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# $Ba_{0.7}Sr_{0.3}TiO_3$–glass–silver percolative composite

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**Abstract**

$Ba_{0.7}Sr_{0.3}TiO_3$–glass–silver (BST–glass–Ag) composites were prepared by the solid state ceramic route. Their percolation behavior and dielectric properties were examined. The pure BST had a percolation limit of 24 vol% of silver whereas an addition of 8 wt% of $50PbO–30B_2O_3–20SiO_2$ (PBS) glass lowered the percolation limit to 14 vol% of Ag. Glass addition lowered the sintering temperature of BST from 1300 to 975 °C and addition of Ag further lowered the sintering temperature to 925 °C, minimizing the Ag loss during sintering. The relative permittivity increased from 2700 for pure BST to about five orders of magnitude in the BST–glass–Ag composites near the percolation threshold.


*Keywords:* B. Composites; C. Dielectric properties; C. Electrical conductivity; D. Glass

## 1. Introduction

Materials with very high relative permittivity are of importance for electromechanical and tunable device applications [1,2]. However, the relative permittivity of ceramics is limited. Therefore the concept of insulator–conductor composites was adopted to increase the relative permittivity [1,2]. Electrical conductivity ($\sigma$) and relative permittivity ($\varepsilon_r$) of the composites change by several orders of magnitude near the percolation limit of the conducting phase. These enhanced electrical properties can be used to develop new devices by exploiting its high $\varepsilon_r$ near percolation threshold [2]. Thus ceramic–metal composites with a simple production process can give better electrical properties and such percolative composites can find useful applications.

The ceramic and metal phases chosen in the present study were $Ba_{0.7}Sr_{0.3}TiO_3$ and silver, respectively. The silver is more suitable for making ceramic–metal composites as compared to copper and aluminum which oxidize at higher temperatures and platinum, palladium are expensive. The effect of silver addition on the electrical properties has been studied in many systems such as in $Pb(Zr,Ti)O_3$, $BaTiO_3$, etc. [3–5]. However, these ceramics are sintered at high temperatures, above the melting point of silver (961 °C). At high temperatures, the silver melts and may get vaporized [5] causing loss of silver in the composites. George et al. [6] reported that the silver loss can be minimized by lowering the sintering temperature of the ceramic below the melting point of silver by the addition of low melting glasses. BST and related compounds with high $\varepsilon_r$, low loss and high tunability, are very promising for applications in multilayer capacitors, DRAMS, phase shifters, etc. [7,8]. The present paper reports the effect of glass addition on the lowering of sintering temperature of BST–Ag composites, which in turn minimizes the silver loss and lowers the percolation limit of BST–Ag composites.

## 2. Experimental

The $Ba_{0.7}Sr_{0.3}TiO_3$ was prepared by solid state ceramic route using $BaCO_3$, $SrCO_3$ and $TiO_2$ (all from Aldrich Chemicals, USA) raw materials. These chemicals were mixed in stoichiometric proportion and calcined at 1100 °C for 4 h. The PBS ($50PbO:30B_2O_3:20SiO_2$) glass was prepared from high purity PbO, $B_2O_3$ and $SiO_2$. These oxides were mixed and melted in a platinum crucible above the melting point (>1000 °C), quenched and powdered. Both pure BST and BST–PBS composites were pelletized and sintered at temperatures in the range 1300–950 °C. The temperature at which the samples sinters with best densification (density) is

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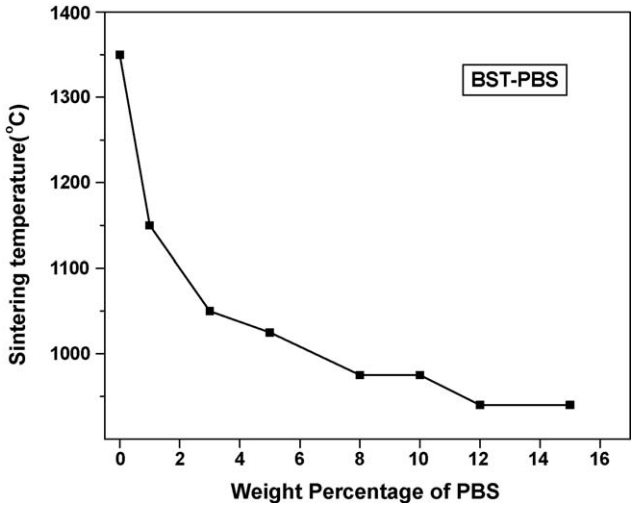


Fig. 1. Variation of sintering temperature of BST with weight percentage of PBS.

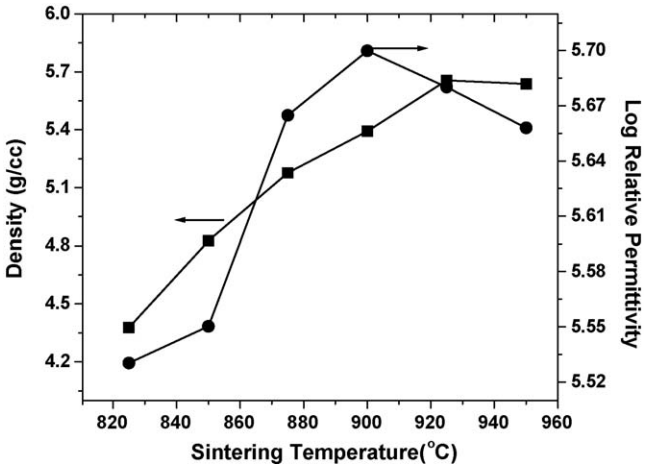


Fig. 2. Variation of density and relative permittivity of BST–8 wt% PBS–14 vol% Ag composite with sintering temperature.

taken as the optimized sintering temperature. The BST–PBS composite with 8 wt% PBS had the best densification and lowest sintering temperature and was selected for preparation of silver containing composites. The BST–8 wt% PBS composite was mixed with different vol% of Ag in distilled water medium. The powders were then dried and mixed with 3 wt% PVA solution and pelletized. These compacts were then sintered at different temperatures in the range 825–950 °C for 4 h. The pure BST–Ag composites were also prepared by sintering at 1300 °C. The crystal structure and phase purity of the samples were investigated using the X-ray diffraction method. The dielectric properties at low frequencies and conductivity were measured using a LCR Meter (HIOKI 3532–50, Japan) in the range 1 kHz–1 MHz.

## 3. Results and discussion

The sintering temperature of BST became lower with the addition of increasing amount of PBS glass. Fig. 1 shows the variation of sintering temperature of BST with different wt% of PBS glass. Addition of 8 wt% of PBS glass lowered the sintering temperature of BST close to the melting point of Ag and the relative permittivity and loss tangent decreased from 2700 to 1050 and 0.023 to 0.017, respectively, at 1 MHz.

The sintering temperature and dielectric behavior of BST–8 wt% PBS–14 vol% Ag composites were optimized by studying the variation in density and $\varepsilon_r$ at different sintering temperatures as shown in Fig. 2. The BST–8 wt% PBS composites containing 5, 10 and 12 vol% of silver sintered to maximum density at 950 °C, while those with 13–16 vol% sintered at 925 °C. The $\varepsilon_r$ was found to increase with sintering temperature and reached a maximum at 900 °C. On further increasing the sintering temperature, the silver melted and diffused to the surface of the pellet degrading the dielectric properties. It is evident from Fig. 2 that addition of silver also lowered the sintering temperature of the composites.

The effect of silver addition on the dielectric behavior of BST was analyzed by studying the variation of $\varepsilon_r$ and $\sigma$ with different vol% of Ag (Fig. 3(a) and (b)). The $\varepsilon_r$ and $\sigma$ of BST–Ag composites sintered at 1300 °C increased gradually up to 20 vol% and at 24 vol% $\varepsilon_r$ and $\sigma$ showed a sharp increase. The $\varepsilon_r$ increased from 2700 to 9790 and $\sigma$ from $3.454 \times 10^{-5}$ to

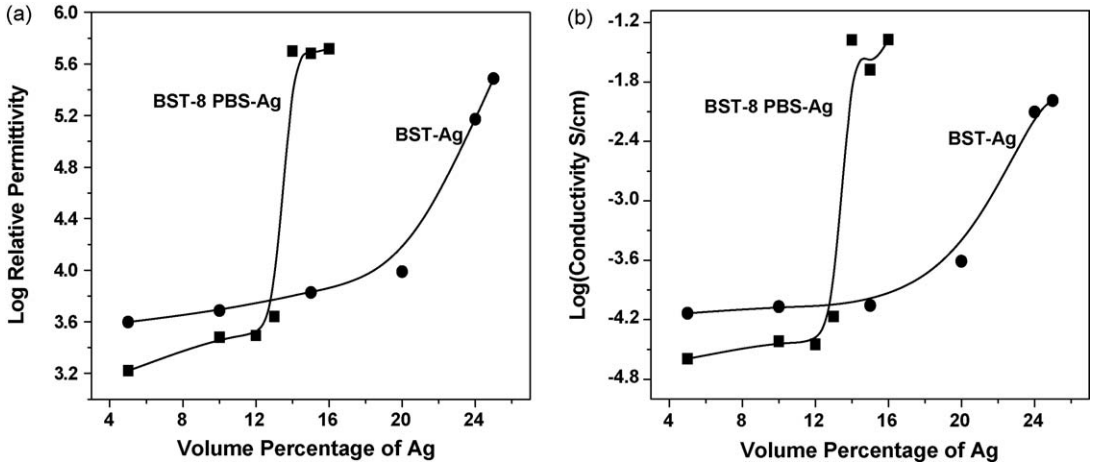


Fig. 3. Variation of (a) relative permittivity, (b) conductivity of BST–Ag and BST–8 wt% PBS–Ag composites with vol% of Ag at 1 MHz.

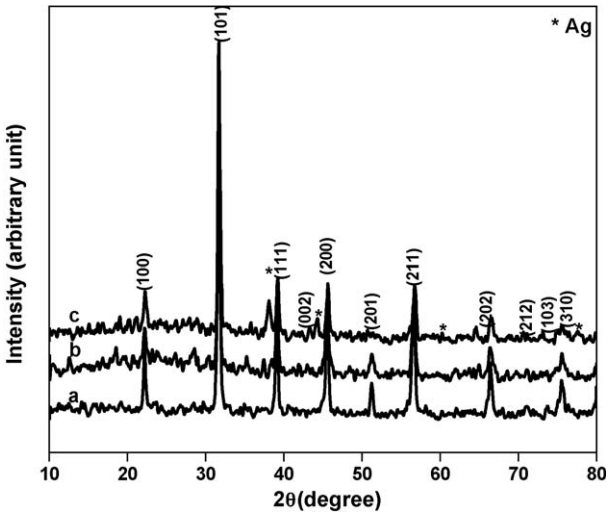


Fig. 4. XRD pattern of sintered samples of (a) BST, (b) BST–8 wt% PBS and (c) BST–8 wt% PBS–14 vol% Ag composite.

$2.46 \times 10^{-4}$ S/cm by the addition of 20 vol% of silver. The $\varepsilon_r$ further increased to $1.4 \times 10^5$ and $\sigma$ to $7.9 \times 10^{-3}$ S/cm as the vol% of Ag increased to 24%. Recently Huang et al. [9] reported a high percolation threshold of 28 vol% of Ag in BST. The glass addition promoted densification of BST even at lower temperatures by liquid phase sintering [10,11]. Fig. 3a and b shows the variation in $\varepsilon_r$ and $\sigma$ of BST–8 wt% PBS composites with different vol% of silver. It is evident from the figure that the percolation threshold achieved lowered to 14 vol% of Ag in BST–8 wt% PBS composites. The $\varepsilon_r$ increased from 4384 to $5 \times 10^5$ and $\sigma$ from $6.8 \times 10^{-5}$ S/cm to $4.2 \times 10^{-2}$ S/cm as the vol% of Ag increased from 13 to 14%. The lowered sintering temperature minimized the silver loss due to sintering at high temperatures. The X-ray diffraction patterns (Fig. 4) did not show any peak other than those corresponding to BST and silver; no peak corresponding to silver oxide was found in the XRD pattern of composites. Silver is more stable than silver oxide at temperatures greater than 189 °C [12] and the chances of formation of $Ag_2O$ during cooling is very little [13]. The SEM microstructure of BST–PBS–Ag composites is shown in Fig. 5a and b. Bright specks of Ag can be seen in the samples BS8-15 and BS8-17 indicating that Ag is uniformly distributed in the composites.

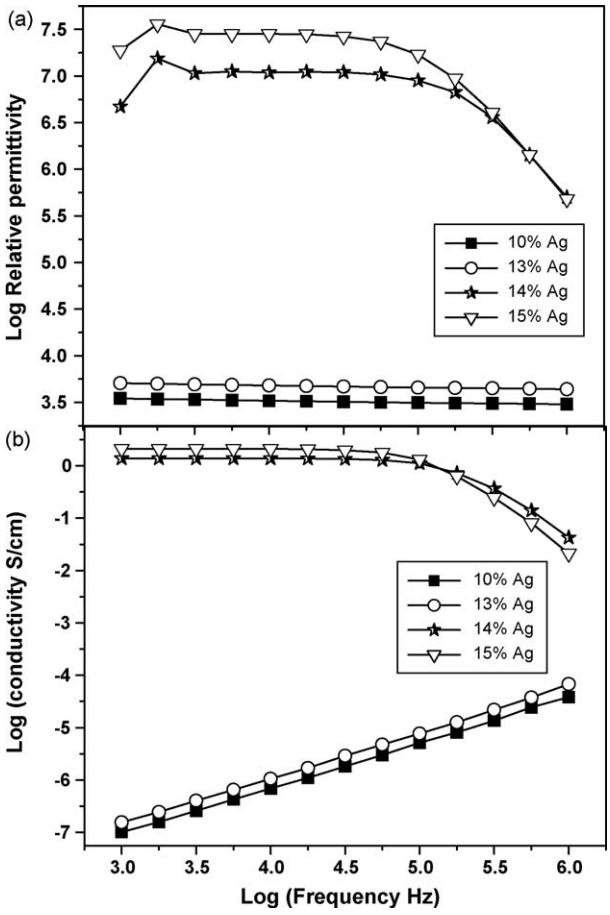


Fig. 6. Variation of (a) relative permittivity, (b) conductivity with frequency for different BST–8 wt% PBS–Ag composites.

The dielectric and conduction behavior of the composites were studied from the frequency dependence of $\sigma$ and $\varepsilon_r$. It is found (Fig. 6a) that at lower vol% of Ag (5–13%) $\varepsilon_r$ decreased gradually with frequency, whereas the $\sigma$ gradually increased with frequency (Fig. 6b). At the percolation threshold (14 vol%), the $\varepsilon_r$ and $\sigma$ remains almost independent of frequency and at higher frequencies they gradually decreased. At lower vol%, the Ag particles are well separated and under applied field the charge carriers move and get accumulated at the grain boundaries causing interfacial polarization. Its

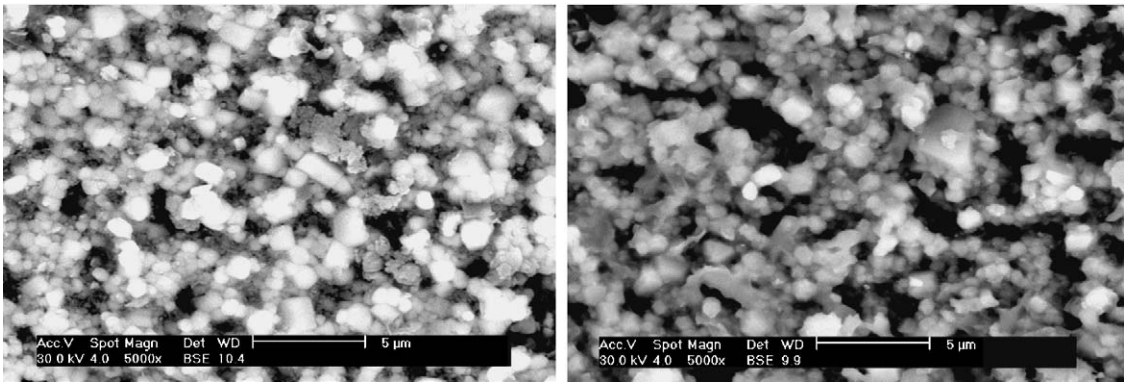


Fig. 5. SEM micrographs (a) BST–8 wt% PBS–15 vol% Ag and (b) BST–8 wt% PBS–17 vol% Ag composites.

relaxation with increase in frequency causes a decrease in $\varepsilon_r$ [14]. The increased current in the Ag particles with frequency causes the gradual increase in $\sigma$ of the composite [2]. With increase in Ag content, the distance between the Ag particles get reduced and near the percolation threshold the diffused double layer around the conducting phase gets overlapped. This diffused double layer [15] is a layer around each Ag particle where the property changes from Ag to BST. This leads to a multipolar interaction between the particles and cause a drastic increase in the permittivity and conductivity (Fig. 3) at the percolation threshold [16]. The interparticle distance is reduced considerably near the percolation threshold and electrons can move freely over a large distance under the applied field giving frequency independent $\varepsilon_r$ and $\sigma$ [14].

## 4. Conclusions

The pure BST–Ag composites showed a percolation limit of 24 vol% of silver. This high value of percolation threshold is due to the apparent escape of silver at higher sintering temperatures. The addition of 8 wt% of PBS glass lowered the sintering temperature of BST from 1300 to 975 °C and addition of Ag further lowered the sintering temperature of the composites to 925 °C. This lowering of sintering temperature prevented the Ag loss during sintering and lowered the percolation threshold from 24 to 14 vol% of Ag. The $\varepsilon_r$ of pure BST composite sintered at 1300 °C increased from 2700 to 9790 at 20 vol% of Ag and at 24 vol% it increased sharply to $1.4 \times 10^5$. However, for BST–8 wt% PBS sintered at 925 °C, the $\varepsilon_r$ increased from 1050 to 4384 at 13 vol% of Ag and showed a sharp increase to $5.1 \times 10^5$ near the percolation limit (14 vol%) of Ag.

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