The effect of Lead-glass Additives on Densification and Dielectric Properties of Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ Ceramics

Q.M. ZHANG, J.D. CUI, G.X. DONG and J. Du
Advanced Electronic Materials Institute, General Research Institute for Nonferrous Metals, Beijing 100088, china
E-mail: dujun@grinm.com

Abstract. Effects of lead-glass additives on the densification, microstructure and dielectric properties of Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ (BST) were investigated. Three simple glass systems including PbO-SiO$_2$, PbO-SiO$_2$-B$_2$O$_3$, and PbO-ZnO-B$_2$O$_3$ were employed. 4 wt% lead-containing glass was added to BST ceramics, which accelerated densification with limited grain growth. The sintering temperatures of lead glass added BST ceramics were lowered to 1000 ºC~1050 ºC with high density above 96%, which were all higher than that of the pure BST sintered at 1350 ºC. The dielectric constant of BST ceramics with PbO-SiO$_2$ glass additives was higher than that of the pure BST ceramics and dissipation factor of all BST samples with lead glass additives was lower than $1 \times 10^{-3}$ at 1 kHz.

1. Introduction
Barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$) is the solid solution of BaTiO$_3$ and SrTiO$_3$ with excellent dielectric properties, which has been used in electronic, electro-optical, optical, acoustic, and microwave devices [1-4]. Most of the above mentioned applications exploit the properties of the ferroelectric phase. Comparatively little attention has been paid to the dielectric characteristics of the paraelectric state, especially for $x \leq 0.4$, which has relatively high dielectric constant, lower dielectric loss, and higher breakdown strength [5-7]. Dielectric loss is often important for dielectrics applications, which is usually lower in the paraelectric state than in the ferroelectric state owing to the disappearance of hysteresis. It is desirable that the Curie temperature of the ferroelectric materials be lower than the operating temperature in order to minimize the loss factor.

In addition, Barium strontium titanate has a high sintering temperature of about 1350 ºC, which causes excess grain growth and increases manufacturing costs, especially for multilayer ceramic capacitors (MLCC) [8, 9]. Coarse grains are also bad for dielectric properties, especially for the breakdown strength [10-12]. Therefore, much effort has been directed towards the investigation of the decrease of the sintering temperature by controlling the sintering conditions and adding sintering aids. One effective method of decreasing the sintering temperature is to add glasses that have low melting points to form liquid phase at the sintering temperature [13-16]. The liquid phase promotes sintering process at a relatively low temperature.

The main purpose of this paper is to investigate the effects of addition of three lead-containing glasses on densification and dielectric properties of Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ ceramics. Three lead-glass systems used in the present study were 60 mol% PbO-40 mol% SiO$_2$ (PS), 40 mol% PbO-20 mol% SiO$_2$-40
mol% B$_2$O$_3$ (PSB), and 36 mol% PbO-18 mol% ZnO-46 mol% B$_2$O$_3$ (PZB), respectively. 4wt% glass was added to BST ceramics.

2. Experimental procedure

Ba$_{0.4}$Sr$_{0.6}$TiO$_3$ powders used in this study were prepared by a conventional solid state reaction. Reagent-grade BaCO$_3$ (≥99%), SrCO$_3$ (≥99%) and TiO$_2$ (≥99%) powders were used as starting materials. The stoichiometric amounts of powder mixtures were ball-milled in ethanol medium using zirconia balls for 24 h. The slurry was then dried, ground well and calcined at 1150 °C in air for 4 h.

Calculated amounts of reagent-grade chemicals for the various glass compositions were weighed, mixed, and melted in quartz crucible in an air atmosphere at 1100 °C for 2 h. The molten glass was quenched in water and then crushed in an agate bowl. Each crushed glass powder was sieved to pass through the 400 mesh screen.

4 wt% glass powders and 96 wt% BST powders were mixed thoroughly as mentioned earlier, dried and then pressed into pellets. Pure BST was sintered at 1350 °C for 3 h, and glass-added pellets were sintered at different temperatures ranging from 900 °C to 1150 °C for 3 h.

Density measurements were made using the Archimedes technique. The crystal structure and phase purity of the samples were analyzed by X-ray diffraction. Microstructures of the ceramics were studied on as-fired surfaces using SEM. Dielectric measurements were performed on plane parallel disks approximately 1 mm thick, which were coated uniformly with a silver paste on both faces, and then fired at 600 °C for 20 min. Room temperature dielectric properties such as dielectric constant and dissipation factor were measured using Hp 4284 LCR meter in the frequency range of 1 kHz to 1 MHz.

3. Results and discussion

Figure 1 shows the change of relative density of the BST ceramics with different lead-containing glass additives and sintering temperatures. It is seen that the melted glass phase accelerated the densification of sintered bodies and lowered the sintering temperature. Addition of 4 wt% PS and PSB glass decreased the sintering temperature to 1050 °C with the maximum relative density of 97.1% and 96.4%, respectively. Addition of 4 wt% PZB glass decreased the sintering temperature to 1000 °C, and the maximum relative density was 96.5%. The relative density of all samples at their optimum sintering temperature was higher than that of the pure BST ceramics sintered at 1350 °C. Throughout the rest of this study, all the glass added samples were sintered at their optimum temperature. From this study, liquid-phase sintering is shown to decrease the sintering temperature by 300 °C ~350 °C with 4 wt% lead-containing glass additives, which can in turn lower the processing costs of BST ceramics and allow for the use of less expensive electrode such as Ni.
Figure 2 shows the XRD patterns of pure BST and BST ceramics with 4 wt% PS, PSB and PZB glass additives. There were no impurity peaks observed in figure 2(a), and all peaks were identified to be due to perovskite BST phase with cubic structure. In figure 2(b)-(d), in addition to the main phase of BST, very small amounts of silicate phases could be founded, which showed reaction between BST and glasses occurred slightly during the sintering process. The lattice constant was calculated by XRD data. The lattice constants of pure BST and BST with 4 wt% PS, PSB and PZB glass additives were 3.9423, 3.9395, 3.9415 and 3.9407, respectively. With the addition of glasses, the lattice constants were slightly decreased. This indicated that the Pb$^{2+}$ ion was substituted into the BST lattice with the chemical reaction between BST and glasses. The microstructure of pure BST and lead-glass added BST is shown in figure 3. Pure BST had a wide grain size distribution, with the average size of about 20 μm. Figure 3(b)-(d) shows the microstructure of 4 wt% PS, PSB and PZB glass added BST ceramics, respectively. The grain size obviously decreased with lead glass addition, of which the average size was only several microns, and the grain size distribution was narrower, which was mainly attributed to lower sintering temperature.

![Figure 2. The XRD patterns of (a) pure BST, (b) BST + 4 wt% PS glass, (c) BST+4 wt% PSB glass, (d) BST+4 wt% of PZB glass.](image)

![Figure 3. The scanning electron micrographs of (a) pure BST sintered at 1350 ºC, (b) 4 wt% PS glass added BST sintered at 1050 ºC, (c) 4 wt% PSB glass added BST sintered at 1050 ºC, (d) 4 wt% PZB glass added BST sintered at 1000 ºC.](image)
Change of room temperature dielectric constant and dissipation factor as a function of measurement frequency for the BST ceramics with lead glass additives at their optimum sintering temperatures is shown in figure 4. The dielectric constant of pure BST sintered at 1350 ºC was about 1087. Dielectric constant of the PS glass added BST sintered at 1050 ºC was about 1143, which was higher than that of the pure BST. This increase was attributed to lower porosity and a refinement of grain size [17]. The dielectric constant of the PSB glass-added BST was 1065, which was slightly lower than that of the pure BST. The PZB glass-added BST had the lowest dielectric constant of about 965. The dissipation factor of BST samples with addition of PS and PZB glasses was lower than that of pure BST, which was about $1 \times 10^{-3}$ at 1 kHz.

![Figure 4](image)

Figure 4. Variation of (a) dielectric constant and (b) dissipation factor as a function of measurement frequency.

Temperature dependence of dielectric properties of the specimens is denoted in figure 5. The Curie temperature of pure BST was found to be about -68 ºC. The addition of three lead glasses led to a slight shift in Curie temperature towards higher temperature, which indicated Pb$^{2+}$ ion diffused into BST lattice and formed the solid solution. Pb$^{2+}$ ion present in the glasses was known to form substitutional solid solution with perovskite compounds, replacing either the A or B site cations in the lattice, which resulted in a shift in Curie temperature [18]. The dielectric loss also showed a peak at the transition temperature, which indicated a well-defined phase transition. The dielectric loss decreased with increase in the temperature beyond the loss peak and reached a minimum at about room temperature. Further increase in temperature increased the dielectric loss again.

![Figure 5](image)

Figure 5. Variation of (a) dielectric constant and (b) dissipation factor as a function of measurement temperature.
4. Conclusions
Three lead glasses were added to BST ceramics in the amount of 4wt%. The relative density of all samples at their optimum sintering temperature was higher than that of the pure BST ceramics sintered at 1350 °C. Dielectric constant of PS glass added BST ceramics sintered at 1050 °C were higher than that of the pure BST ceramics, and the dielectric loss of all samples with glass addition was lower than $1 \times 10^{-3}$ at 1 kHz. It was observed that a small amount of glasses effectively lowered the preparation temperature and improved the dielectric properties of BST ceramics, especially for PS glass.

References
[1] Thakur O P, Chandra Prakash, and Agrawal D K 2002 Materials Science and Engineering B 96 221-5
[2] J. W. Liou and B. S. Chiou 1997 J. Am. Ceram. Soc. 80 3093-9
[3] Ali N J and Milne S J 1993 J. Am. Ceram. Soc. 76 2321-6
[4] Chen Y C and Huang C L 2006 Materials Letters 60 451-4
[5] Liou J W and Chiou B S 1997 Materials Chemistry and Physics 51 59-63
[6] Pohanka R C, Freiman S W, and Bender B A 1978 J. Am. Ceram. Soc. 61 72-5
[7] Tomoko Kito and John U T 1995 J. Mater. Res. 10 1411-7
[8] Jeon H P, Lee S K, Kimb S W, and Choi D K 2005 Materials Chemistry and Physics 94 185–9
[9] Prakash D, Sharma B P, Rama Mohan T R, and Gopalan P, 2000 Journal of Solid State Chemistry 155 86-95
[10] Yang Y, Zhang S C, and Dogan F 2003 Pulsed Power Conference Digest of Technical Papers 1 719–22
[11] Beauchamp E K 1971 J. Am. Ceram. Soc. 54 484–7
[12] Tunkasiri T and Rujijanagul G 1996 Journal of Materials Science Letters 15 1767 -9
[13] Priya Rani B R and Sebastian M T 2008 J. Mater. Sci: Mater Electron 19 39–44
[14] Armstrong T R, Young K A and Buchanan R C 1990 J. Am. Ceram. Soc. 73 700-6
[15] Zhang B,Yao X, and Zhang L Y, 2004 Ceramics International 30 1767 –71
[16] Zhai J w, Yao X, Cheng X G and Zhang L Y 2002 Journal of Materials Science 37 3739 – 45
[17] Arlt G, Hennings D, and Dewith G, 1985 J. Appl. Phys. 58 1619
[18] Hirata A and Yamaguchi T 1997 J. Am. Ceram. Soc.80 79-84