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Effects of glass additions on the microstructure and dielectric properties of barium strontium titanate (BST) ceramics

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Abstract

Commercial glass frits (lead borosilicate glasses) were employed as the sintering aids to reduce the sintering temperatures of BST ceramics. The effects of the glass content and the sintering temperature on the microstructures, dielectric properties and tunabilities of BST ceramics have been investigated. Densification of BST ceramics of 5 wt% glass content becomes significant from sintering temperature of 1000 °C. The glass content shows a strong influence on the Curie temperature T_c, permittivity and the diffuse transition. X-ray results show all BST ceramics exhibit a perovskite structure and also the formation of a secondary phase, $Ba_2TiSi_2O_8$. The shift of BST diffraction peaks towards higher angle with increasing the glass content indicates the substitution of Pb^{2+} in Ba^{2+} site, which mainly accounts for the diffuse transition observed in these BST ceramics. BST ceramics with 10 wt% glass additives possess the highest tunability at all four sintering temperatures. A tunability of 12.2% at a bias field of 1 kV/mm was achieved for BST ceramics with 10 wt% glass content sintered at 900 °C.

Keywords: Dielectric properties; Sintering; Glass frit; (Ba, Sr)TiO_3

1. Introduction

In the past decades, barium strontium titanate, (Ba, Sr)TiO_3, has attracted much attention in the development of tunable microwave devices as it exhibits a large change in dielectric constant with an applied dc electric field. Thick film processes, with the potential of being cost-effective and to integrate with low temperature co-fired ceramic (LTCC) systems, have recently been applied to BST in delivering tunable components such as filters, varactors, and phase shifters for microwave telecommunication applications[1–3] alongside the well-studied thin film process.[4] Conventional solid state synthesis of BST ceramics requires high sintering temperatures of 1350–1450 °C. This has become an apparent barrier in developing BST thick film devices for frequency agile microwave applications because, at this temperature range, BST films inter-react strongly with alumina substrates and most electrodes will suffer severe damage.

Glass compositions such as B_2O_3–SiO_2,[5,6] BaO–Al_2O_3–SiO_2,[7] and B_2O_3–Li_2CO_3,[3] etc. have been utilised as additives in BST ceramics and thick films to reduce the sintering temperature and promote densification. It was reported that the doping of PbO could increase the T_c of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films,[8] and the further increase of the lead content to a composition of $(Ba_{0.25}Pb_{0.25})Sr_{0.5}TiO_3$ could enhance the tunability and induce the diffuse phase transition of such BPST thin films.[9]

In previous work, a commercial glass frit, lead borosilicate, was demonstrated to be useful for $Ba_{0.55}Sr_{0.45}TiO_3$ thick films sintered at 900 °C with a compatible performance to undoped $Ba_{0.7}Sr_{0.3}TiO_3$ thick films sintered at 1260 °C.[10] The current work has been undertaken to investigate the effects of such a commercial lead borosilicate glass frit and the sintering temperatures on the microstructures, dielectric properties and tunabilities of the $Ba_{0.55}Sr_{0.45}TiO_3$ ceramics, in order to improve our understanding of the development of BST thick films employing such a glass phase.

2. Experimental

BST powders with Ba/Sr = 55/45 made by conventional solid-state routes were supplied by Powerwave Technologies. Glass frit (42C1, Johnson Matthey Colour Technologies,

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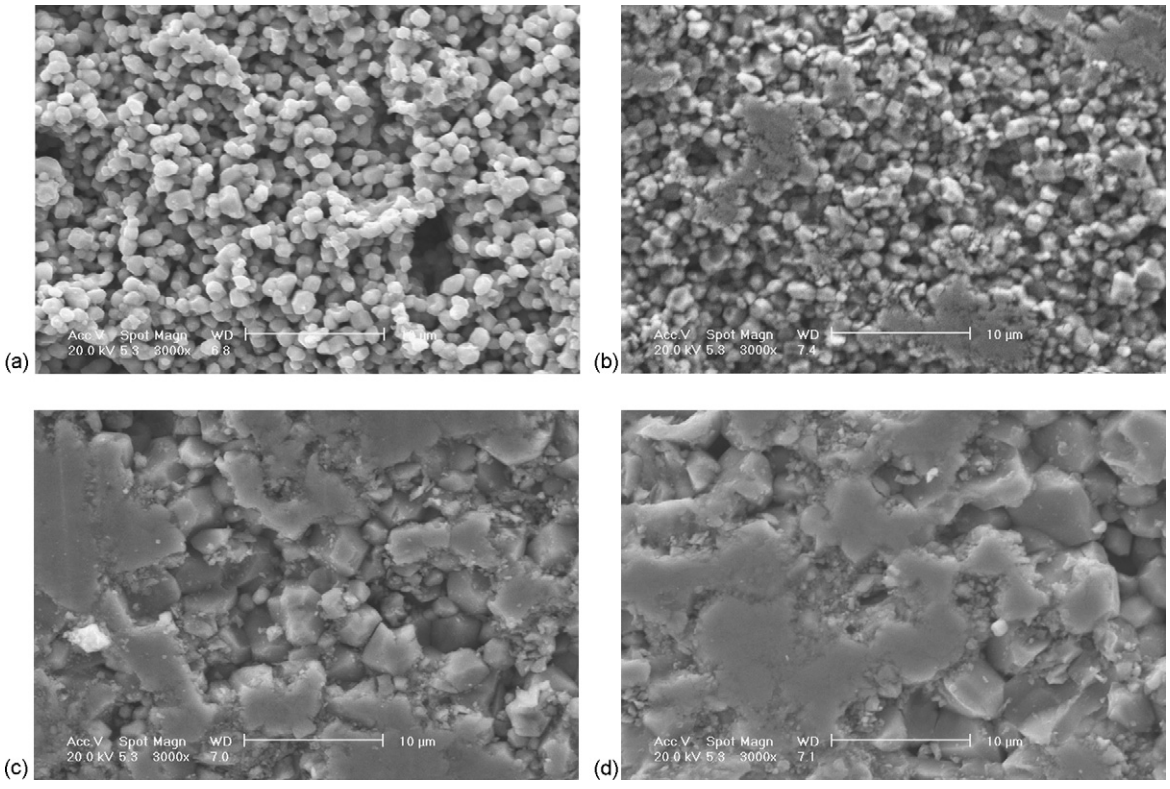

Fig. 1. SEM micrographs of BST ceramics with 5 wt% glass frit sintered at temperatures of (a) 900 °C; (b) 1000 °C; (c) 1100 °C; and (d) 1200 °C for 2 h, respectively.

Stoke-on-Trent, UK) was used as the sintering aid. This frit has a density of 6.1 g cm^{-3}, comprising primarily of oxides of Pb, Si and B, and has a melting point ~520 °C.[11] The glass frits were added to BST powders in proportion of 5–30 wt%. The weighed BST and glass frit powders were ball milled for 16 h in isopropanol with zirconia media. After drying, the powders were die-pressed into pellets and fired in air at temperatures from 850 to 1200 °C for 2 h using a heating rate of 5 °C/min.

A Philip X'pert X-ray diffraction was used to characterise the crystallisation of the sintered ceramics with monochromatic Cu K_α radiation with a step size of 0.02° and a speed of 1.2°/min. The density and shrinkage were calculated from the measured weights and dimensions. The microstructures of the BST-glass ceramics were observed using a Philips XL30 scanning electron microscopy and the samples were prepared by sectioning a thin slice using a diamond wafer. The dielectric properties were characterised using an impedance analyser (HP 4914A) with a metal-ferroelectric-metal (MFM) capacitor configuration at frequencies from 100 Hz to 10 MHz and over the temperature range from −70 to 70 °C. The tuneability of the BST-glass ceramics was measured at 10 kHz with a bias electric field up to 1 kV/mm and calculated from $1 - \varepsilon(V)/\varepsilon(0)$, where $\varepsilon(V)$ and $\varepsilon(0)$ is the relative permittivity with bias V volts and without bias, respectively.

3. Results and discussion

The cross-sectional SEM micrographs of BST ceramics with 5 wt% glass frit sintered at different temperatures are shown in Fig. 1. The sample sintered at 900 °C (in Fig. 1(a)) shows an obvious porous microstructures and the smallest grain size. Increasing the temperature by 100 °C greatly promoted the densification while the grain size still remained small (Fig. 1(b)). Further increase of the sintering temperature led to much denser microstructures and considerably increased grain sizes. This indicates the glass phase can provide the liquid when the sintering temperature is above 900 °C, and enhance the densification of BST at lower sintering temperatures through a liquid phase sintering mechanism.

Fig. 2 shows cross-sectional SEM micrographs of BST ceramics sintered at 1100 °C for 2 h with different content of glass frit. All the samples exhibit a similar microstructure at this temperature despite the large difference in the sintering aid content. The samples containing lower glass frit contents of 5 and 10 wt% exhibited slightly larger grain sizes than those of higher glass contents. No obvious glass phase can be found in these samples with even high glass content, possibly indicating a strong volatilization of PbO at this sintering temperature.

The glass frit introduced as the sintering aid contains a large amount of PbO and SiO_2 and very small amount of B_2O_3 and TiO_2. Fig. 3 shows the X-ray diffraction patterns of the BST ceramics which contain various glass frit contents and were sintered at 1100 °C for 2 h. All the samples exhibited a perovskite structure and also the formation of a secondary phase, which shows increased intensity with increasing glass content. Divya and Kumar[6] reported the formation of such a secondary phase, $Ba_2TiSi_2O_8$, in the BST ceramics would occur when borosilicate glass content was over 5 mol% and the firing temperature was above 850 °C, with which our results are consistent. It is common for the formation of $Ba_2TiSi_2O_8$ secondary phase in

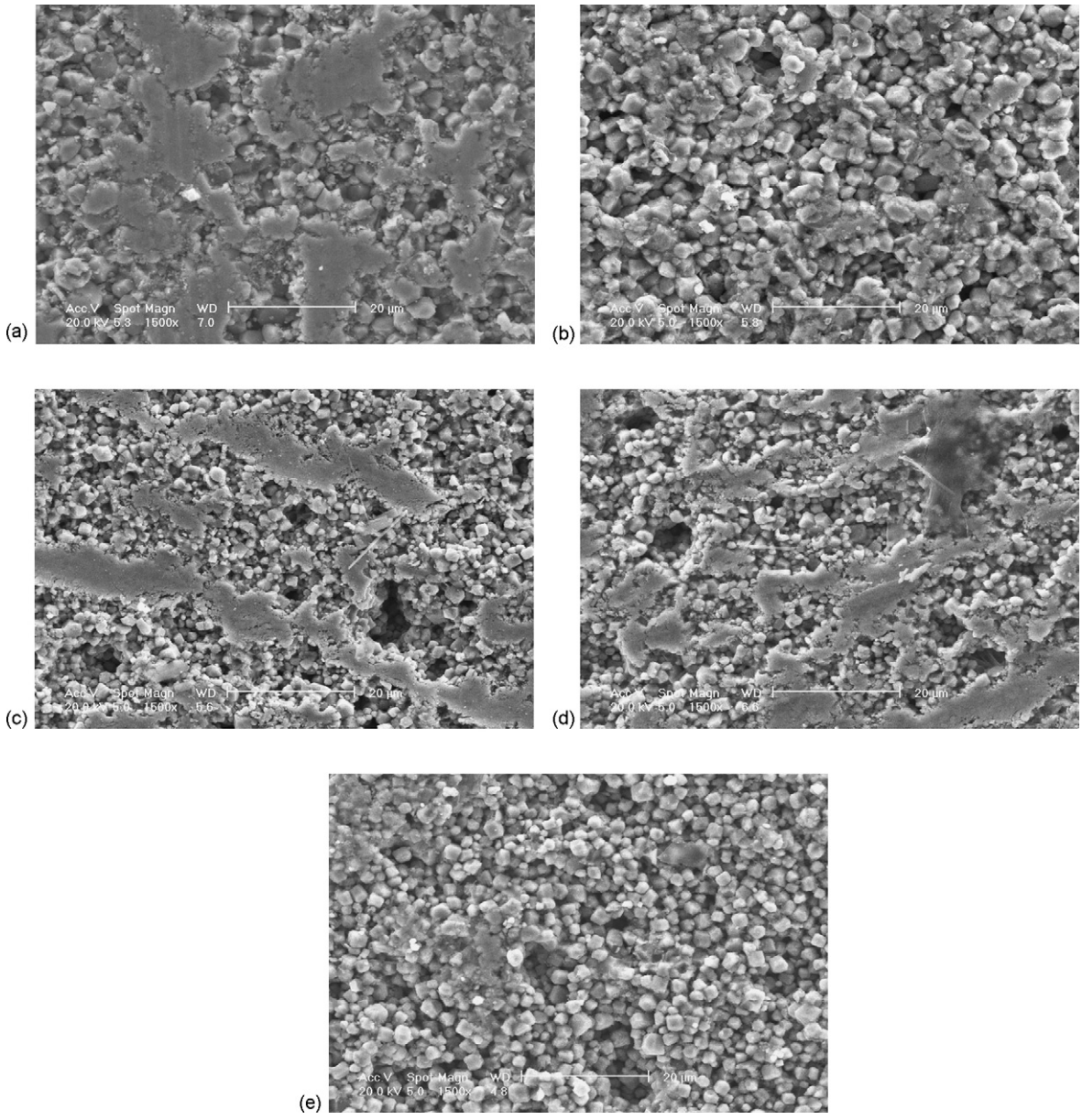

Fig. 2. SEM micrographs of BST ceramics sintered at 1100 °C for 2 h with different amount of glass frit: (a) 5 wt%; (b) 10 wt%; (c) 15 wt%; (d) 20 wt%; and (e) 30 wt%.

the BST ceramics when introducing the glass composition containing SiO_2.[6,7,12] The sample with the lowest glass frit content of 5 wt% only shows a slight trace of the secondary phase. The glass frit contains a large amount of PbO. During the sintering, much lead oxide will be lost due to its volatile nature in an unprotected environment. In addition, some lead may enter the BST lattice and substitute with Ba site. It was noted that all peaks of BST shift slightly towards higher angle with increasing glass content, revealing the smaller lattice parameters of BST with the increase of the glass content. This is due to the smaller ionic radius of Pb^{2+} (1.19 Å) as compared to the ionic radius of Ba^{2+} (1.35 Å).[9]

The temperature dependence of dielectric properties, ε_r and $\tan\delta$, of the BST ceramics containing different amount of glass frit sintered at 1100 °C are shown in Fig. 4. With the increase of the glass content, the Curie temperature T_c shifted to higher temperature and the transitions became more diffuse, and the permittivity at T_c decreased accordingly. The variation in Curie temperature with glass content is plotted in Fig. 5, revealing an approximately linear relationship between T_c and the glass content in the BST ceramics. The shift of T_c is around 75 °C from 5 to 30 wt% glass contents. It has been reported that the clamping effect on the ferroelectric crystallites by the glass matrix could cause small deviations in T_c around 2 °C.[13] However, the large shift of T_c observed here indicates the compositional change of the ferroelectric phases. With the addition of PbO contained glass frit, Pb^{2+} will substitute on the Ba^{2+} site and result in the formation of regions of $PbTiO_3$, which has higher T_c of 485 °C than that of BST with the possible maximum T_c of 120 °C for $BaTiO_3$. This can explain the shift of T_c of BST ceramics to

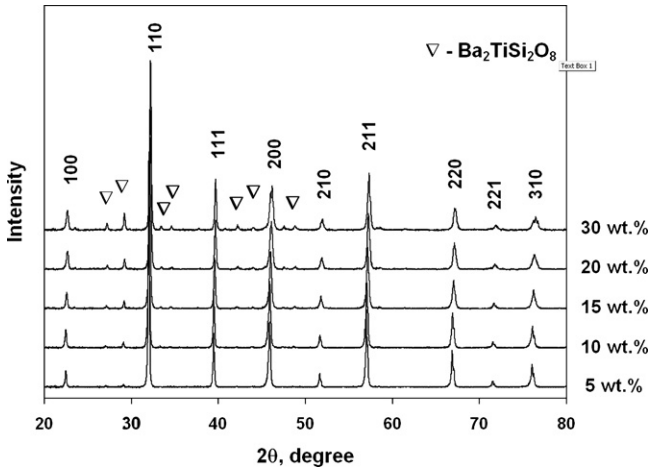

Fig. 3. XRD results of BST ceramics with different glass frit contents sintered at 1100 °C for 2 h.

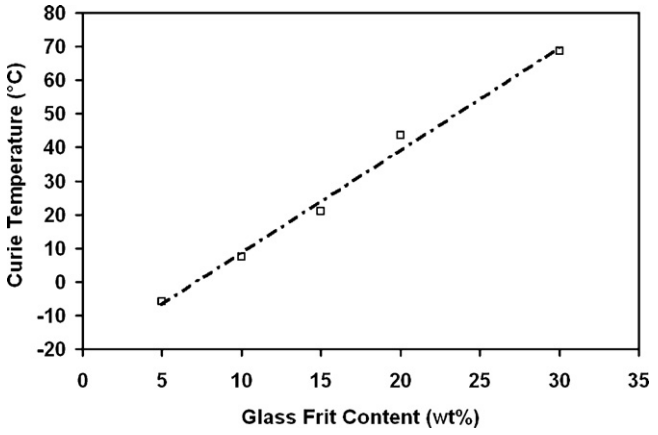

Fig. 5. Effects of glass frit contents on the Curie temperature of BST ceramics sintered at 1100 °C for 2 h.

higher temperatures with the addition of the glass frit, which was also observed in Pb doped BST thin films.[9]

The diffuse phase transition is related strongly to the addition of the glass phase. The cations introduced with the glass phase can enter into BST lattices, leading to the change of dielectric properties, and the observation of relaxor behaviour and diffuse transitions.[7] With increasing the amount of the glass content, the peaks of the secondary phase became stronger, as shown in Fig. 3 of the XRD result, and meanwhile, as shown in Fig. 2, the BST grain sizes reduced. Both the effects can lead to the decrease in permittivity and the broadening of the transition peak. More importantly, the substitution of Pb^{2+} in Ba^{2+} site and consequently, the formation of $PbTiO_3$ phase in BST can generate an uneven distribution of BST composition, leading to an enhancement of the broadening effects.

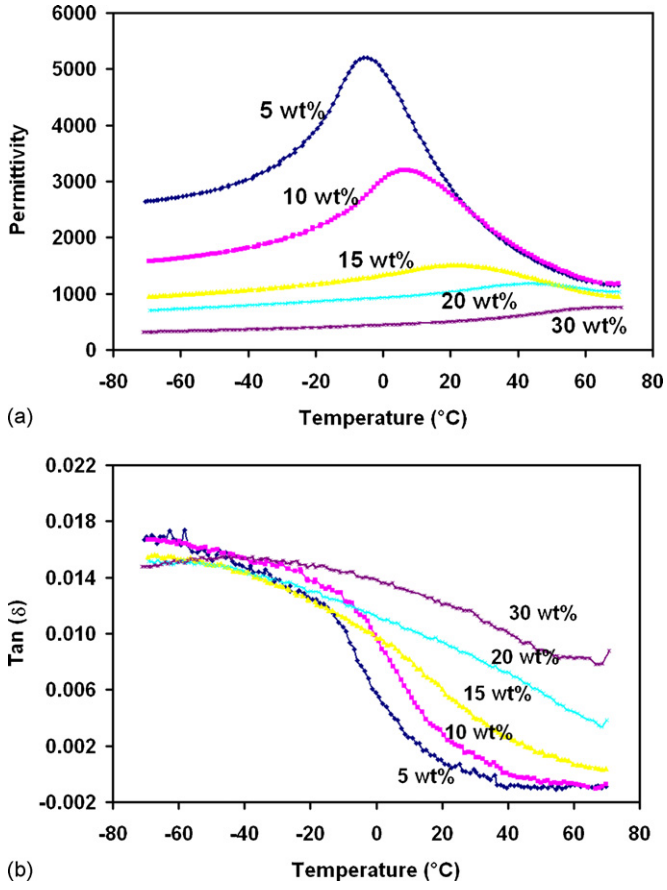

Fig. 4. Effects of glass frit contents on the dielectric properties of BST ceramics sintered at 1100 °C: (a) permittivity as a function of temperature and (b) loss tangent as a function of temperature. The measurements were carried out at 10 kHz.

The effect of glass content on the dielectric loss is shown in Fig. 4(b). In the low temperature ferroelectric regions, the dielectric losses were almost independent of glass content and can be attributed to the domain wall movement in the ferroelectric phase. It can also be noted that the BST ceramics with higher glass contents show slightly lower loss, suggesting the effect of the high electrical resistance and low dielectric loss by adding the glass phase.[14] On the contrary, this effect is reversed at room temperature as the loss increased steadily with increasing glass content. Increased Pb^{2+} substitutions lead to additional $PbTiO_3$ with increasing glass content, and contribute to stronger polar behaviour at room temperature.

The properties of the BST ceramics with different amount of glass frit sintered at different temperatures are summarized in Table 1. For each given composition, increasing the sintering temperature led to higher density of BST ceramics, and generally improved dielectric properties with higher permittivity and lower dielectric loss. At the same sintering temperature, higher glass contents generally resulted in increased density of BST ceramics, and this effect is more obvious in the samples sintered at lower temperatures.

Although higher glass contents are effective in promoting liquid phase sintering at low sintering temperatures and enhancing the densification of the BST ceramics, the dielectric properties deteriorate markedly, becoming particularly poor for materials with glass contents >20 wt%. However, BST ceramic samples with 5 and 10 wt% glass additives exhibit much lower dielectric losses at room temperature. The tunability of BST ceramics with different glass contents sintered at different temperatures are listed in Table 1 and calculated based on the value obtained at the electric field of 1 kV/mm. The samples with 10 wt% glass

Table 1
Properties of BST ceramics with different amount of glass frit.

Content of glass frits (wt%)	Sintering temperature (°C)	Shrinkage (%)	Density (g cm^{-3})	ε_r (20 °C)	Tan δ (20 °C)	Tunability (%) at 1 kV/mm
5	900	5.89	3.44	802	0.004	7.3
	1000	12.64	4.43	1691	0.002	11.8
	1100	16.43	5.14	2932	0.001	13.8
	1200	17.13	5.21	3056	0.0001	17.4
10	900	8.14	3.78	748	0.005	12.2
	1000	14.65	4.81	1807	0.006	13.0
	1100	17.05	5.18	2796	0.003	19.7
	1200	17.91	5.23	2982	0.004	21.8
15	850	7.67	3.42	413	0.007	–
	900	13.18	4.28	721	0.007	5.1
	1100	18.99	5.10	1512	0.006	14.3
20	850	5.97	3.39	333	0.008	–
	900	11.16	4.02	504	0.009	5.1
	1100	17.29	5.07	1033	0.009	11.0
30	850	6.59	3.66	189	0.010	–
	900	13.41	4.49	335	0.012	–
	1100	16.43	4.96	504	0.012	5.1

The dielectric property and tunability were measured at 10 kHz and 20 °C.

additives show the highest tunability of 12–22% at all four sintering temperatures. Interestingly this composition sintered at 900 °C shows reasonably high tunability compared to those sintered at much higher temperatures, although its density is rather low. However, its reasonable good dielectric loss property and much lower permittivity make it a good candidate for microwave tunable applications. This composition is consistent with our previous report of employing 10 wt% of such a glass frit in BST thick films for the purpose of lowering the sintering temperatures, revealing a competitive tunability of the films sintered at 900 °C.[10]

4. Conclusions

Lead borosilicate glasses additives have a strong influence on the microstructures, dielectric properties and tunabilities of BST ceramics. Densification of BST ceramics containing 5 wt% glass content becomes significant from sintering temperature of 1000 °C. At a sintering temperature of 1100 °C, BST ceramics containing lower glass contents exhibited larger grain sizes, and showed no obvious trace of glass phase, indicating a strong volatilisation of PbO at this sintering temperature. A perovskite structure was revealed for all BST samples but the formation of a secondary phase, $Ba_2TiSi_2O_8$ becomes apparent when the glass content is more than 10 wt%. The phase evolution and microstructural analysis suggest that much PbO volatised during the sintering at 1100 °C and the substitution of Pb^{2+} in Ba^{2+} lattice site. The formation of $PbTiO_3$ causes an uneven distribution of BST composition, giving rise to the strong broadening effects of the phase transition. BST ceramics with 10 wt% glass additives exhibit the highest tunability at all four sintering temperatures. A tunability of 12.2% at a bias field of 1 kV/mm was achieved for BST ceramics with 10 wt% glass content sintered at 900 °C. These results provide useful information for the design of the microwave devices and an enlarged processing window for BST thick films with the potential of low temperature co-fired ceramic (LTCC) process.

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