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Effect of the addition of B_2O_3 and $BaO–B_2O_3–SiO_2$ glasses on the microstructure and dielectric properties of giant dielectric constant material $CaCu_3Ti_4O_{12}$

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Abstract

The effect of the addition of glassy phases on the microstructure and dielectric properties of $CaCu_3Ti_4O_{12}$ (CCTO) ceramics was investigated. Both single-component (B_2O_3) and multi-component (30 wt% BaO–60 wt% B_2O_3–10 wt% SiO_2 (BBS)) glass systems were chosen to study their effect on the density, microstructure and dielectric properties of CCTO. Addition of an optimum amount of B_2O_3 glass facilitated grain growth and an increase in dielectric constant. However, further increase in the B_2O_3 content resulted in its segregation at the grain boundaries associated with a reduction in the grain size. In contrast, BBS glass addition resulted in well-faceted grains and increase in the dielectric constant and decrease in the dielectric loss. An internal barrier layer capacitance (IBLC) model was invoked to correlate the dielectric constant with the grain size in these samples.
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1. Introduction

Electroceramics associated with high dielectric constants (ε_r') accompanied by low dielectric loss (D) have been in increasing demand owing to their potential applications in miniaturized electronic devices. Hence, the recently synthesized giant ε_r' material $CaCu_3Ti_4O_{12}$ (CCTO) has attracted much attention. It showed an extremely high ε_r' ($> 10^5$) at room temperature [1–5]. Impedance studies that were carried out on CCTO ceramics demonstrated their electrical heterogeneous nature (the existence of semiconducting grains and relatively high resistive grain boundaries) and the large ε_r' was attributed to the internal barrier layer effects at the grain boundary [4,5].

The ε_r' of CCTO was reported to be strongly dependent on the processing conditions such as sintering temperature, duration of sintering, cooling rate, etc. ε_r' ranging from 2000 to 2,80,000 was obtained by increasing the sintering temperature/duration and was explained based on the

grain boundary barrier layer capacitance effects [5,6]. Despite exhibiting high ε_r', unfortunately, CCTO ceramics suffer from considerably high D especially at high temperatures, which was attributed to the existence of leaky grain boundaries. According to the internal barrier layer capacitance model, the apparent ε_r' of such an electrically heterogeneous ceramic is given by

$$\varepsilon_r' = \varepsilon_{gb}\left(\frac{(d_g + d_{gb})}{d_{gb}}\right), \qquad (1)$$

where ε_{gb} is the dielectric constant of the grain boundary layer, d_g and d_{gb} are the thicknesses of the grain and the grain boundary layer, respectively. Therefore, even a small ε_{gb} could lead to a giant ε_r' if the ratio $(d_g + d_{gb})/d_{gb}$ is large [7]. It is clear from the above equation that ε_r' is strongly dependent on the microstructure and can therefore be maximized by enhancing the grain size (increasing d_g), by thinning down the grain boundary (decreasing d_{gb}), or by deliberately creating a grain boundary phase associated with high dielectric constant (increasing ε_{gb}). It would be desirable to have CCTO ceramics consisting of large grains and highly resistive grain boundaries to achieve high ε_r'

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associated with low D. In general, these requisites are accomplished by adding suitable additives. Low-melting glass additives were often used for lowering the sintering temperature and engineering the microstructures of the electroceramics [8–15].

It was reported that the glassy material in ceramics forms grain-to-grain bridges via liquid-phase formation during sintering. This would facilitate the grain growth and help in the elimination of inter-grain pores [16,17]. In addition, since some of the glasses have high electrical resistance and low D [18,19], these could assist in the lowering of D and in improving the overall dielectric properties of the poly-crystalline ceramics. However, this greatly depends on the kind of chemical reaction between the glassy phase that is added and the rest of the dielectric, densification and the microstructure. The desirable characteristics of the additive used as a sintering aid for the densification of the ceramic are low melting point, low viscosity at the sintering temperature and no/less reactivity with the ceramics [20]. Though the glass additives reduce the sintering tempera-ture, they may introduce certain undesirable effects, such as a decrease in the ε'_r due to the presence of continuous low ε'_r grain boundary glassy phase, the formation of undesir-able secondary phases, etc. [21].

The present study aims at obtaining high-density CCTO ceramics by relatively low-temperature sintering in the presence of an optimal amount of liquid phase without any undesirable phase formation. In order to obtain high-quality dielectric ceramics associated with high densifica-tion, limited grain growth and reduced porosity, the crucial step has been to optimize the volume fraction of the low ε'_r

glass additive and the sintering temperature. In the present work, the effect of boric oxide (B_2O_3)—a well-known glass former—on the density, microstructure and ε'_r of CCTO ceramics has been studied. The reason for choosing B_2O_3 is owing to its low melting point (450 °C), as it might significantly bring down the sintering temperature of CCTO. On the other hand, based on the literature indicating that the multi-component glasses are more effective than single-component glasses in reducing the sintering temperature of the ceramics without considerably affecting the physical properties of the matrix, we have also performed the above studies using a ternary glass system, $BaO–B_2O_3–SiO_2$. In addition, since borosilicate glasses have continuous network structures with SiO_4 and B_2O_3 configurations to form (–Si–O–B–O–) linkages, they are expected to have high electrical resistance and low D.

2. Experimental

Polycrystalline ceramic powders of CCTO were prepared via the conventional solid-state reaction route using stoichiometric amounts of high-purity $CaCO_3$, CuO and TiO_2. These were thoroughly mixed in an acetone medium using a ball mill. Subsequently, these mixtures were oven dried for about 2 h. This was followed by calcination of the powder in an alumina crucible at 1000 °C for 10 h with intermittent grinding. The formation of the monophasic compound was confirmed via X-ray powder diffraction (XRD). The XRD data were collected employing the CuKα radiation using Philips X-ray diffractometer at the scan rate of 1°/min.

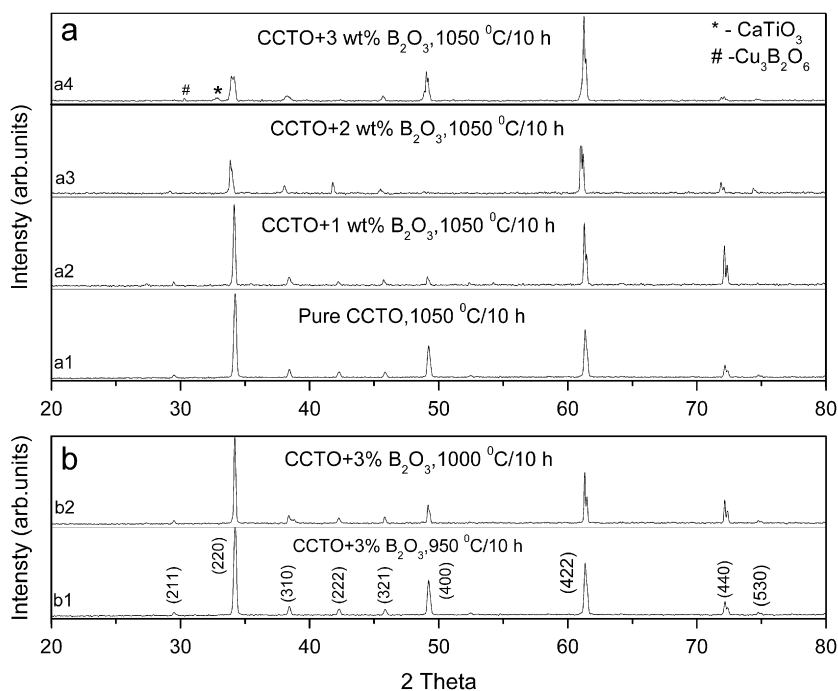

Fig. 1. X-ray powder diffraction patterns for (a) 1050 °C/10 h sintered $CaCu_3Ti_4O_{12}$ ceramics containing (a1) 0, (a2) 1, (a3) 2, (a4) 3 wt% B_2O_3 and (b) 3 wt% B_2O_3-added $CaCu_3Ti_4O_{12}$ ceramics sintered for 10 h at (b1) 950 °C (b2) 1000 °C.

B_2O_3 glass powder in wt% (1, 2, 3, 5, 7.5 and 10) was added to the prereacted CCTO powder. Also, the glasses of the composition, 30 wt% BaO–60 wt% B_2O_3–10 wt% SiO_2 (BBS), were prepared using $BaCO_3$, H_3BO_3 and SiO_2 as starting materials by the melt-quenching technique. The stoichiometric composition of the batch material (10 g) was melted at 1300 °C in a platinum crucible and maintained this temperature for 30 min in a glass-melting furnace (Lenton). The molten material was then poured onto a stainless steel plate which was preheated to 100 °C and pressed by another one. The BBS glass exhibited a density of 4.02 g cm^{-3} associated with a melting point of around 850 °C. The powder that was obtained by ball milling the as-quenched glass was added to pure CCTO powder in wt% ratio of 1, 2, 3 and 5. The powders of CCTO and glass (B_2O_3/BBS) were thoroughly mixed for 2 h in acetone medium using a ball mill. The mixed powder was dried and then cold pressed into the pellets of 10 mm in diameter and 2 mm in thickness, at a pressure of 300 kg/cm^2 using PVA as a binder. The pressed pellets were slowly heated to 600 °C to get rid of the binder. The pellets with different concentrations of glass (B_2O_3/BBS) were then individually heated at 950, 1000, 1050 °C for 10 h to optimize the glass content and the sintering temperature to achieve the highest possible density and desired dielectric properties. Archimedes' principle was used to measure the density of the sample using Xylene as the liquid medium.

XRD studies were performed on the sintered pellets also to confirm the retention of the monophasic nature of the CCTO powder even after sintering using glass additives. The microstructural features and grain size distribution in the sintered pellets were studied by scanning electron microscopy (SEM) (Cambridge S360, Quanta 200 and JEOL 840). Capacitance measurements were carried out at 300 K as a function of frequency (100 Hz–10 MHz) using impedance gain phase analyzer (HP4194A) at signal strength of 0.5 V_{rms}. For this purpose, polished smooth parallel surfaces were sputtered with gold. Subsequently, silver epoxy was employed to bond the copper leads to the sample.

3. Results and discussion

Fig. 1a (a1–a4) shows the XRD patterns for the phase pure CCTO and 1, 2 and 3 wt% B_2O_3-added CCTO pellets
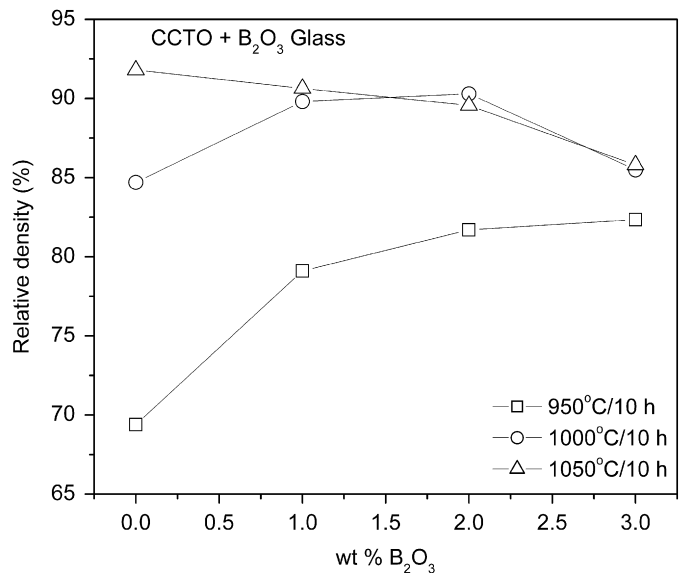
Fig. 3. Variation in the density of the $CaCu_3Ti_4O_{12}$ ceramics as a function of B_2O_3 content which are sintered at three different temperatures.

Fig. 2. X-ray powder diffraction patterns for $CaCu_3Ti_4O_{12}$ ceramics sintered at 1050 °C/10 h containing (a) 0 wt%, (b) 1 wt%, (c) 2 wt%, (d) 3 wt% , (e) 5 wt% of BBS glass.
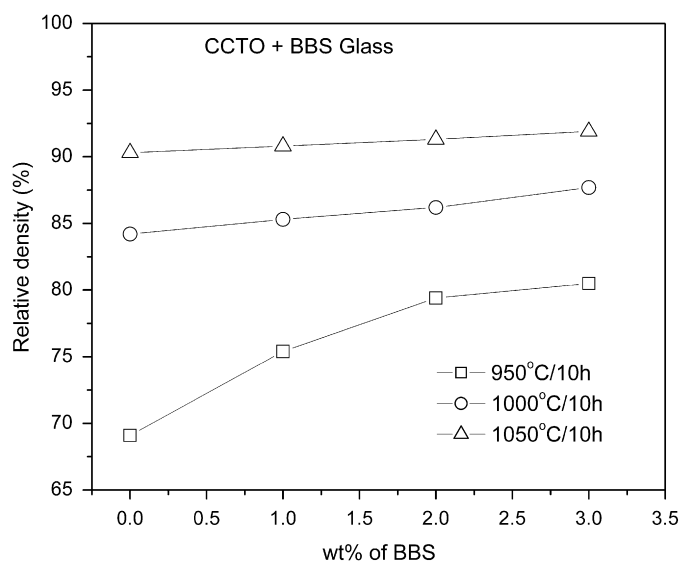
Fig. 4. Variation in the density of the $CaCu_3Ti_4O_{12}$ ceramics as a function of BBS content which are sintered at three different temperatures.
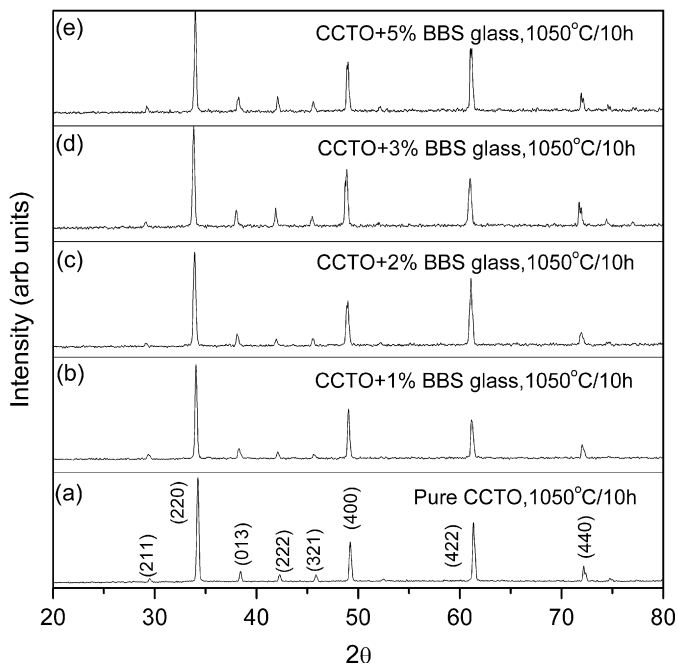
that were sintered at 1050 °C/10 h. It is evident from these patterns that the addition of B_2O_3 to CCTO helps in bringing about a planar orientation which has strong concentration dependence. Increasing the B_2O_3 content to 3 wt% in CCTO seems to have adverse affects as X-ray peaks corresponding to undesirable impurity phases start appearing (indicated by * and #), suggesting a possible chemical reaction between B_2O_3 and CCTO at higher concentrations. These Bragg peaks were identified to be originating from the presence of $CaTiO_3$ and $Cu_3B_2O_6$ phases. On further increasing the concentration of B_2O_3 to 5 wt%, the intensities of these particular peaks increase significantly (not included in the figure).

In order to visualize the influence of sintering temperature on the formation of the impurity phase, the 3 wt% B_2O_3-added CCTO pellets were sintered at 950 and 1000 °C for 10 h. The XRD patterns that are obtained for these samples are shown in Fig. 1b (b1 and b2). For the pellets sintered at 950 and 1000 °C (Fig. 1b (b1 and b2)), there is no significant change in the peak positions and the intensity

with respect to that of the pure CCTO. On further increasing the sintering temperature to 1050 °C, relative intensities of the X-ray peaks corresponding to CCTO change drastically (Fig. 1a (a4)). For instance, there is a significant decrease in the relative intensity of the peak corresponding to (220) reflection of CCTO, while there is a great deal of increase in the intensity of (422) reflection.

The XRD patterns obtained for pure CCTO and 1, 2, 3 and 5 wt% BBS glass-added CCTO pellets that were sintered at 1050 °C/10 h are shown in Fig. 2(a–e). The XRD pattern obtained for 5 wt% BBS glass-added CCTO pellet (Fig. 2e) is identical with that obtained for pure CCTO (Fig. 2a), indicating the absence of any chemical reaction between CCTO and the glass additive. In contrast, as mentioned earlier, B_2O_3, which melts at much lower temperatures (450 °C) when compared to BBS (850 °C), reacts with CCTO, due to its low viscosity at elevated sintering temperatures (around 1050 °C and above).

The variation in the relative density of CCTO with B_2O_3 content and sintering temperature is illustrated in Fig. 3.
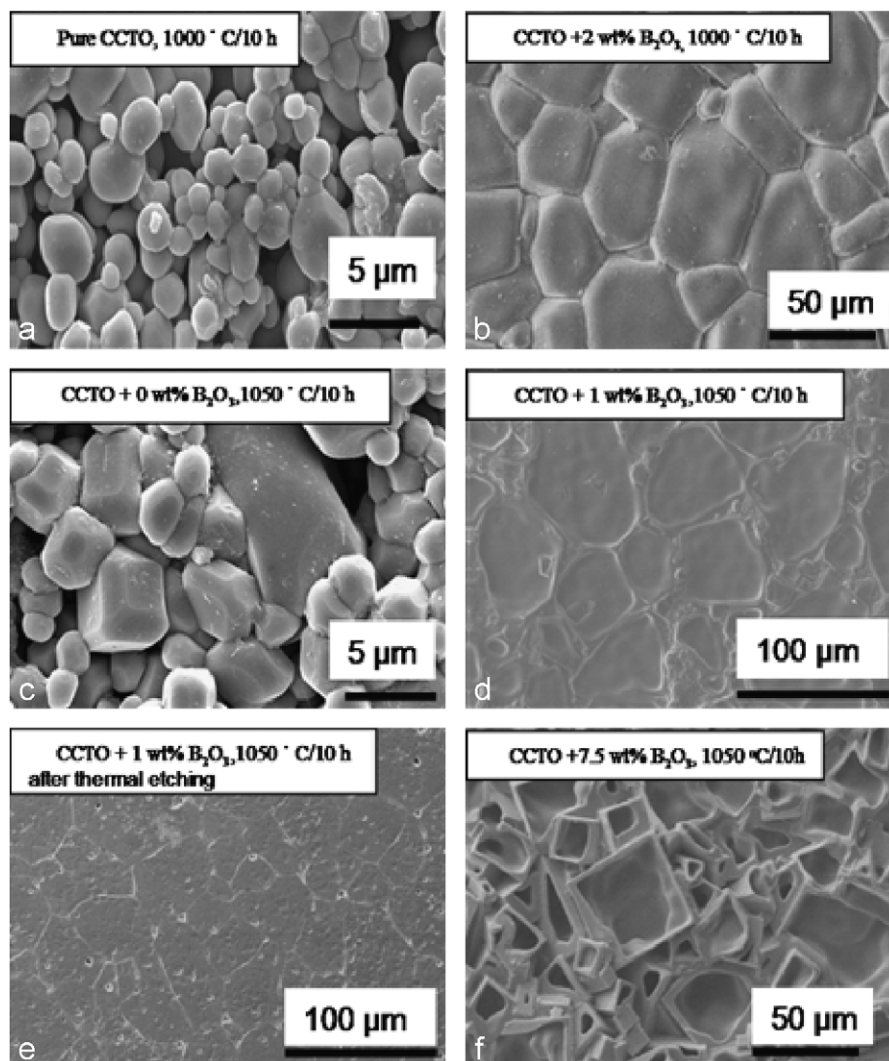

Fig. 5. Scanning electron micrographs of $CaCu_3Ti_4O_{12}$ pellets containing different amounts of B_2O_3 and sintered at different temperatures.

For the pellets sintered at 950 °C, the density increases with increase in B_2O_3 content, while for the pellets sintered at 1000 °C, the density increases only until 2 wt%. On further increasing the B_2O_3 content to 3 wt%, the density decreases. In the case of pellets sintered at 1050 °C, the density decreases continuously with increase in the B_2O_3 content. These observations suggest that heating the pellets with optimum amount of B_2O_3 at optimum temperature is essential for the sintering process via liquid-phase formation. In liquid-phase sintering, grain-to-grain material transport enhances, if the additives wet the grains of the matrix material. In such cases the transient glassy phase formed at lower temperatures would facilitate the densification via the pore elimination process. On the other hand, the presence of excess amount of B_2O_3 glassy phase would result in the lowering of the density as its theoretical density is much lower (1.819 g/cm^3) than that of CCTO (5.096 g/cm^3). The decrease in the density on increasing the B_2O_3 glass content could also be due to the rapid grain growth accompanied by pore entrapment. Excess liquid

phase makes the grain growth rate faster than the removal rate of entrapped inter/intra-grain pores, leading to a lower density. Evaporation of the glass component and the chemical reactions between the glass and the matrix may lead to the formation of traces of secondary phases of lower densities which might lower the total density of the composite, particularly at higher percentages of glassy phase. The variation in the relative density of CCTO with BBS content and sintering temperature is depicted in Fig. 4. The density increases continuously with increase in BBS content irrespective of the sintering temperatures involved, which is in contrast with that of B_2O_3-added ceramics.

Microstructures of the CCTO pellets that were sintered at different temperatures with various amounts (weight percentages) of B_2O_3 are depicted in Fig. 5(a–f). The micrographs for pure and 2 wt% B_2O_3-added CCTO ceramics sintered at 1000 °C/10 h are shown in Fig. 5(a and b). It is to be noted that B_2O_3 addition has resulted in the enhancement of the grain size. Average grain size of
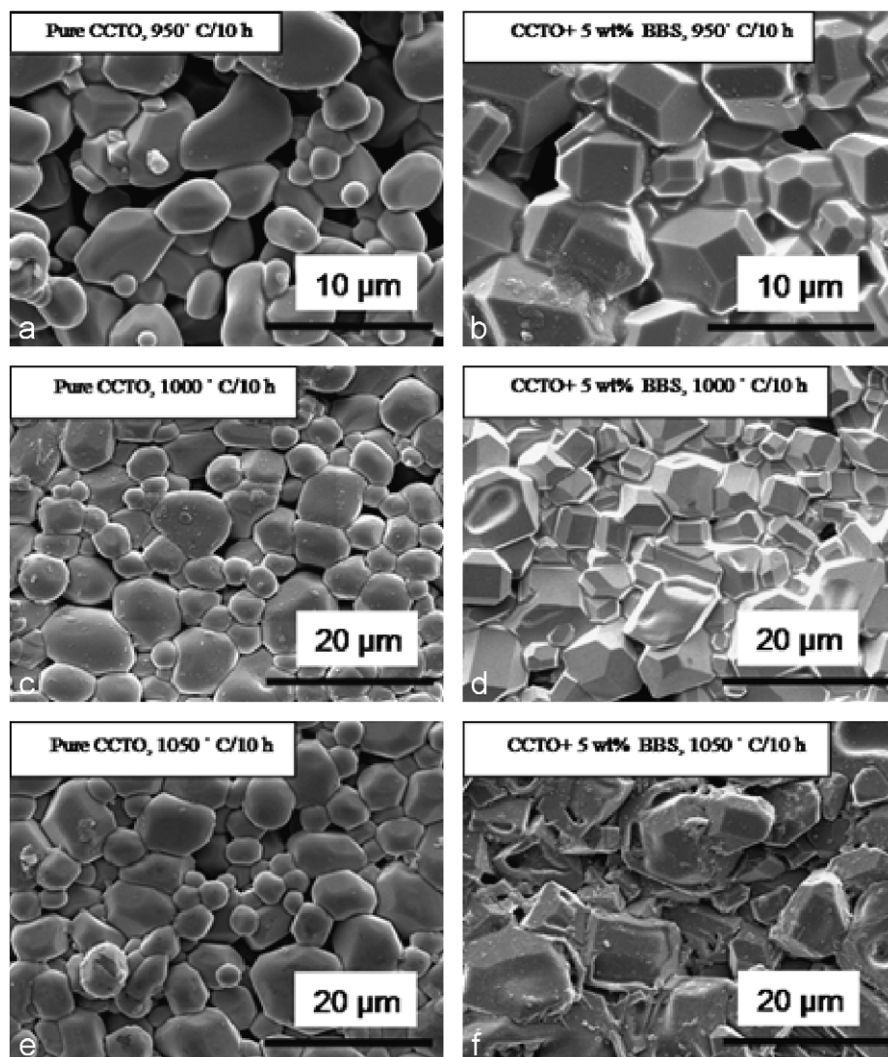

Fig. 6. Scanning electron micrographs of pure CaCu$_3$Ti$_4$O$_{12}$ and BBS-added CaCu$_3$Ti$_4$O$_{12}$ pellets sintered at 950 °C/10 h, 1000 °C/10 h, 1050 °C/10 h.

B_2O_3-containing CCTO is in the 45–55 μm range (Fig. 5b), which is nearly ten times higher than the average grain size (3–5 μm) that is observed in pure CCTO ceramics sintered at the same temperature (Fig. 5a). This increase in the grain size on the addition of B_2O_3 is expected to influence the dielectric properties of CCTO ceramics as the grain size is an important parameter in IBLCs. Fig. 5(c and d) shows the microstructures of the pure and 1 wt% B_2O_3-added CCTO sintered at 1050 °C/10 h. As in the case of the samples sintered at 1000 °C/10 h, there is an enhancement of grain size to a great extent even in the case of 1050 °C/ 10 h sintered B_2O_3-added CCTO samples. In addition, the morphology of the grains in B_2O_3-added CCTO ceramics (Fig. 5d) is distinctly different from that of the pure CCTO (Fig. 5c), even though these were sintered at the same temperature. In fact, on critical examination, it is noticed that there is an inward buckling of the surface of the grains in these samples (Fig. 5d). The micrograph of the well-polished and thermally etched pellets of 1 wt% B_2O_3-added CCTO pellets sintered at 1050 °C/10 h is shown in Fig. 5e. It reveals the presence of trapped intragrain pores. These

entrapped pores would account for a reduction in the apparent density of the pellets. Higher amounts (3–7.5%) of glass phase, however, led to the grain size reduction (Fig. 5f). There are symptoms of second phase evolving around CCTO grains, which is very clear in the samples containing higher amounts of B_2O_3 (Fig. 5f). The segregation of increasing amount of B_2O_3 especially at the grain boundaries hinder the movement of CCTO particles and hence restrict the grain growth. Indeed, for higher concentrations of B_2O_3, flaky-shaped structures develop and segregate around grains (Fig. 5f).

The effect of BBS glass addition on the microstructure of the sintered pellets of CCTO is shown in Fig. 6(a–f). It is evident from these micrographs that the grain size increases only marginally with increase in both sintering temperature and the addition of glass phase. A noteworthy aspect of this microstructure is the presence of faceted grains (Fig. 6(b and d)), which is attributed to the existence of surface energy anisotropy. Also, liquid phase would minimize the total surface energy per volume due to wetting. The simple thermodynamic criterion for grain
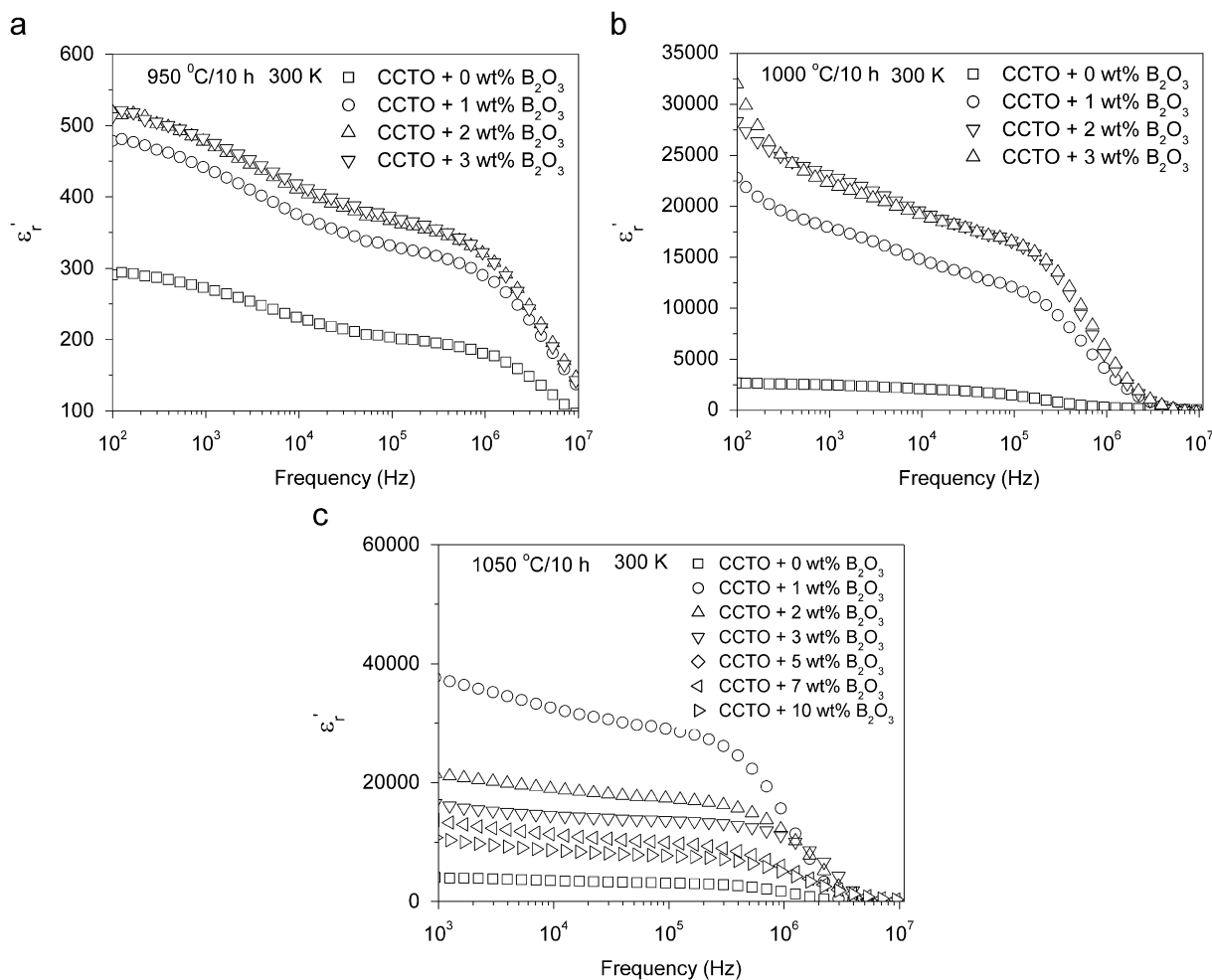

Fig. 7. Variation of dielectric constant (ε'_r) with frequency at 300 K for the $CaCu_3Ti_4O_{12}$ ceramics containing various amounts (in wt%) of B_2O_3, sintered at (a) 950 °C/10 h, (b) 1000 °C/10 h, (c) 1050 °C/10 h.

boundary wetting is based on the relative energies, per unit area, of the grain boundary, γ_{gb}, and the two solid–liquid interfaces, γ_{sl}, which replace the grain boundary on wetting and the criterion is $2\gamma_{sl} < \gamma_{gb}$. Due to the presence of liquid phase, the CCTO grains, which were nearly spherical in the absence of glass, became faceted as they were wet by the liquid. The change in the morphology of the grains (faceting) resulted in the reduced contact area between the neighboring grains. For the samples with higher concentration of glass and sintered at higher temperature, most CCTO grains are bounded by large-scale facets and are separated by thick layers of glassy phase (Fig. 6f).

The variation of ε'_r with frequency at 300 K for the CCTO ceramics containing various amounts (in wt%) of B_2O_3, sintered at 950, 1000 and 1050 °C for 10 h are shown in Fig. 7(a–c). For all the samples, the ε'_r decreases with increasing frequency up to 1 MHz and a rapid decrease in the ε'_r occurs at frequencies higher than 1 MHz. The dielectric relaxation takes place nearly at the same

frequency for all the samples, irrespective of the amount of B_2O_3 added and the sintering temperature. The observed dielectric phenomenon is similar to the one that is reported in the literature for pure CCTO and is attributed to the grain boundary relaxation [4–6]. For the pellets sintered at 950 and 1000 °C, the ε'_r increases with increasing amounts of B_2O_3 in the entire frequency range under study. However, for the samples sintered at 1050 °C, the ε'_r does not follow the above trend with an increase in amount of B_2O_3 (Fig. 7c).

The variation of D as a function of frequency at 300 K for the CCTO ceramics containing various amounts (in wt%) of B_2O_3, sintered at 950, 1000 and 1050 °C for 10 h are shown in Fig. 8(a–c). The D for 950 °C sintered pellet is found to decrease with increase in B_2O_3 content at all the frequencies under study. It is to be noted that for each sample, the drop in ε'_r (Fig. 7(a–c)) in the MHz frequency range is accompanied by a rapid increase in the D values. Also, for each sintering temperature the D is sensitive to the amount of B_2O_3 added.
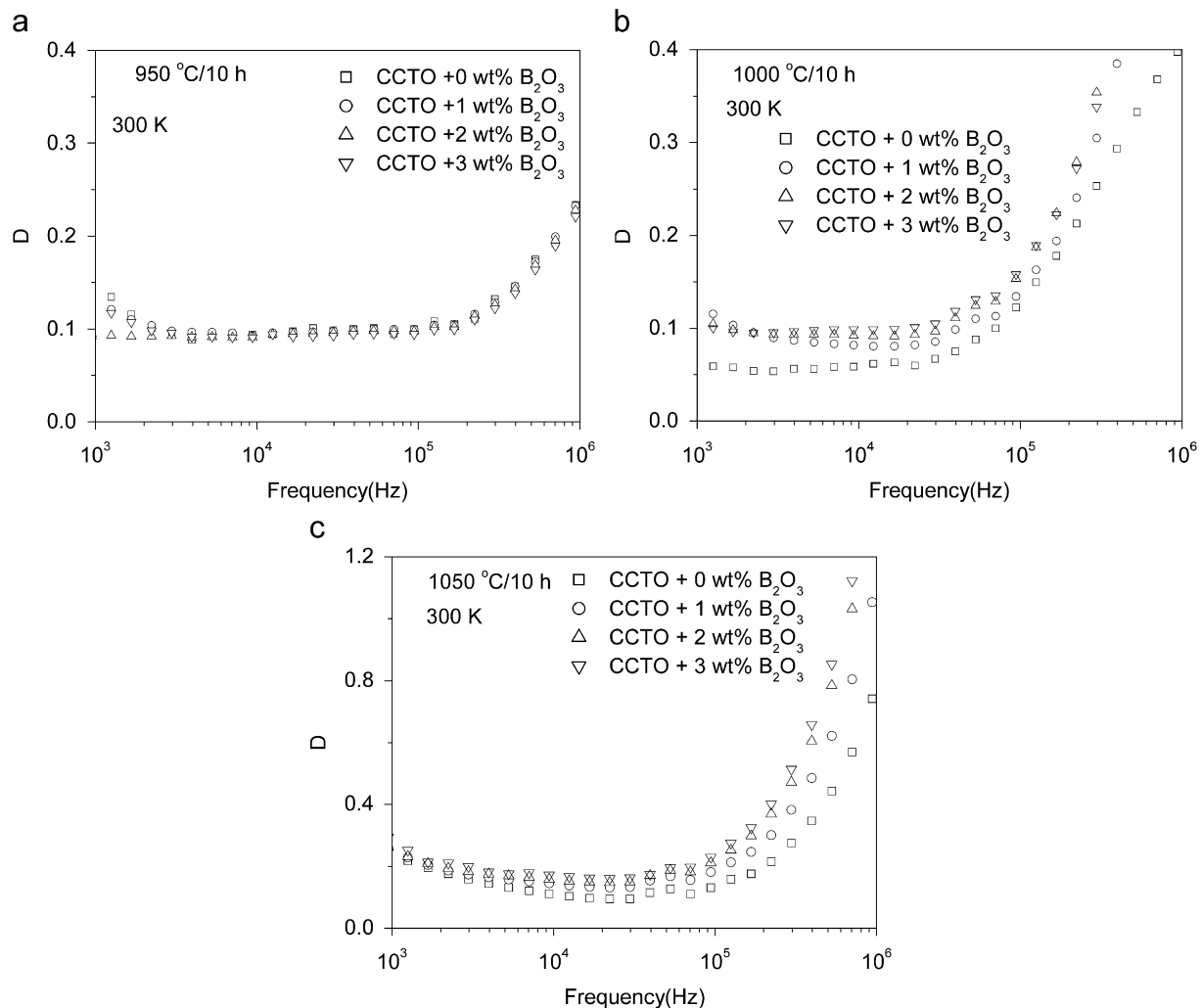

Fig. 8. Variation of dielectric loss (D) with frequency at 300 K for the $CaCu_3Ti_4O_{12}$ ceramics containing various amounts (in wt%) of B_2O_3, sintered at (a) 950 °C/10 h, (b) 1000 °C/10 h, (c) 1050 °C/10 h.
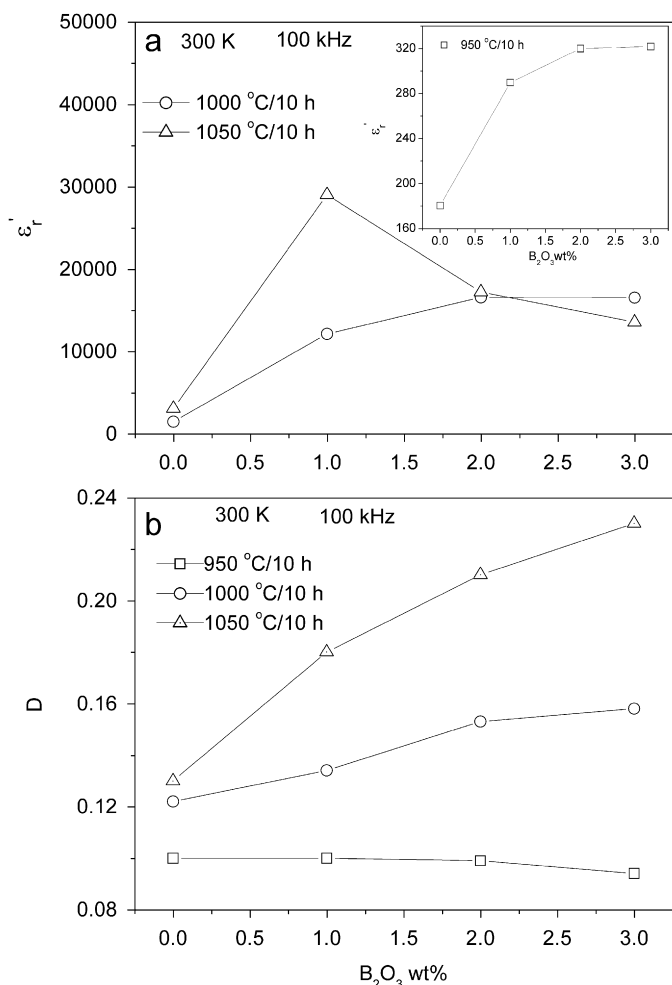
Fig. 9. Variation of (a) the dielectric constant (ε_r') and (b) the dielectric loss (D) for CaCu$_3$Ti$_4$O$_{12}$ ceramics (1000 and 1050 °C) at 100 kHz as a function of concentration (in wt%) of B$_2$O$_3$. The inset of (a) shows the variation of ε_r' with B$_2$O$_3$ content for the pellets sintered at 950 °C.

The observations in Figs. 7 and 8 have been summarized in Fig. 9(a and b), where ε_r' and D at 100 kHz of CCTO have been plotted as a function of concentration (in wt%) of B$_2$O$_3$ and the sintering temperature. The trend in the variation of the ε_r' as a function of concentration (in wt%) of B$_2$O$_3$ (Fig. 9a) is nearly consistent with that of density variation with B$_2$O$_3$ content (Fig. 3). The deviation from this trend for some of the compositions under study might have arisen from two opposing factors. One is increase in the grain size, which results in an increase in the ε_r'. On the contrary, a decrease in the density due to intra-grain porosity results in a reduction in the ε_r'. Interestingly, for the pellets sintered at 950 °C/10 h, the ε_r' increases and the loss decreases with increase in the B$_2$O$_3$ content. B$_2$O$_3$ addition has a greater influence on the pellets sintered at 1000 °C/10 h. At 100 kHz, pure CCTO sintered at 1000 °C/ 10 h has a relatively low ε_r' of about 1474. Addition of 1 wt% B$_2$O$_3$ results in an increase in the ε_r' from 1474 to 12,078. However, further addition of B$_2$O$_3$ has only a nominal influence on the ε_r'. On increasing the B$_2$O$_3$ content

to 3 wt%, the ε_r' decreases to a small extent. These observations are consistent with the variation in the density of the sample with the B$_2$O$_3$ content. For the pellets sintered at 1050 °C/10 h, the ε_r' of pure CCTO is about 3078. Addition of 1 wt% of B$_2$O$_3$ increases its ε_r' from 3078 to 29,032. On further increase in the B$_2$O$_3$ content, the ε_r' decreases continuously, which is consistent with the decrease in the density of the sample. The excess quantity of glass addition would inhibit the grain growth and decrease the density and grain size, thus resulting in a low ε_r'. A marginal decrease in the D for 950 °C sintered samples at 100 kHz with increase in B$_2$O$_3$ content (up to 3 wt%) is attributed to the accumulation of higher amounts of B$_2$O$_3$ segregating at the grain boundaries and thereby minimizing the grain-to-grain contact of CCTO, whereas for the sample sintered at 1000 °C and 1050 °C, the increase in D with increase in B$_2$O$_3$ content is ascribed to the presence of secondary phase (Fig. 1), especially Cu$_3$B$_2$O$_6$ whose electrical conductivity is higher than that of B$_2$O$_3$.

The variation of ε_r' with frequency at 300 K for the CCTO ceramics containing various amounts (in wt%) of BBS, sintered at 950, 1000 and 1050 °C for 10 h are shown in Fig. 10(a–c). It is evident from these figures that the ε_r' increases considerably with increase in sintering temperature and the amount of glass addition. However, the influence of BBS glass addition on the ε_r' of CCTO is not as much as that observed for B$_2$O$_3$-added samples. Nevertheless, a more interesting and positive aspect of the BBS glass addition in CCTO is noticed in its D behavior. It is clear from Fig. 11 (a and b) that the loss decreases substantially with the amount of glass added. Also, it is prominently seen that the low-frequency increase in D in pure CCTO decreases considerably with increase in the amount of BBS glass. The decrease of loss in BBS-added samples could be because of a decrease in the grain-to-grain contact, which is due to the evolution of faceted grains. The observations in Figs. 10 and 11 have been summarized in Fig. 12(a and b), where ε_r' and D at 100 kHz for CCTO have been plotted as a function of concentration (in wt%) of BBS glass and the sintering temperature.

CCTO being a centrosymmetric compound, the exhibition of high ε_r' has been attributed to the formation of the grain boundary IBLC and, in the present case, dependence of ε_r' on the glass content could be explained based on the Eq. (1) by invoking the grain size effect. B$_2$O$_3$-containing CCTO samples have largest grains and are likely to show a high ε_r' according to the IBLC model. For instance, 1 wt% B$_2$O$_3$-containing samples sintered at 1050 °C/10 h consist of large grains as compared to the rest of the samples and hence they exhibit the highest ε_r'. Addition of higher amounts (3–7.5%) of glassy phase, however, led to reduction in the grain size due to the segregation of increasing amount of B$_2$O$_3$, especially at the grain boundaries. The ε_r' of these samples decreased accordingly. On the other hand, in the case of BBS-added CCTO samples, grain size increased only marginally with increase in the BBS content, which is also reflected in the trend
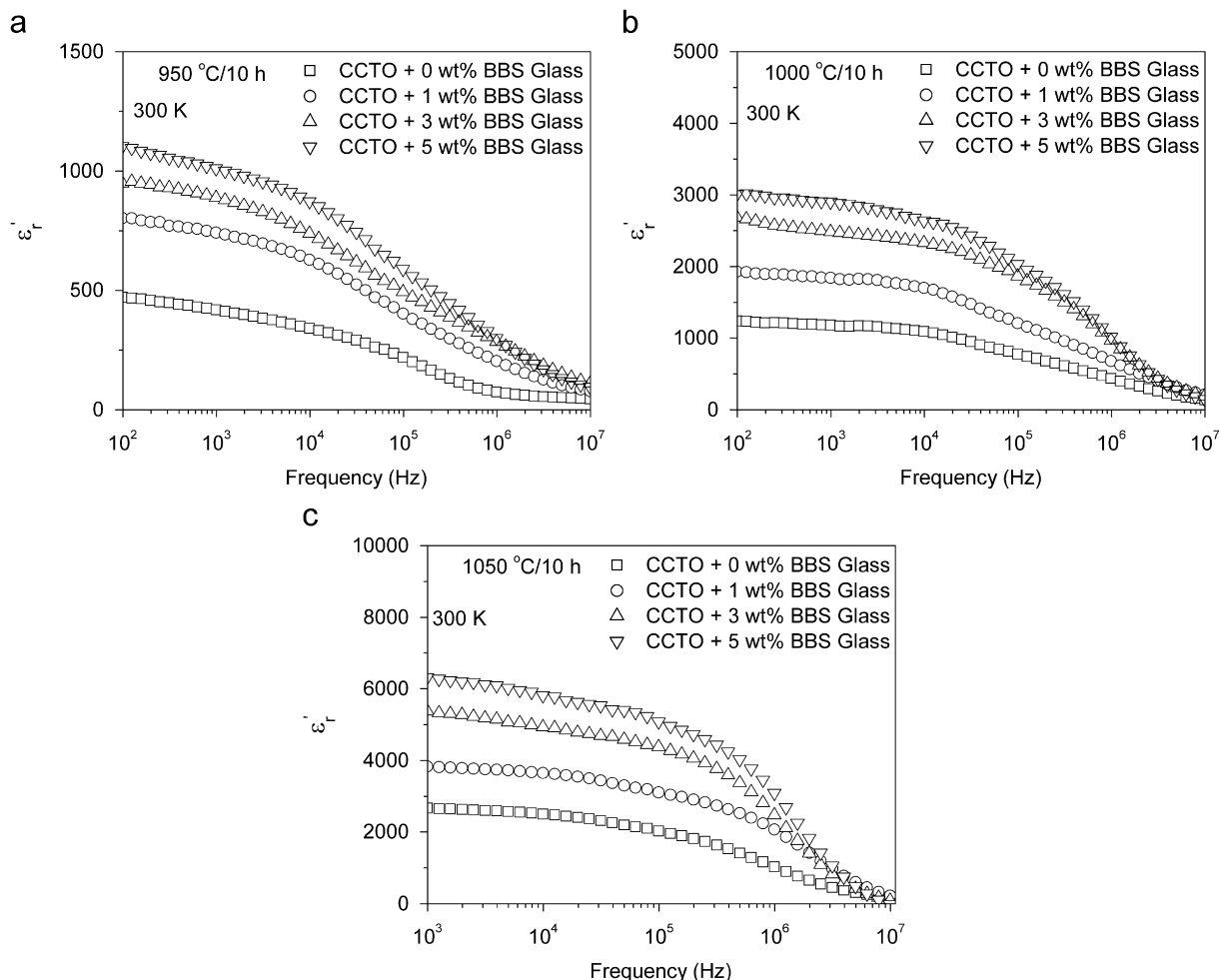
Fig. 10. Variation of dielectric constant (ε'_r) with frequency at 300 K for the CaCu$_3$Ti$_4$O$_{12}$ ceramics containing various amounts (in wt%) of BBS, sintered at (a) 950 °C/10 h, (b) 1000 °C/10 h, (c) 1050 °C/10 h.

followed by ε'_r value. The above observations strongly justify the usage of IBLC model in explaining the dielectric behavior of these samples.

Among the two types of glasses used in the current study (primary (B$_2$O$_3$) and ternary (BaO–B$_2$O$_3$–SiO$_2$)), B$_2$O$_3$ addition led to a rapid increase in the grain growth and hence resulted in a high ε'_r via IBLC mechanism. However, increase in the ε'_r was associated with the increase in the D also. Good dielectric materials should have high ε'_r and low D. Hence, among the B$_2$O$_3$-added samples, 1050 °C/10 h sintered CCTO containing 1 wt% of B$_2$O$_3$ exhibit good dielectric properties as it has high ε'_r (~29,000) and reasonably low D (0.18). Increase in the B$_2$O$_3$ content beyond 1% led to a decrease in the ε'_r and an increase in the D. Hence samples with higher concentrations of B$_2$O$_3$ are not worth considering for device applications. Interestingly, in the case of BaO–B$_2$O$_3$–SiO$_2$ (BSS)-added samples, ε'_r increases only marginally but more importantly D decreases with increase in the BSS content a desirable feature which could be exploited in the design of capacitor applications.

4. Conclusions

The effect of the addition of glassy phases, B$_2$O$_3$ and BaO–B$_2$O$_3$–SiO$_2$ (BBS), on the sintering behavior, microstructural features and dielectric characteristics of giant ε'_r material CaCu$_3$Ti$_4$O$_{12}$ was studied. B$_2$O$_3$ addition had a subtle positive effect on the density and ε'_r of the pellets sintered at 950 °C. However, it had a substantial influence on the pellets sintered at 1000 °C. Density and ε'_r increased on increasing the B$_2$O$_3$ content to 2 wt%. On increasing the B$_2$O$_3$ content to 3 wt%, there was entrapment of intragrain pores due to rapid grain growth, resulting in decreased density and increased D. For the pellets sintered at 1050 °C, there was continuous decrease in the density with increase in the B$_2$O$_3$ content due to the segregation of glassy phase in the matrix material. On the other hand, BBS-added samples exhibited faceted grains, thus reducing the grain-to-grain contact. The ε'_r of these samples increased with increase in BBS content due to the increased grain size, but the D decreased due to the reduction in the contact area between the grains. The increase or decrease in the ε'_r in
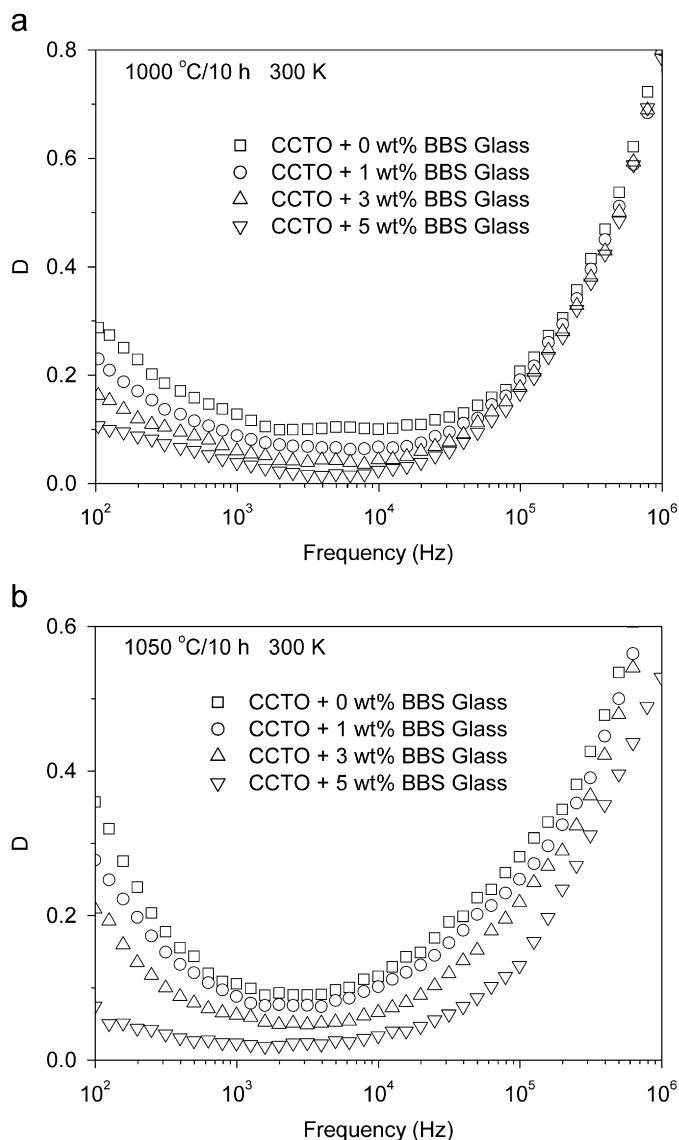
Fig. 11. Variation of dielectric loss (D) with frequency at 300 K for the CaCu$_3$Ti$_4$O$_{12}$ ceramics containing various amounts (in wt%) of BBS, sintered at (a) 950 °C/10 h, (b) 1000 °C/10 h.

these samples was explained based on the internal barrier layer capacitance model.

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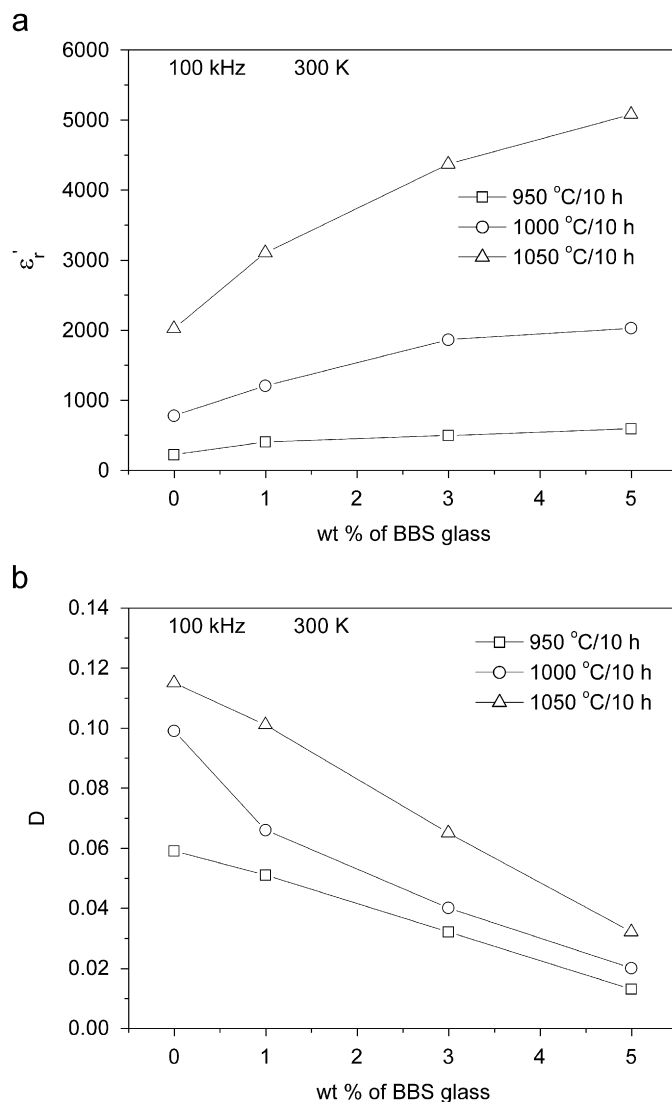[7] J. Liu, C.-G. Duan, W.-G. Yin, W.N. Mei, R.W. Smith, J.R. Hardy, Phys. Rev. B 70 (2004) 144106-1–144106-7.

Fig. 12. Variation of (a) the dielectric constant (ε'_r) and (b) the dielectric loss (D) for CaCu$_3$Ti$_4$O$_{12}$ (sintered at 950, 1000 and 1050 °C) at 100 kHz as a function of concentration (in wt%) of BBS.

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