



Influence of liquid phase lead borate glass on dielectric response of lead iron niobate



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ABSTRACT

Lead iron niobate $[\text{Pb}(\text{Fe}_{1/2}^{+3}\text{Nb}_{1/2}^{+5})\text{O}_3]$ (PFN) is well recognized lead-based complex-double perovskite $[\text{A}(\text{B}_1\text{B}_{11})\text{O}_3]$ ferroelectrics. In the present work, the influence of liquid phase of lead borate glass $4\text{PbO}-\text{B}_2\text{O}_3$ (LB) on sinterability and dielectric behaviours of PFN are systematically investigated. The PFN powder was synthesized by combustion route (SHS synthesis) and LB-glass by conventional quenching technique, separately. The compositions of PFN and LB-glass (0–3 wt%) were prepared by ball milling. The crystalline structure of as-synthesized PFN, PFN–LB and amorphous nature of LB-glass are confirmed by XRD and well fitted by Rietveld refinement with *monoclinic* structure of 'Cm' space group. Microstructure was examined by SEM and TEM; indicates nanoscale dimensions of as-synthesized PFN. The green pellets of PFN and PFN–LB were sintered at various sintering conditions. Liquid phase sintering by LB-glass in PFN is found to strongly influence on the morphology, compactness and dielectric behaviour of nanostructure PFN. Semiquantitative correlation between microstructure and dielectric behaviour was established.

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1. Introduction

Lead iron niobate $[\text{Pb}(\text{Fe}_{1/2}^{+3}\text{Nb}_{1/2}^{+5})\text{O}_3]$ (PFN) belongs to lead-based complex-double perovskite $[\text{A}(\text{B}_1\text{B}_{11})\text{O}_3]$ ferroelectric family. It was found most attractive due to their exceptionally high dielectric constant for making multilayer ceramic capacitor [1–3]. Suitability of PFN to yield cost effective multilayer capacitors has been realized by lowering the sintering temperature (<1000 °C); it makes to use non-noble inexpensive materials (viz., 70:30 Ag; Pd, etc.) as electrode for multilayer capacitor [4–6]. A diffuse phase transition (DPT) with a non-relaxor type behaviour has been observed in PFN [7]. This makes the research on PFN-system more attentive and attempts have been mostly focused on development of high quality PFN-based system having low sintering temperature with enhancing dielectric constant, less loss and controlling lead loss during processing [8–12]. Optimizing processing conditions to obtain high quality PFN for device application is a major challenge.

Recent literature reveals that the liquid phase sintering (LPS) of ceramic using B_2O_3 , Bi_2O_3 , LiF, etc as sintering aids has been found to be a highly effective way to decrease sintering temperature with improving dielectric constant and minimizing lead loss during

sintering [13–16]. In general, liquid phase sintering in ceramics has been observed to induce complete densification at much lower temperature [17–19,15]. In addition to that, enhancement in dielectric and piezoelectric properties of ceramics has been reported in very few cases by liquid phase sintering [20–27].

A systematic review of recent literatures on use of glass as sintering aids to improve sinterability and dielectric behaviour in ferroelectric ceramics is given in [Supplementary data file-1](#). Amongst the available glasses system, PbO-based glasses have been observed to have lowest softening temperature, around 500 °C, high ionic polarizability and low dielectric losses and thus are more appropriate for liquid phase sintering [16,28].

With this motivation, in the present work, PbO-based glass are selected as sintering aids in the PFN double perovskite system. Structure is confirmed by X-ray diffraction study. Microstructures are examined by SEM and TEM. Sinterability of the PFN–LB system is systematically investigated by using liquid phase sintering and results are compared with pure PFN system. Effects of liquid phase sintering on dielectric behaviour are investigated. Semiquantitative correlation between microstructure and dielectric behaviour is established.

2. Experimental

The initial ingredients used in this work were $\text{Pb}(\text{NO}_3)_2$ (99% Merck), $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99% Merck) and Nb_2O_5 (99.5 Sigma–Aldrich) as cation precursors and urea, $\text{CO}(\text{NH}_2)_2$ (99% Merck) as a fuel. The precursor were initially mixed in 50 ml distilled

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water and stirred for 15 min to obtain a homogeneous mixture. The homogeneous solution was heated at 250 °C (optimized temperature), the liquid frothed for a while, followed by ignition with evolution of gases and combustion occurred. To complete the combustion reaction, the reactants were further heated at 550 °C for 10 min in muffle furnace; reddish brown product of PFN was obtained. The product was grounded at room temperature in a mortar. The LB-glasses were prepared by following earlier reported conventional quenching technique; ingredients B₂O₃ and PbO (Merck) were used for synthesis [15]. LB-glass in different weight percentages (0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt%) were dispersed in PFN to form different compositions. The compositions were mixed in presence of acetone with the help of ball mill (Pulverisette-6 Fritz, Germany). During ball milling, the milling rate was maintained at 600 rpm per hour. The powder was compacted using pressure of 5 ton/cm². The compacted pellets were sintered at temperature more than that of glass softening temperature. The density of the sintered pellet was determined using Archimedes principle [29] relative density was calculated. Table 1 lists the nomenclature used in the present work to represent various compositions of PFN, LB and their sintering conditions. When the LB-glass percentage in PFN was increased above 3 wt%, then sintered pellet was found to melt, above 700 °C. This is due to softening temperature of LB-glass around 500 °C. Hence, maximum upto 3 wt% LB is added in PFN as sintering aids in the present work.

The crystal structure was confirmed by X-ray powder diffraction (XRD) using Cu K α radiation, with the help of PANalytical X-ray powder diffractometer at 40 kV and 30 mA. Microstructure and surface morphology was examined by Transmission Electron Microscopy (TEM) CM200 TEM and Scanning electron microscope (JEOL: JSM-6380 Analytical SEM) equipped with an electronic probe analyzer system (Accelerating voltage 30 kV). For dielectric study, samples were coated with platinum for good ohmic contact. The dielectric constant (ϵ_r) and dissipation factor ($\tan \delta$) were measured at different frequencies from 10 Hz to 1000 kHz in 25–200 °C temperature range by using computer controlled HP-4192A LF impedance analyzer. The temperature during the measurements was controlled with an accuracy of ± 1 °C using Eurotherm temperature controller.

3. Results

The XRD patterns of pure PFN, 4PbO:B₂O₃ (40:60 wt%) LB-glass and PFN-3-LB-83 systems are shown in Fig. 1(a–c), respectively. XRD patterns of PFN (Fig. 1a) is well matched with the JCPDS data (file no. 0.032-0522) confirm the formation of single phase with monoclinic structure of PFN in “Cm” space group symmetry. The observed XRD peaks are well matched with the lines of perovskite phase of PFN. No additional impurity phases are found. The amorphous nature of the LB-glass is clearly depicted by Fig. 1b. XRD pattern of PFN-3-LB-83 reveals the presence of sharp crystalline peaks of PFN (Fig. 1c). The XRD data of both the samples (pure PFN and LB glass-dispersed PFN) are well fitted with Rietveld by “Cm” space group symmetry (shown in Fig. 2).

TEM image of the as-synthesis PFN shows (Fig. 3) oval shape of particles having diameter around 50 nm. The diffusive characteristics of PFN as viewed in the inset of Fig. 3 demonstrate the random distribution of Fe³⁺ and Nb⁵⁺. It is a clear evidence of existence of compositions fluctuation of the Fe³⁺ and Nb⁵⁺, which leads to formation of many microscopic regions on the B-sites. The same trends of results have earlier been reported by Cross [30].

SEM images of sintered pellets of PFN-0-LB-83 and PFN-2-LB-83 samples are shown in Fig. 4(a and b), respectively. Both the images

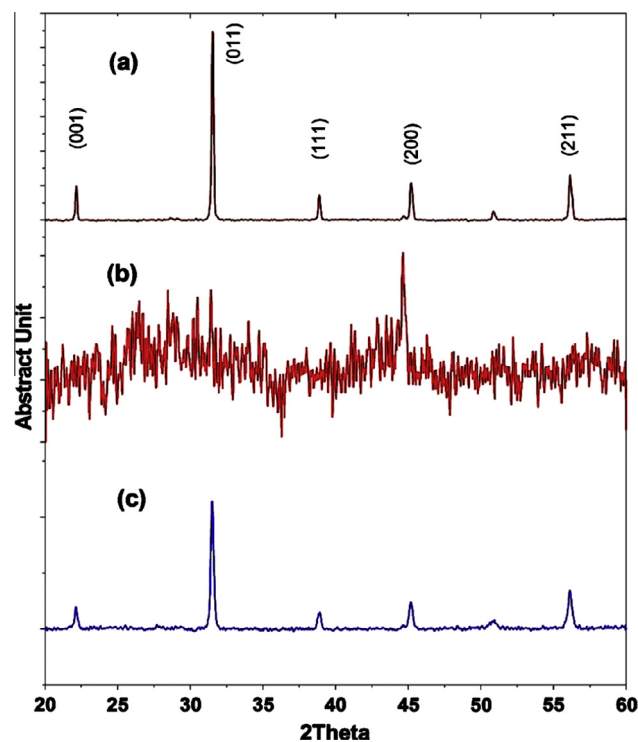


Fig. 1. XRD patterns of (a) PFN (b) 4PbO:B₂O₃ glass and (c) PFN-3-LB-83.

reveal highly compacted structure with well defined grain and grain boundaries. However, glass deposition on the grain boundary can be clearly detected in SEM image of PFN-2-LB-83. Grain size was determined by manual image analysis, matching digital pixel scale across each grain. The average grain size of PFN-0-LB-83 and PFN-2-LB-83 is obtained to be 1.9 μ m and 2.4 μ m, respectively. This clearly shows that under the same sintering conditions grain size of PFN-2-LB-83 is more than PFN without LB. Relative density of both the system are determined and found more in PFN-2-LB-83. Same trends of variation of grain size and relative density are observed in almost all samples (tabulated in Tables 2 and 4). However, if the LB concentration increases above 2 wt%, relative density and grain size both are found to decrease.

The observed enhancement of sinterability of PFN by LB is understood on the basis of liquid phase sintering (LPS) process. The glass softening temperature of LB is around 500 °C, at which LB starts melting. In the present work sintering were performed above the glass softening temperature (at 700 °C and 800 °C), at which LB melt and liquid form of LB move around the grain boundaries of PFN grain due to capillary action. In capillary action, the capillary force arises due to surface tension at the interface (liquid–solid–vapour) leads the flow of liquid phase. On the same line, in the present case flow of LB through grain boundary fills the pores of PFN which leads to densification and grains-growth [31–36]. Thus increase in relative density using LB clearly shows that in PFN–LB sintering process is dominantly due to the liquid phase sintering (LPS) rather than solid-state sintering. However with an increase LB concentration above 2 wt%, decrease of sinterability is due to bridging of particle by glass materials, which can disintegrate the solid particles into smaller grains at the liquid–solid interface. The PFN-2-LB-83 is found to optimize glass percentage in the liquid phase sintering.

The temperature profile of dielectric constant at 1 kHz frequency of PFN–LB samples sintered at 700 and 800 °C are displayed in Figs. 5 and 6, respectively. Dielectric anomaly around 100 °C can be clearly observed for both the samples. The dielectric maxima are

Table 1

List of Compositions of PFN–LB with its nomenclature PFN–LB.

Composition	Sintering conditions		Nomenclature
	Sintering temperature (°C)	Sintering time (h)	
PFN+0 wt%LB	700	2	PFN-0-LB-72
	700	3	PFN-0-LB-73
PFN+1 wt%LB	700	3	PFN-1-LB-73
PFN+2 wt%LB	700	3	PFN-2-LB-73
PFN+3 wt%LB	700	3	PFN-3-LB-73
PFN+0 wt%LB	800	2	PFN-0-LB-82
	800	3	PFN-0-LB-83
PFN+1 wt%LB	800	3	PFN-1-LB-83
PFN+2 wt%LB	800	3	PFN-2-LB-83
PFN+3 wt%LB	800	3	PFN-3-LB-83

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