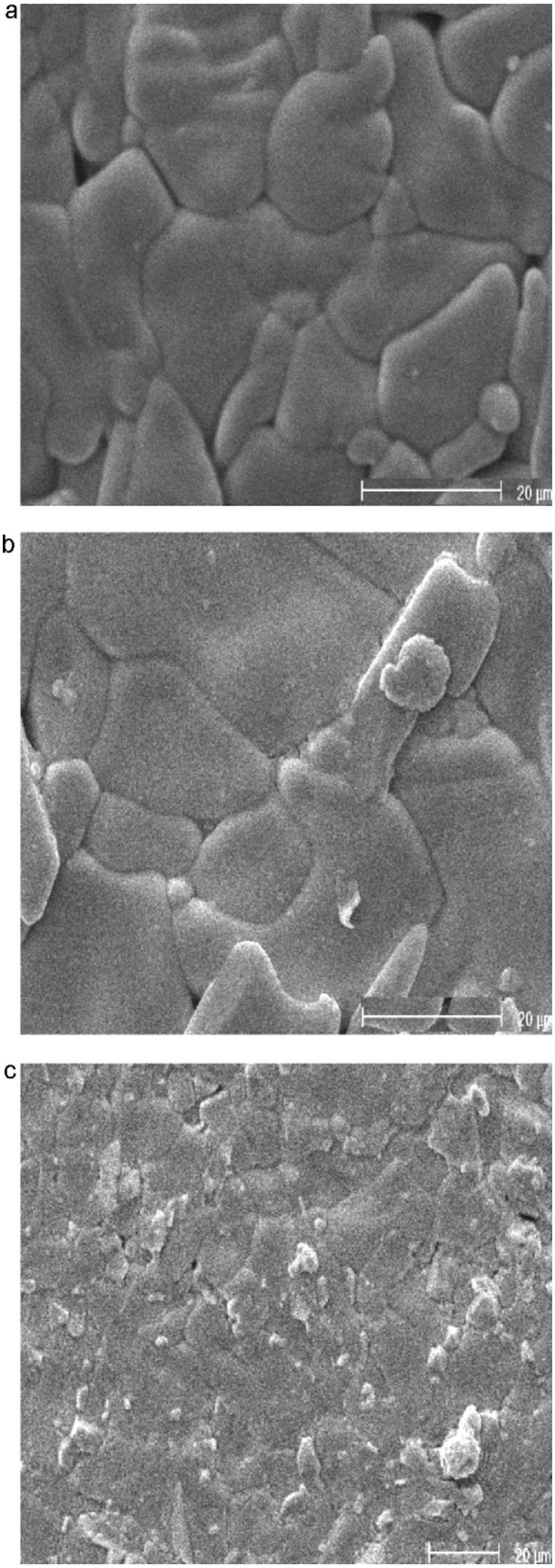

Fig. 3. SEM pictures of the ZST ceramics added with B_2O_3, sintered at 1150 °C for 3 h. (a) 0.2 wt.% of B_2O_3, (b) 0.5 wt.% of B_2O_3, (c) 1.0 wt.% of B_2O_3.

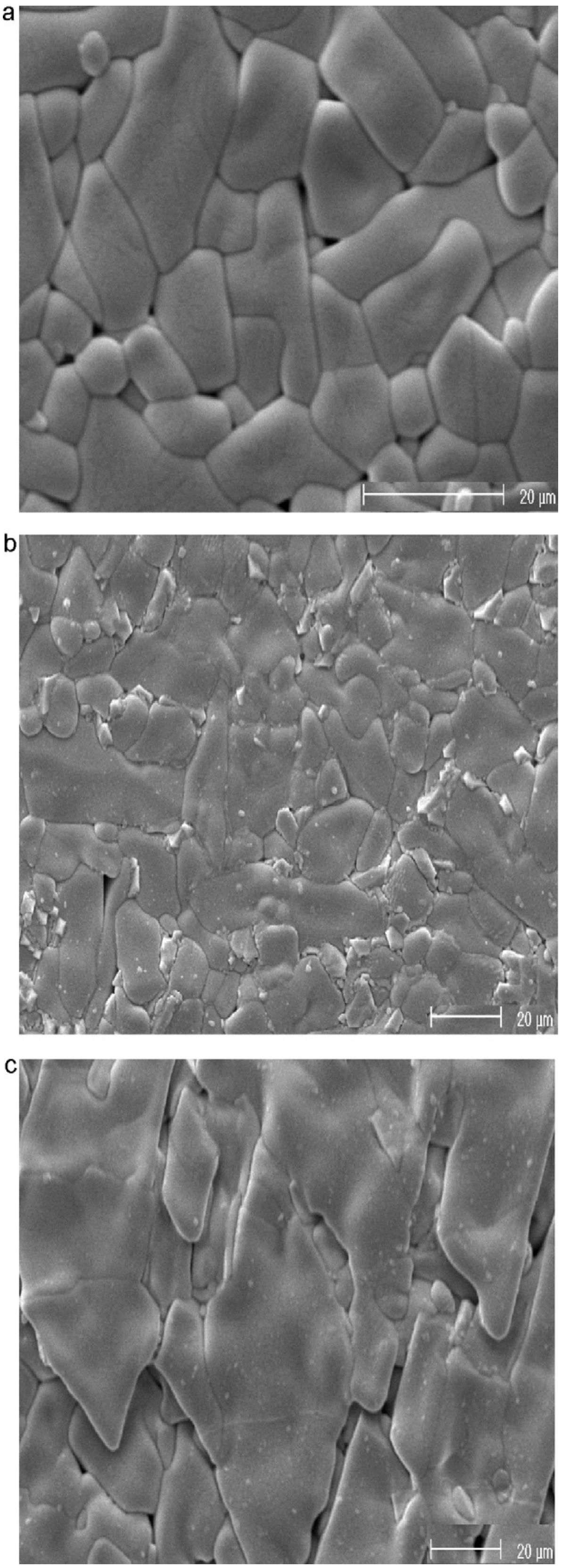

Fig. 4. SEM pictures of the ZST ceramics added with ZnO–B_2O_3, sintered at 1200 °C for 3 h. (a) 0.2 wt.% of ZnO–B_2O_3, (b) 0.5 wt.% of ZnO–B_2O_3, (c) 1.0 wt.% of ZnO–B_2O_3.

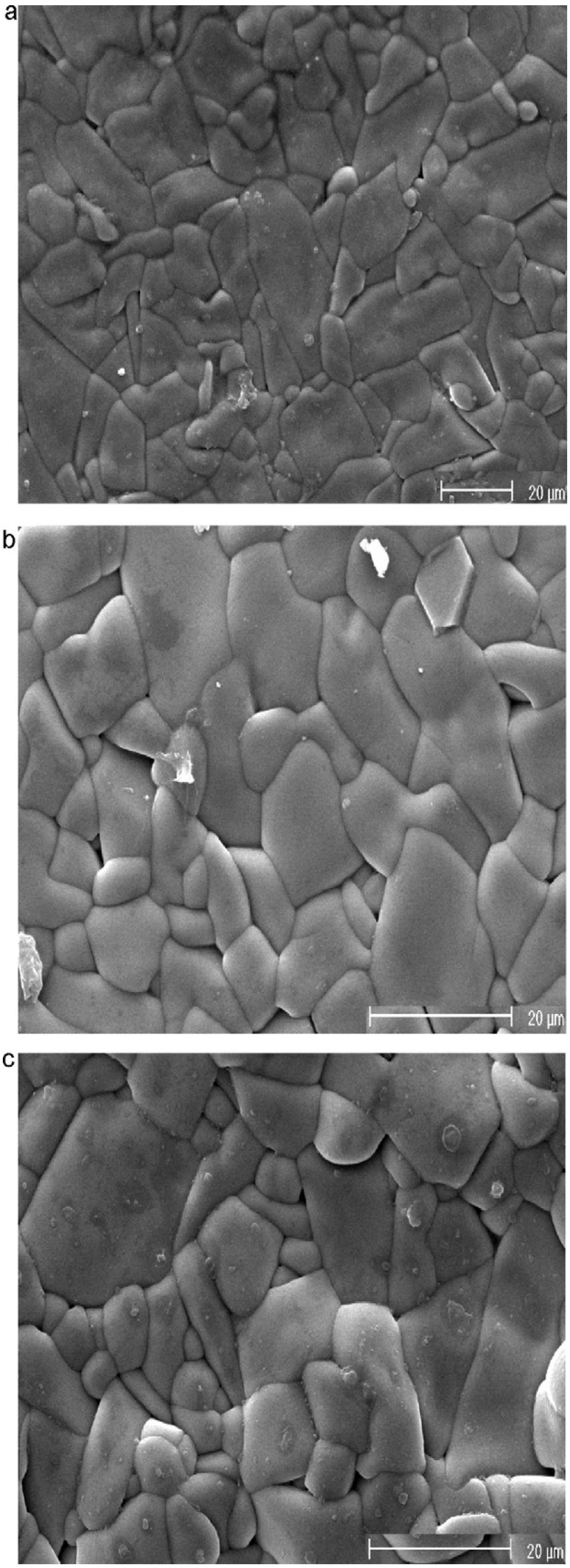

Fig. 5. SEM pictures of the ZST ceramics added with $5ZnO–2B_2O_3$, sintered at 1250 °C for 3 h. (a) 0.2 wt.% of $5ZnO–2B_2O_3$, (b) 0.5 wt.% of $5ZnO–2B_2O_3$ and (c) 1.0 wt.% of $5ZnO–2B_2O_3$.

better and that is attributed primarily to the reduced particle size (220 nm) of the powders used in this study. As the particle size decreases the driving force for the densification process increases because of the increased surface area resulting in increase in relative bulk density. It is interesting to note that higher relative bulk density cases gives uniform grain growth with higher average grain size which is ideal for good microwave dielectric resonator characteristics.

3.4. Microwave dielectric properties

The microwave dielectric constants of the ZST ceramics added with different glass additives are plotted in Fig. 6(a–c) for B_2O_3, $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$, respectively as a function of sintering temperature. In all the cases it is observed that the dielectric constant vs. sintering temperature with different wt.% of the additive concentration followed a similar trend as that of the relative bulk density vs. sintering temperature with different wt.% of the additive concentration. The dielectric constants of the ZST ceramics added with B_2O_3 are ranged from 32.3 to 38.7 and for the samples added with $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$, they are ranged between 29–38.2 and 31.5–39.1, respectively.

The $Q \times f_o$ values of the ZST ceramics added with different wt.% of B_2O_3, $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$ as a function of sintering temperature are shown in Fig. 7(a–c), respectively. The maximum $Q \times f_o$ values of the ZST ceramics added with different glass additives are found to be 61,500, 48,500 and 51,900 GHz for the samples added with B_2O_3, $ZnO–B_2O_3$ and $5ZnO–2B_2O_3$, respectively showing that B_2O_3 gave the best results in this series. The lower $Q \times f_o$ values with increase in the concentration of $ZnO–B_2O_3$ is due to the secondary phases segregated at the grain boundary and the non-uniform grain growth as clearly observed from the SEM picture (Fig. 3b and c). However it is worth noting that with only 1 wt.% $ZnO–B_2O_3$, the abnormal grain growth is observed in the SEM picture, which is an indication of secondary phase, giving rise to increase in losses.

3.5. Discussions

In general, the microwave dielectric losses have the intrinsic and extrinsic origins. The intrinsic losses are due to the anharmonic forces that mediate the interaction between crystal lattice modes and electromagnetic radiation, which leads to damping of the optical phonons. On the other hand the extrinsic losses are caused by the extended dislocations, grain boundaries, porosity, oxygen vacancies and secondary phases [10,11], which are heavily dependent on processing conditions. These losses are caused mainly by the dipolar relaxation of the defect-oriented polarizations concentrated at the interfaces [12].

In the present study the increase in $Q \times f_o$ values goes with the increase in relative bulk density and the uniform grain size. Significantly, with smaller particle size and with small amounts of glass additives the microstructure and the microwave dielectric properties of the ZST ceramics improved even at lower sintering temperatures. There is not much variation in dielectric constant among the samples where maximum densification is achieved, but the $Q \times f_o$ values are affected with these additives. The specimen with large grain size is expected to have a high $Q \times f_0$ value because the grain growth decreases the grain boundary area [12]. The comparison between the properties of the unmodified and modified $(Zr_{0.8}Sn_{0.2})TiO_4$ ceramics along with their sintering conditions, bulk densities and the microwave dielectric properties are given in Table 1 [13]. The milling conditions were kept constant except for pure ZST ceramics. In the case of pure ZST ceramics, the powders were milled for 10 h. From Table 1, it is clear that the samples added with 0.2 wt.% B_2O_3 alone and 0.2 wt.% $5ZnO–2B_2O_3$ exhibited better microwave dielectric properties compared to pure

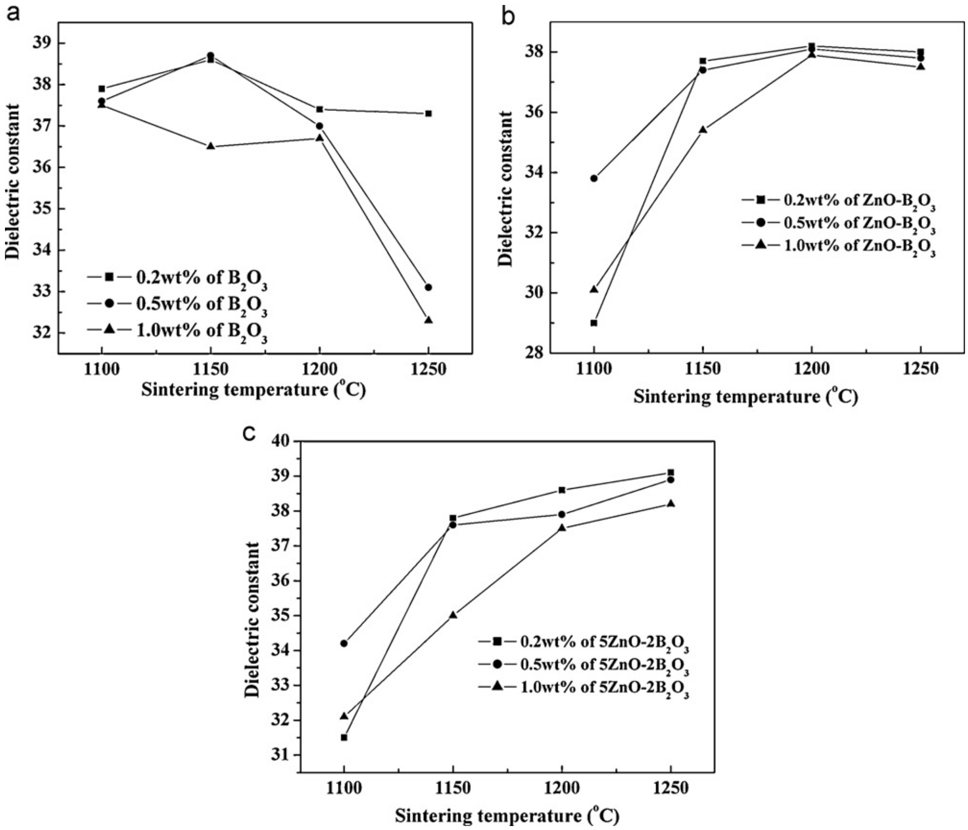

Fig. 6. (a) Variation in dielectric constant as a function of sintering temperature with different wt.% of B_2O_3, (b) variation in dielectric constant as a function of sintering temperature with different wt.% of ZnO–B_2O_3 and (c) variation in dielectric constant as a function of sintering temperature with different wt.% of 5ZnO–$2B_2O_3$.

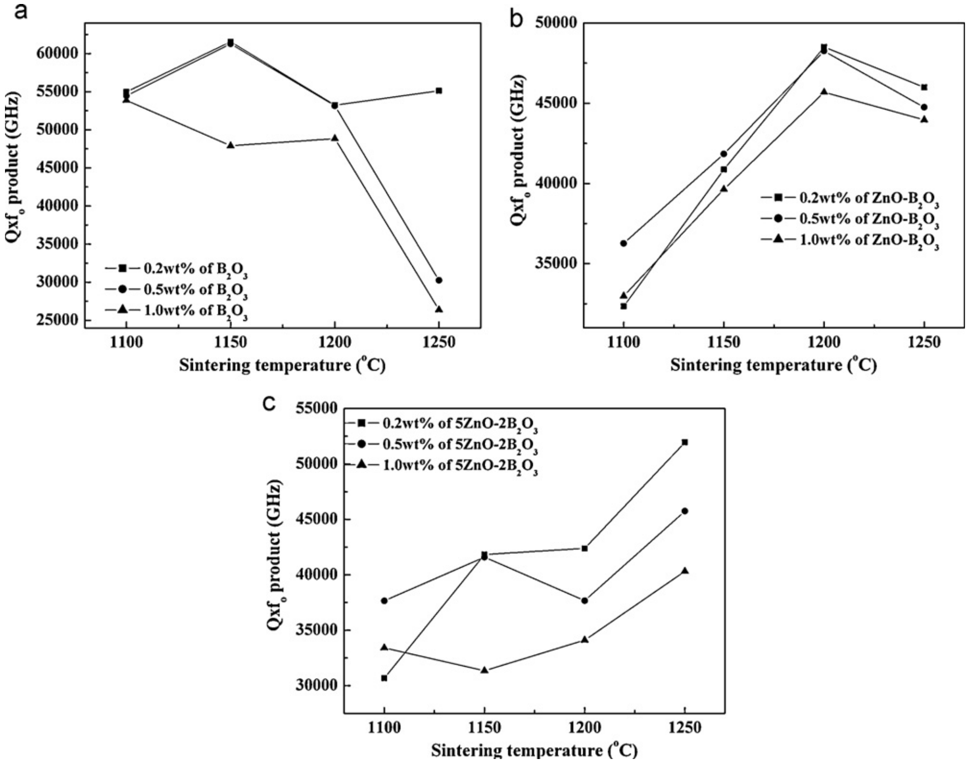

Fig. 7. Variation in (a) $Q \times f_0$ as a function of sintering temperature with different wt.% of B_2O_3. (b) $Q \times f_0$ as a function of sintering temperature with different wt.% of ZnO–B_2O_3. (c) $Q \times f_0$ as a function of sintering temperature with different wt.% of 5ZnO–$2B_2O_3$.

Table 1
Comparison between doped and undoped ZST ceramics.

Sintering additive	Sintering temperature and duration	Density (ρ%)	Dielectric constant (ε_r)	Quality factor product, $Q \times f_0$ (GHz)	Grain size (μm)
Pure ZST	1650 °C–3 h	94.1	36.1	39000	14
ZST + 1 wt.% ZnO	1350 °C–4 h	97.4	39.3	49600	18
ZST + 1 wt.% ZnO + 0.2 wt.% B_2O_3	1150 °C–3 h	98.8	38.7	61500	12
ZST + 1 wt.% ZnO + 0.2 wt.% ZnO–B_2O_3	1200 °C–3 h	98.7	38.27	48500	9.5
ZST + 1 wt.% ZnO + 0.2 wt.% 5ZnO–2B_2O_3	1250 °C–3 h	98.9	39.1	51900	11

ZST and 1 wt.% ZnO added ZST ceramics. In the case of the samples added with ZnO–B_2O the SEM pictures showed abnormal grain growth which is an indication of the presence of secondary phases. From this study it is clear that addition of glassy additives reduced the extrinsic losses of the ZST ceramics. At higher sintering temperatures (1400 °C) ZnO volatizes which may create some loss due to the variation in stoichiometry in the ceramics whereas in the present study the samples were sintered around 1100 °C which prevents the volatization of ZnO. Table 1 shows that with ZnO and ZnO + B_2O_3 additives, the $Q \times f_0$ value increases progressively while sintering temperatures decreases, a very attractive change for this material. In addition, cooling rate also plays a role in the dielectric properties of ZST as a slow cooling allows settling-in of a local cation ordering [14,15]. This is also consistent with the results by Petzelt et al. [16], Wang et al. [17] and Azough et al. [18], that annealing and slow cooling could decrease the dielectric loss. The increase in the $Q \times f_0$ value also possibly due to the reduction in oxygen vacancies during the slow cooling. This goes well with the observation here that larger grains gives smaller losses as larger grain can be more ordered with properties approaching that of a single crystal. In the present study, a slow cooling rate of 2 °C/min is employed. An ordered structure tends to exhibit less anhormonicities and hence reduced losses and temperature dependence. In the present study the increase Q value is primarily attributed to the increase in relative bulk density and increase in uniform grain size. It is found that the ZST ceramics added with B_2O_3 would be a suitable candidate for LTCC applications.

The temperature coefficient of resonant frequency (τ_f) is known to be related to the composition and secondary phases in the material. Since ZST ceramics are temperature stable and the addition of B_2O_3, ZnO–B_2O_3 or 5ZnO–2B_2O_3 did not cause any noticeable secondary phases, the (τ_f) values did not change much. The addition of B_2O_3 showed negative value of τ_f (−1 to −4 ppm/°C), as the concentration of ZnO–B_2O_3 increases, τ_f value changed from positive value to negative value (+2 to −5.4) and the addition of 5ZnO–2B_2O_3 showed positive value of τ_f (+1 to 3 ppm/°C).

4. Conclusions

Microwave dielectric properties of the ZST ceramics with the addition of B_2O_3, ZnO–B_2O_3 or 5ZnO–2B_2O_3 have been studied systematically. It is observed that the sintering temperature of the ZST ceramics have been reduced to 1150, 1200 and 1250 °C with the addition of B_2O_3, ZnO–B_2O_3 and 5ZnO–2B_2O_3, respectively. The effect of glassy additives on structure, microstructure and microwave dielectric properties has been discussed. The microstructure of the ZST ceramics has been improved with low concentrations of these additives. The maximum $Q \times f_0$ values of the ZST ceramics added with different glass additives are found to be 61,500, 48,500 and 51,900 GHz for the samples added with B_2O_3, ZnO–B_2O_3 and 5ZnO–2B_2O_3, respectively. The phenomena behind the increase in grain size and relative bulk density were explained by Ostwald ripening. The improvement in $Q \times f_0$ value is primarily attributed to the increase in uniform grain size and the relative bulk density.

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References

[1] R. Zou, L. Li, Z. Gui, Ceram. Int. 26 (2000) 673–676.
[2] N. Setter, R. Waser, Acta Mater. 48 (2000) 151–178.
[3] W.C. Tzou, C.F. Yang, Y.C. Chen, P.S. Cheng, J. Eur. Ceram. Soc. 20 (2000) 991– 996.
[4] T. Takada, S.F. Wang, S.Y. Yoshikawa, S.J. Jang, R.E. Newnham, J. Am. Ceram. Soc. 77 (1994) 2485–2488.
[5] K.P. Surendran, P. Mohanan, M.T. Sebastian, J. Solid State Chem. 177 (2004) 4031–4046.
[6] B.W. Hakki, P.D. Coleman, IEEE Trans. Microwave Theory Technol. 18 (1960) 402–410.
[7] W.E. Courtney, IEEE Trans. Microwave Theory Technol. 18 (1970) 476–485.
[8] D. Kajfez, P. Guillon, Dielectric Resonators, Artech House, Dedham, MA, 1986.
[9] L.K. Suk-Joong, Sintering, Elsevier, Burlington, MA, 2005.
[10] W.S. Kim, T.H. Hong, E.S. Kim, K.H. Yoon, Jpn. J. Appl. Phys. 37 (1998) 5367–5371.
[11] K.H. Yoon, Y.S. Kim, E.S. Kim, J. Mater. Res. 10 (1995) 2085–2090.
[12] C.L. Huang, M.H. Weng, H.L. Chen, Mater. Chem. Phys. 71 (2001) 17–22.
[13] D. Pamu, G. Lakshmi Narayana Rao, K.C. James Raju, Adv. Appl. Ceram. 106 (2007) 203–208.
[14] R. Christoffersen, P.K. Davis, J. Am. Ceram. Soc. 75 (1992) 563–569.
[15] A.E. McHale, R.S. Roth, J. Am. Ceram. Soc. 69 (1986) 827–832.
[16] I. Petzelt, S. Pacesova, J. Fousek, S. Kamba, V. Zeleny, V. Koukal, J. Schwarzbach, B.P. Gorshunov, A.A. Volkov, Ferroelectrics 93 (1989) 77–85.
[17] C.L. Wang, H.Y. Lee, F. Azough, R. Feer, J. Mater. Sci. 32 (1997) 1693–1701.
[18] F. Azough, R. Freer, J. Petzelt, J. Mater. Sci. 28 (1993) 2273–2276.