Effect of Lead Borosilicate Glass addition on the Crystallization, ferroelectric and dielectric energy storage properties of $\text{Ba}_{0.9995}\text{La}_{0.0005}\text{TiO}_3$ Ceramics

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Abstract

This article presents the effect of lead-borosilicate glass (65PbO-20B₂O₃-15SiO₂, mol%) (PBS) addition on the structure, microstructure, dielectric, ferroelectric and energy storage properties of $\text{Ba}_{0.9995}\text{La}_{0.0005}\text{TiO}_3$ (BLT) ceramics system has been systematically investigated. XRD analysis revealed the tetragonal (T) phase at room temperature. Addition of PBS glass results in decrease in ferroelectricity and improved breakdown properties. High maximum polarization ($P_s \sim 21.53 \mu\text{C}/\text{cm}^2$) and remnant polarization values ($2P_r \sim 8.75 \mu\text{C}/\text{cm}^2$) were obtained from ferroelectric (P-E) hysteresis loops for the BLT ceramics. Two dielectric anomalies at 420 K and 600 K were observed due to the phase transformation. The glass-ceramics heat treated at 900 °C for 3h was found to possess optimal properties with breakdown strength of $> 300 \text{ kV}/\text{cm}$ and energy storage density of $0.564 \text{ J}/\text{cm}^3$, which is a promising glass-ceramic ferroelectric capacitor material for high energy storage density dielectrics.

Key words: Dielectrics, Energy Storage, BaTiO_3 , Glass-Ceramics, Capacitors

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I. Introduction

Capacitive electric energy storage in materials is a novel approach for large-scale electrical energy storage applications. The dielectric constant and breakdown strength of the materials play a vital role in the amount of electrostatics energy to be stored in capacitors. Materials with high dielectric constant and high breakdown strength are required for high-energy density capacitors in stationary power electronics, mobile devices and pulsed power applications [1,2]. There is a great need and high demand for next generation electrical energy storage devices in the aforementioned applications. In addition to these properties, it is also important that the materials with a low dielectric loss against temperature are also important for an ideal capacitor [2]. Ferroelectric ceramic materials exhibit high dielectric constant ($\epsilon > 1000$) and they are considered as suitable materials for electrical and electronics applications, but conventional ceramics have low dielectric breakdown strength. There are several extrinsic factors that contribute to lowering the dielectric breakdown strength of polycrystalline materials which include pores, grain boundaries, and anisotropic permittivity in randomly oriented crystals [3]. Both polymers and glasses are considered as potential candidate materials for energy storage application and both have advantages and disadvantages for aforementioned applications. Dielectric polymers have relatively low dielectric constant ($\epsilon \leq 12$) with high dielectric breakdown strength ($\text{DBS} > 2 \text{ MV/cm}$), however their operating temperatures are rather very low [4]. However, PVDF is the most studied ferroelectric polymer due to its spontaneous polarization with relatively high dielectric constant ($\epsilon = 12$) and higher breakdown strength ($\text{DBS} \geq 5 \text{ MV/cm}$) [2]. Glass is also considered as a promising candidate for high-

temperature capacitor applications, due to its inherent high thermal stability, excellent insulating properties, and potential for self-healing during dielectric breakdown, however it has low dielectric constant [5]. Low melting glass with high dielectric constant is critical for high energy density storage capacitors. In general a glass-ceramic material consists of at least one high dielectric breakdown strength glass phase and one crystalline phase high dielectric constant ceramic.

By controlled crystallization (i.e nucleation and growth of glass) glass-ceramics can be processed [6]. Highest energy density in a ferroelectric capacitor can be achieved in glass–ceramic materials by combining high dielectric breakdown strength glass with high dielectric constant ceramic, in which a ferroelectric phase is crystallized by the devitrification of a glass matrix [6]. Pore free microstructures can be obtained by combining glass and ceramic materials in glass-ceramics with improved energy density properties than that of the conventional ceramic dielectrics.

Several dielectric and ferroelectric ceramic filler materials have been employed to fabricate a capacitors: silicone nitrate (Si_3N_4), silicon oxide (SiO_2), titanium dioxide (TiO_2), aluminum oxide (Al_2O_3), zinc oxide (ZnO) barium titanate (BaTiO_3 -BTO), lithium niobate (LiNbO_3), lead titanate (PbTiO_3) and lead zirconate titanate ($\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$) [2]. Ternary TiO_2 – BaO – B_2O_3 glasses were first studied for the crystallization pathways and kinetics due to their potential as ferroelectric glass–ceramics containing BTO crystals [7-9]. There have been many investigations on high dielectric constant glass–ceramics containing ferroelectric phases such as barium titanate and its solid solutions barium strontium titanates (Ba,SrTiO_3 (BST), [10-13], barium calcium/ barium zirconium titanate ($\text{Ba,Ca}(\text{Zr,Ti})\text{O}_3$ (BZT-BCT) [14], and lead strontium barium niobate [15] have focused

on crystallization, microstructure, ferroelectric, dielectric and energy storage properties. Few advantages in preparing glass–ceramics with a crystallized ferroelectric phase in a glass matrix include finer crystallites, more homogeneous mixture of the crystalline and glass phases, and low porosity [13]. The ferroelectric glass-ceramics are considered, the most promising energy storage capacitors due to their synergistic effect of high dielectric constant from crystalline ceramic phase and high dielectric breakdown strength due to the pore-free nature of the residual glass content in the composition [14]. The crystallization behavior can be enhanced by using certain nucleating agents such as La_2O_3 , Nb_2O_3 , Fe_2O_3 and Bi_2O_3 and they also promote crystallization of major perovskite phase and reduce the amount of secondary phase [16]. From literature it is also identified that various glass containing metal oxides (PbO , BaO , SrO , B_2O_3 , SiO_2 , ZnO , CdO , Al_2O_3) have been used to lower the sintering temperature and as well as they have been employed to improve dielectric breakdown strength (DBS) with improved dielectric constant and high energy density properties [14,17-19]. The addition of glass ($3\text{BaO}-3\text{TiO}_2-\text{B}_2\text{O}_3$) in small amounts (1wt.%) to vanadium doped BTO ceramics increased saturation polarization, with a significant increase in the energy storage density and a thermally invariant ferroelectric properties were reported by Satyanarayan Patel et. al., [20]. Better dielectric properties were reported for alio-valent (La_2O_3) substituted barium strontium titanate (Ba,SrTiO_3) (BST) ferroelectric glass-ceramics made by melt-quenching method followed by controlled crystallization [21]. Effect of lanthanum doping in BST glass ceramics has been investigate by differential scanning calorimeter (DSC), X-ray diffractometer and Raman spectroscopy [22]. Controlled crystallization of 1.0 wt% La_2O_3 content in BST glass ceramics is also reported with optimized energy storage density (3.18 J/cm^3) which is 2.56 times higher than pure BST glass-ceramics (1.25 J/cm^3) [23].

This study extends the previous work to understand the effect of PBS glass on La_2O_3 doped BTO. Here in this paper, we report crystallization kinetics, microstructure, dielectric, ferroelectric and energy storage properties of BTO, BLT, and PBS-BLT glass-ceramics.

II. Experimental Procedure

BaTiO_3 doped with 1.5 at% lanthanum was prepared by using a conventional solid-state synthesis route. Reagent grade (99.9% pure) powders of BaCO_3 , TiO_2 , and La_2O_3 (Alfa Aesar USA) were used as raw materials. The powders were mixed in stoichiometric ratios and milled in acetone to obtain physical homogeneity. Afterwards, the slurry was dried and the mixture was calcined in an alumina crucible at 1250°C for 10 h in air. The calcined powder was then ground and analyzed using powder X-ray diffraction using $\text{CuK}\alpha$ radiation (Rigaku, Rigaku Tokyo, Japan). The glass composition lead borosilicate (65PbO - $20\text{B}_2\text{O}_3$ - 15SiO_2 , mol%)-PBS was used in present study. It was fabricated by means of a conventional melt quenched technique. For this purpose, reagent-grade powders of PbO , SiO_2 , and B_2O_3 were weighed according to the stoichiometric formula. The powders were thoroughly mixed and melted in a platinum crucible at 1300°C in air. The mixture was held at 1300°C for 30 min, and then the melt was quenched between stainless steel plates. The obtained glass samples were ground into a fine powder. The amorphous nature of the quenched glass was confirmed by using X-ray powder diffraction. The sintered lanthanum doped BTO powder was ground and separated into 4 individual batches. The ground lead borosilicate glass powder was added to four of these batches in quantities of 15, 20, 30 and 40 wt%., and thoroughly mixed to achieve homogeneity. Then 4 wt.% polyvinyl alcohol (PVA) binder was added to the powder and pressed into green pellets of 12 mm_0.3 mm (diameter_thickness). The glass-ceramics samples were sintered at 750°C for 3 h.

The pure lanthanum doped BTO pellets were sintered at 1350°C for 6 h. The addition of glass could reduce the sintering temperature owing to viscous sintering effect. Therefore, pellets with added glass were successfully sintered at **1350°C** in air for 6 h. The sintered samples were phase identified using X-ray diffraction analysis. To confirm the morphology of the sintered pellets, scanning electron microscopy (SEM; FEI SEM NOVA Nanosem 450, Pacific Tech Center, Singapore) images were taken. The polarization-electric field (P–E) hysteresis loops were obtained for the poled samples by using a modified Sawyer–Tower circuit at different electric field strengths (Radiant Technologies, NM, USA).

Characterization Techniques

To evaluate crystalline structure, the X-ray powder diffraction (XRD) profiles of the film samples were recorded using Cu K α radiation from a highly stabilized and automated Rigaku X-ray generator operated at 40 kV and 40 mA. The XRD data were recorded at a step size 0.02 and step scan 1°/ min, for the entire angular range 10°–80°.

Ferroelectric (P-E) measurements were performed with a Radiant Technologies (RT 6000 HVA-4000V) amplifier. The electrical breakdown voltage of the capacitor metal-insulator-metal (MIM) configuration was measured at room temperature using Trek (10kV) high voltage amplifier. Moreover, the dielectric characterization of the samples was conducted by Broadband Dielectric Spectroscopy (BDS) in the frequency range of 100 Hz to 1 MHz using a HP4294A LCR meter.

3. Results and discussion

Crystallization and Morphology

Phase evolution of the glass (PBS), ceramic BTO, BLT and glass–ceramics [BLT-PBS (15%, 20%, 30%, 40%)] at room temperature was characterized by X-ray diffraction (XRD). XRD patterns of PBS, BTO, BLT and BLT-PBS (15%, 20%, 30%, 40%) glass-ceramic samples acquired are shown in Fig.1. PBS glass ceramic materials have shown fully amorphous phase and XRD patterns of the BTO, BLT and BLT-PBS (15%, 20%, 30%, 40%) glass-ceramics are indexed to the desired perovskite tetragonal phase. These XRD patterns are in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card numbers 05-0626. The sharp and well-defined diffraction peaks indicate that this ceramic material has a good degree of crystallinity in the long range order. No secondary peaks in La doped BTO indicates that La^{3+} is completely diffused into Ba^{2+} site in BTO crystal lattice. The splitting of (002) and (200) diffraction peaks in all the compositions confirmed the tetragonal structure of the ceramics at room temperature. A small amount of glass-ceramics phase along with polycrystalline perovskite was observed for 40 wt% of BLT-PBS and this peak is detected at around $20\sim 29^\circ$ (marked with # symbol). The glass-ceramics samples were observed to be fully crystalline when sintered at 900°C for 3 h.

Figure 2a–d shows the microstructural (SEM) images of BTO, BLT and BLT ceramics with different amounts of PBS (15, 20, 30, 40 wt.%)–BLT glass-ceramics. The SEM micrograph of BTO, BLT ceramics and PBS-BLT glass-ceramics has shown uniform distribution of grains throughout the surface of the sample. The grains and grain boundaries are well defined in the BTO, BLT samples. Homogeneous and dense microstructure with minimum number of voids was observed in SEM micrographs as the glass content increased. Dense microstructure

in this ceramics system is attributed effective sintering of the ceramics. However there exist some big voids among the grains and ensuing oxygen vacancies during the synthesis at high temperature for BTO, BLT ceramics. Overall grain growth with dense microstructures in these BTO, BLT ceramics might be attributed to higher sintering temperature. Bimodal grain size distributions with large grains distributed among small grains were observed in these ceramics. As the glass content increased in the glass-ceramics, the distribution of the grain size is non-uniform and glass may be filling the space between the grain and the grain-boundaries. By this way highly dense and pore free microstructures can be achieved in glass-ceramic samples (via melting re-crystallization methods) [24-26].

Fig. 3 (a) depicts the ferroelectric P–E hysteresis loops for all studied compositions measured at an applied frequency of 50 Hz, which were measured up to their breakdown field. Pure BTO and BLT ceramics have shown typical ferroelectric hysteresis loops. Figure 3(b) shows the electric field dependent polarization (P–E) ferroelectric hysteresis loops as observed for 15, 20, 30, and 40 wt% BLT-PBS glass-ceramics at room temperature. It can be seen that pure BTO and BLT shows a large saturation polarization of 13.4, 21.5 $\mu\text{C}/\text{cm}^2$, while the saturation polarization of BLT-PBS15, BLT-PBS20, BLT-PBS30 and BLT-PBS40 is 11.84, 6.40, 5.85, 2.60 $\mu\text{C}/\text{cm}^2$, respectively. In contrast to the BTO and BLT ferroelectric hysteresis loops, the P–E loops of the PBS-BLT glass-ceramics are nearly linear under a low electric field around $\sim 300 \text{ kV cm}^{-1}$ and a deviation from non-linearity was observed. The suppression of ferroelectric switching in linear ferroelectric hysteresis loops in dense nanocrystalline BTO was first reported by Buscaglia et. al., [27,28]. More recently Su et. al., also reported similar behavior for their Bi-BT nanocomposites. Ferroelectric polarization suppression for nanocrystalline BTO was closely related to a) the decrease of the local electric field due to the presence of low dielectric constant grain boundaries and b) domain wall pinning movement

and the hindrance of domain switching resulting from the grain boundaries or the defects present at the grain boundaries.

Compared to both BTO, BLT ceramics, glass added BLT ceramics substantially reduced remnant polarization and saturation polarization along with an increase in applied electric field. This indicates that as the glass content increased, the material shows a gradual transition from ferroelectric to linear dielectric behavior. However, the reduction in the value of saturation polarization, with increasing glass content in BLT ceramics can be attributed to increasing grain separation and due to widening grain boundaries the intergranular domain interaction is weakened [20]. The ferroelectric (P–E) hysteresis loops exhibited a good remnant polarization, saturation polarization and coercive field. This result indicates that a good quantity of ferroelectric phases is formed from the glass matrix. As the glass content increased in these glass-ceramic samples, the semi-linear behavior of the P–E hysteresis loops is observed mainly due to weak ferroelectric phase particles in micrometer and strong paraelectric glass phase.

The energy density was obtained by integrating the area between the polarization axis and the discharge curve in a polarization versus electric field (P-E) hysteresis loops. The energy density (the energy storage capability) of non-linear ferroelectric ceramics is calculated from its P-E hysteresis loop by using the following equation (1):

$$J = \oint_{P_r}^{P_{max}} E dP = \frac{1}{2} \varepsilon_0 \varepsilon_r E_b^2 \quad (1)$$

Here, J represents the electrical energy density stored in the material, E or E_b refers to the applied external electric field (breakdown strength), P_r and P_{max} are the remnant and maximum polarization values, respectively. From the above equation

(1), a high energy density can be obtained by a huge difference between P_r and $P_{\max}$ [4]. The discharged energy density (J_d) is obtained from upper curve (discharge curve) of P-E ferroelectric hysteresis loop which is equal to integral of the area enclosed by discharge curve and y-axis. The charged energy density (J_c) is obtained from bottom curve (discharge curve) of P-E ferroelectric hysteresis loop which is equal to integral of the area enclosed by charge curve and y-axis. The energy storage efficiency of these glass-ceramics was also calculated the ratio of re-coverable energy storage density to that of charge curve energy density from ferroelectric P-E hysteresis loops using the following equation (2) [4]. The smaller the energy storage efficiency (η) corresponds to higher the loss in P-E hysteresis loop.

$$\eta = \frac{J_d}{J_c} * 100\% \quad (2)$$

The breakdown strength of capacitor materials depends on several factors which include: porosity, grain size, and extrinsic measurement conditions such as sample thickness, sample area, and electrode configuration [29]. Dielectric breakdown is a failure phenomenon and the electric field concentration is found in the vicinity of pores, electrode edge and other structural defects. It is necessary to eliminate defects in the structure and as well the electrical field concentration near defects to enhance the dielectric breakdown field [30]. Electrical energy storage prosperities (the charge curve and discharge curve energy densities) for BTO, BLT and PBS-BLT glass–ceramic samples were evaluated from integral area of ferroelectric P-E hysteresis loops. **The recoverable energy densities (discharged curve energy density), charge curve energy densities and energy storage efficiencies of the PBS-BLT glass–ceramics are listed in Table.1.**

As the glass content increased from 15 to 40 wt.%, dielectric breakdown strength, and energy efficiency of the glass-ceramic capacitors were improved with glass content. However, their energy densities were reduced from 0.564 J/cm³ to 0.06 J/cm³. The early saturation polarization limits further increase in energy storage of PBS-BLT glass-ceramics under higher electric fields. As shown in the energy storage density equation, E_d is proportional to dielectric constant and square of the electric field for a linear dielectric.

Clearly, the dielectric breakdown strength PBS-BLT ceramics increases with the increase of glass content. However, the energy storage density decreased with increasing glass content. The interfacial polarization may be the source of the hysteresis and thus, contribute to the low energy density values in the PBS-BLT glass-ceramics. The presence of silica glass with higher resistivity and low dielectric permittivity in the PBS-BLT glass-ceramic composition might be the other reason for low electrical energy density in the current capacitors due to uneven field distribution even though these glass-ceramics are highly densified [30].

Dielectric properties

Fig.4 illustrates the temperature dependence of the dielectric constant at various selected frequencies (100 Hz-1 MHz) for BTO, BLT (300 K to 500K) and PBS-BLT (300 K to 725K) glass- ceramics. Dielectric constant (ϵ), was calculated from the measured, capacitance (c) using the following equation (3):

$$\epsilon = \frac{C * d}{\epsilon_0 * A} \quad (3)$$

Where, C is the capacitance in farad, F , ϵ_0 is the permittivity of free space ($8.85 \times 10^{-14} \text{ F/cm}$), d is the thickness (cm) and A is the surface area (cm^2) of the samples.

Both BTO and BLT ceramics have shown ferroelectric to paraelectric phase transition at around (T_c) $\sim 410\text{-}420 \text{ K}$. However, glass-ceramics have shown the two dielectric anomalies at 420 K and 600 K . It is also seen from the temperature dependent dielectric properties, that with increase in PBS glass content in BLT ceramics, the T_c shifts to lower temperatures and the transitions also become more diffused. The 40 wt.% PBS-BLT glass–ceramic composition has shown the lowest temperature dependence of dielectric constant. The reason for the shift in the T_c , is attributed to compositional variation in the ferroelectric phase due to incorporation of elements between the ceramic and glass phases [13]. Temperature dependent dielectric constant measurements clearly demonstrated that dielectric constant increases slowly with increase in temperature, and a maximum dielectric constant (ϵ_{max}) ~ 18000 was observed at (T_c) $\sim 420 \text{ K}$ for BLT ceramics. It is observed that the dielectric constant decreases monotonically with increase in frequency at all temperatures for both BTO, BLT ceramics and is the signature of polar dielectric materials. It is also found that the value of the dielectric constant is significantly increased by La^{3+} doping at the Ba^{2+} -site, when compared to undoped BTO ceramics [31]. Higher values of dielectric constant at room temperature and at phase transition temperature for all these ceramics and glass-ceramics were attributed to many factors which include: (a) grain size; (b) change in density; (c) the grain boundary layer; (d) the release of internal stress; (f) the defect and domain wall motion; (g) good densification [32]. Temperature dependent dielectric constant curves also confirm broadening in the dielectric constant (ϵ) versus temperature (T) with diffuse phase transition (DPT) behavior. Similar results were reported by Divya et. al., [13]. The suppression of Curie temperature may attributed

to the clamping of the BaTiO₃ grains by the glass matrix [33, 34]. There is no shift in the dielectric constant with temperature curves at all frequencies measured, which ruled out relaxor behavior for these ceramics and as well as glass-ceramic compositions. From dielectric measurements it is also found that a drop in dielectric constant at high temperature and at high frequency (**Fig.4**), attribute is to the disappearance of spontaneous polarization as the ferroelectric tetragonal structure of ceramics transforms to a paraelectric cubic phase [35,36].

Fig.5 illustrates the temperature dependence of the dielectric loss, measured at 100 Hz-1 MHz for BTO, BLT and PBS-BLT glass-ceramics. Low dielectric loss ($\tan \delta \sim 0.034-0.16$) was observed throughout the measured temperature range. This low dielectric loss values might be due to non-existence of pores in the SEM image. High $\tan \delta$ at low frequencies with temperature might be due to the increase in the thermally generated free charge carriers in the sample. The increase in $\tan \delta$ at high frequencies is extrinsic in nature. It can also be seen from the **Fig.5** that a small variation in $\tan \delta$ values throughout the measured temperature. However $\tan \delta$ value at 100 Hz increased above 400 K. This increase in dielectric energy loss is attributed to, the interfacial polarization, caused by the difference in the electrical conductivity and permittivity of grain and grain boundary [37].

4. Conclusions

The objective of this work was to investigate the effect of glass addition for the possible improvement of the electrical energy storage density and storage efficiency into BLT bulk ceramics. The energy density of the composites was calculated using ferroelectric hysteresis loops. It was observed that a significant improvement in the energy storage density can be obtained by addition of lead borosilicate glass (65PbO-20B₂O₃-15SiO₂, mol%)-PBS. PBS-BLT nanocomposites

showed high polarization, high dielectric breakdown strength, high polarization saturation, and low remnant polarization with the discharge energy density of $\sim 0.564 \text{ J/cm}^3$ at around 300 kV/cm. Thus, further PBS-BLT glass-ceramic composite materials appear to be a promising material system for energy storage capacitors. Glass-ceramic composites are more advantageous to reduce the defect concentrations than the current state of art polymer-ceramic composites and as well in eliminating interfacial defects due to the absence of organic-inorganic interfaces.

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Figure Captions

Fig.1 The room temperature XRD patterns of PBS-BLT glass–ceramics sintered at 900°C, with 2θ angle ranging from 10° to 80° .

Fig.2 SEM micrographs of PBS-BLT glass–ceramics sintered at 900°C.

Fig.3 The room temperature P-E loops of BTO, BLT ceramics and PBS-BLT glass-ceramics sintered at 900°C.

Fig.4 The temperature dependence of the dielectric permittivity of PBS-BLT glass–ceramics sintered at 900°C.

Fig.5 The temperature dependence of the dielectric loss of PBS-BLT glass–ceramics sintered at 900°C.

Table 1

Remnant Polarization, Saturation Polarization, Coercive Field, Recoverable energy density, energy storage efficiency of PBS-BLT glass–ceramics sintered at 900°C.

Table.1

Composition	Remanent polarization - Pr($\mu\text{C}/\text{cm}^2$)	Saturation polarization- Ps($\mu\text{C}/\text{cm}^2$)	Coercive field (kV/cm)	Discharge Energy Density – (Ed) _d (J/cm^3)	Charge Energy Density (Ed) _c (J/cm^3)	Energy storage efficiency (%) ($\eta = (\text{Ed})_{\text{d}} / (\text{Ed})_{\text{c}}$)
BaTiO ₃ (BTO)	2.00	13.41	4.28	0.292	0.757	38.5
Ba _{0.9995} La _{0.0005} TiO ₃ (BLT)	3.10	21.55	3.8	0.342	0.873	39.1
BLT-PBS15	3.70	11.84	27.35	0.306	0.564	54.2
BLT-PBS20	2.50	6.40	39.30	0.139	0.262	53.0
BLT-PBS30	2.38	5.85	46.83	0.110	0.173	63.5
BLT-PBS40	0.82	2.60	43.85	0.044	0.06	73.3

Fig.1

Fig.2

Fig.3

Fig.4

Fig.5

Graphical Abstract