

## Effect of lead silicate 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 recognized as lead-based complex-double perovskite [ $\text{A}(\text{B}_I\text{B}_{II})\text{O}_3$ ] ferroelectrics. The PFN powder was synthesized by combustion route (SHS synthesis) and LS-glass by conventional quenching technique, separately. The compositions of PFN and LS-glass (0 to 3 wt %) were prepared by ball milling. The crystalline structure of as-synthesized PFN and PFN-LS and amorphous nature of LS-glass are confirmed by XRD. Microstructure was examined by SEM; indicates nanoscale dimensions of as-synthesized PFN. The dielectric property of PFN is found to be enhanced by liquid phase sintering.

**Keyword:** Sintering, nano-particle, Perovskites, Dielectric properties, Scanning electron microscope

### 1. Introduction

Lead iron niobate (PFN) is a member of the lead-based perovskite ferroelectric family used in multilayer ceramic capacitors, sensors, memory chips (FRAM, DRAM) and novel transducers etc. In present investigation 4PbO-SiO<sub>2</sub> (LS) glass is used as a sintering aid work liquid phase sintering (LPS) induce complete densification of PFN, which improve the dielectric properties of materials. Earlier, B<sub>2</sub>O<sub>3</sub>, Bi<sub>2</sub>O<sub>3</sub> and LiF have been successfully used as sintering aids [1-3]. In present investigation 4PbO-SiO<sub>2</sub> (LS) glass is used as a sintering aid, having a eutectic temperature around 500°C. The properties of PbO-based glass have been reported by Fajans and Kreidl [4]. According to them, such glasses not only have low flow temperature, but also show a high ionic polarizability, which helps in polarization of ferroelectric material. Moreover, the PbO based glass without alkali ions has a low dielectric loss [5].

All above factors prompted us to synthesis lead borate (LB) glass dispersed PFN, which helps in increasing the dielectric constant of PFN, reduce the dissipation loss and decreases the dielectric maxima by liquid phase sintering.

### 2. Experimental

In the present work PFN was synthesized by combustion method. The initial ingredients were Pb(NO<sub>3</sub>)<sub>2</sub> (>99% Merck), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (99% Merck) and Nb<sub>2</sub>O<sub>5</sub> (99.5 Sigma-Aldrich) as cation precursors and urea, CO(NH<sub>2</sub>)<sub>2</sub> (99% Merck) as a fuel. Later, 50 ml of distilled water was added to it and stirred with the glass rod (previously cleaned by chromic acid) for 15 min so as to obtain homogeneous mixture. The mixture then heated at temperature 550°C, and was kept at this temperature for 10 minutes. The reaction occurred and yielded reddish brown product in the form of fragile foam that was easily crumbled into the powder. The lead silicate glass (4PbO:SiO<sub>2</sub>) was prepared by following the conventional quenching technique [3]. The initial ingredients used for the preparation of glasses were SiO<sub>2</sub> and PbO (Merck). The obtained fine powder of PFN was mixed with the lead silicate glasses (4PbO:SiO<sub>2</sub>) in different weight percentages to prepare composition. The mixtures of PFN and LS-glass (0.0, 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 wt %) were pulverized in presence of acetone, with the help of Planetary minimill (Pulverisette-6 Fritz, Germany). During the ball milling, the milling speed and duration were 600 RPM and 1 hr, respectively. The well ground samples thus obtained were finally sintered at 700°C and 800°C for 3hrs. The composites of PFN: 4PbO:SiO<sub>2</sub>: 99:1, 98:2, 97:3 sintered at 700°C are designated as F7G1, F7G2 and F7G3 respectively. Whereas, samples with different composition but sintered at 800°C are designated as F8G1, F8G2 and F8G3, respectively.

All the sintered samples were characterized by X-ray powder diffraction (XRD) using Cu-Kα<sub>1</sub> radiation, with the help of PANalytical X-ray powder diffractometer at 40kV and 30mA. The surface morphology of synthesized samples was examined by scanning electron microscope (JEOL:JSM-6380 Analytical SEM) equipped with an electronic probe analyzer system (Accelerating voltage 30kV). The dielectric

constant ( $\epsilon_r$ ) and dissipation factor ( $\tan\delta$ ) were measured at different frequencies from 10Hz to 1000 kHz in the temperature range from 25 to 200<sup>o</sup>C using computer controlled HP-4192A LF impedance analyzer.

### 3. Results and Discussion.

The XRD patterns of PFN, 4PbO:SiO<sub>2</sub> (40:60 wt %) and (1-x) (PFN)+x(4PbO:SiO<sub>2</sub>) composites are shown in figures.1.(a), (b) and (c), respectively. The XRD pattern of PFN synthesized in this work are compared with JCPDS data (file no. 0.032-0522) of perovskite PFN. All the XRD peaks observed in the pattern match well with the corresponding JCPDS data of PFN as shown in Table.1. No additional diffraction line(s) were seen other than

**Table. 1. Comparison of 'd' value of sintered with the standard JCPDS data**

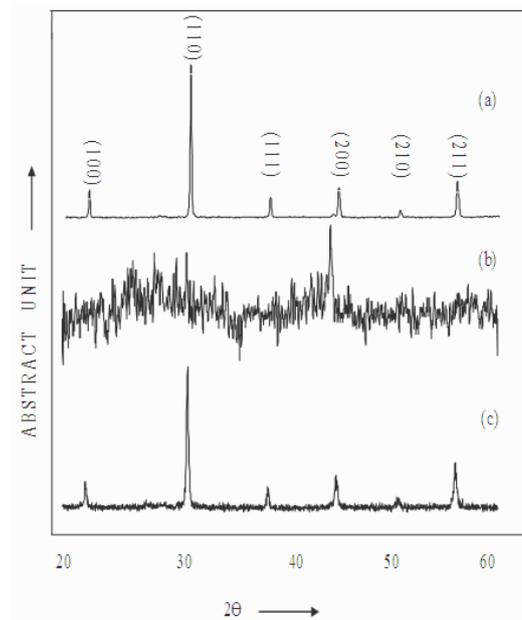
Sr. No	Experimental data			JCPDS (No.16-522)		[ h k l ]
	d	(I/I <sub>o</sub> )	(A <sup>o</sup> )	d <sub>JCPDS</sub> (A <sup>o</sup> )	(I/I <sub>o</sub> ) <sub>JCPDS</sub>	
1.	4.0539		18.18	4.015	16	[ 1 0 0 ]
2.	2.8586		100	2.838	100	[ 1 1 0 ]
3.	2.3291		12.97	2.318	25	[ 1 1 1 ]
4.	2.0142		2.33	2.008	40	[ 2 0 0 ]
5.	1.7911		18.91	1.796	9	[ 2 1 0 ]
6.	1.6324		23.45	1.639	55	[ 2 1 1 ]

perovskites; suggesting non-formation of any byproduct due to reaction between glass and PFN. The absence of diffraction lines due to either presence of secondary pyrochlore phase or unreacted compounds [Pb(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O and Nb<sub>2</sub>O<sub>5</sub> ] rule out their precipitation in PFN. A good agreement between observed and JCPDS values of 'd' and relative intensity confirms the formation of perovskite PFN. A close look at the Fig.1.b suggests the amorphous nature of the 4PbO:SiO<sub>2</sub> sample. On the other hand, Fig. 1.c reveals the presence of sharp crystalline peaks in the background of noise due to amorphous phase.

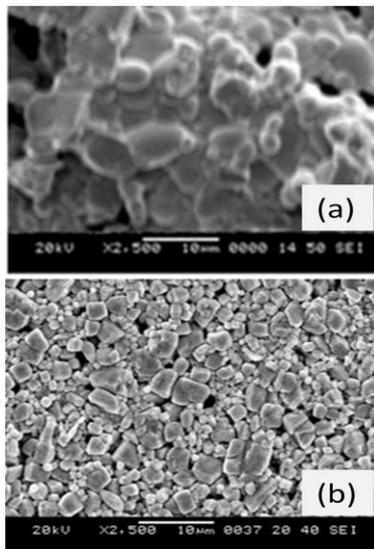
In case of SEM micrograph of pure PFN powder sintered at 800<sup>o</sup>C, the particles agglomerate and convert to spherical and oval shape with the average grain size that increased upto < 3 $\mu$ m, which is much smaller than that synthesized by the conventional solid state oxide reaction method [6-8](Fig 2(a)).

A further point of discussion is derived from the fact that, the use of sintering aid as a LS-glass will affect the ceramics dielectric response due to its influence on the grain size. The densification is obtained predominantly through the liquid-phase rather than solid-state sintering. In order to quantify the significance of this effect SEM cross-section of PFN-LS glass (1 and 2 wt %) composites were examined, which were sintered at 800<sup>o</sup>C.

A comparison of Fig.2 (a,b,) reveals that the solid state sintering (Fig.2 (a)) and liquid phase sintering (Fig.2(b)) processes, which involved capillary action, due to capillary forces and wetting by the liquid glass. The capillary force and wetting is dominant in sample F8G3, due to higher percentage of liquid-phase glass (Fig.2b). In sample F8G1, with the increase in temperature, solid-state sintering process becomes dominant than the liquid phase sintering. Physically solid state sintering translates into a large grain size. However many sub-micro grains having grain size >3 $\mu$ m are observed in sample F8G1. Thus the variation in dielectric property is due to grain surface area and potential drop between grains.



**Fig.1: XRD patterns of (a) PFN (b) 4PbO:SiO<sub>2</sub> glass and (c) 0.99{PFN}-0.1{4PbO: SiO<sub>2</sub>}**



**Fig.2: Scanning electron microphotograph of (i) F83 (ii) F8G1 and (iii) F8G2**

It has been reported that the glass materials bridge particle - particle and disintegrate the solid particles into smaller grains by the liquid-solid interface. The resulting properties are known to be strongly dependent upon the chemical composition of the liquid phase. However, it is still difficult to make precise prediction about the liquid phase sintering behaviour [9,10].

A typical variation of dielectric constant ( $\epsilon_r$ ) and dielectric loss ( $\tan\delta$ ) with temperature at various frequencies 10 Hz to 1000 kHz for samples, F7G3 and F8G3 are shown in Fig. 3(a,b), respectively. Almost all samples show similar behavior. It is observed that with increasing temperature, the value of  $\epsilon_r$  initially increases and attains a certain maximum value at Curie temperature (110<sup>o</sup>C) and then decreases, where ferroelectric to paraelectric phase transition takes place. The dielectric loss increases with the increase in temperature. The variation of transition temperature ( $T_c$ ) Vs concentration of PS glass (1 to 3wt %) at 700 and 800<sup>o</sup>C sintered temperature as shown in Fig.4

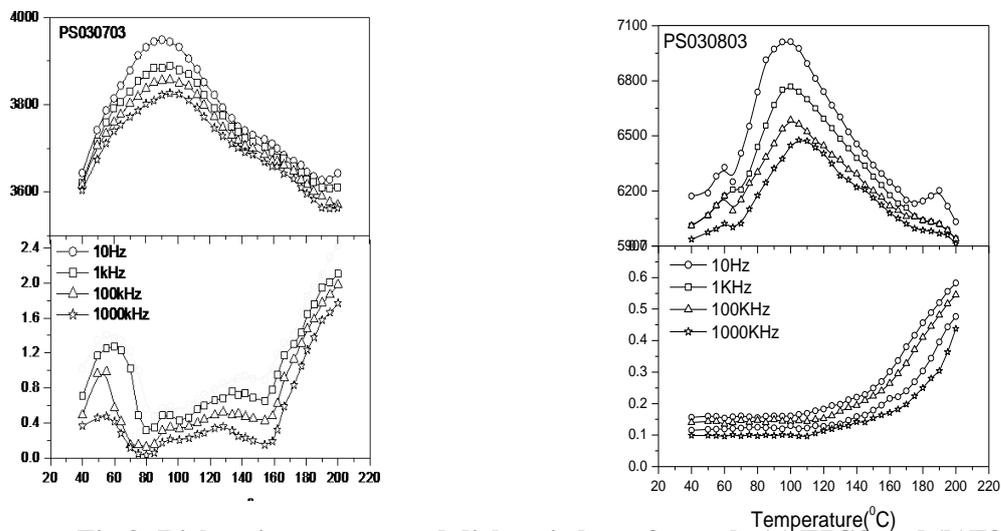
In pure PFN sample sintered at 700 and 800<sup>o</sup> C at 2 and 3hrs i.e F72, F73, F82 and F83, the value of dielectric maximum ( $\epsilon_{rmax}$ ) and  $\tan\delta_{max}$  at 1kHz are given in **Table.2**. The appearance of diffused phase transition in the temperature range from 105<sup>o</sup>C to 115<sup>o</sup>C indicates the non-relaxor behaviour of pure-PFN in all the F72, F73, F82 and F83 samples, due to inbuilt compositional micro

**Table.2: A comparison of relative permittivity and loss for PFN prepared by changing the preparative parameters sintering temperature and time.**

Sr. No	Sample name	T <sub>sinter</sub> (°C)	t <sub>sinter</sub> (Hrs)	$\epsilon_{rmax}$	$\tan\delta_{max}$
1	F72	700	2	13500	1.2
2	F73	700	3	11348	0.06
3	F82	800	2	14000	6
4	F83	800	3	15500	0.4

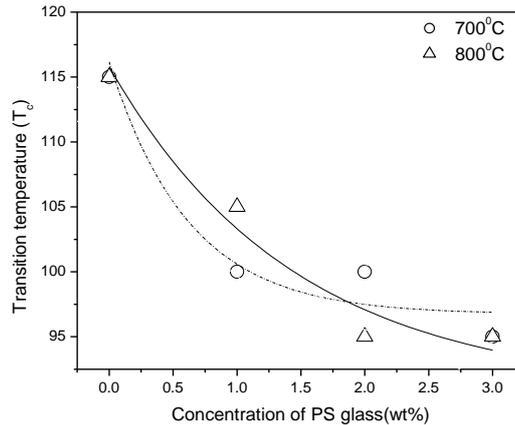
(a)

(b)

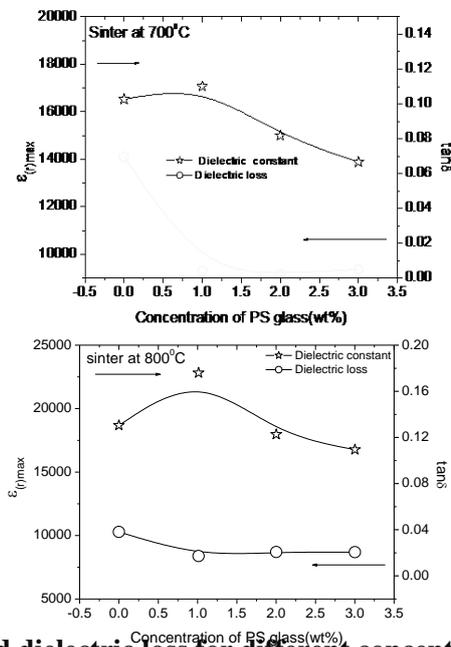


**Fig.3: Dielectric constant and dielectric loss of sample (a) F7G3 and (b)F8G3**

inhomogeneity amongst the B-site cations (i.e. Nb/Fe) of unit cell, which agrees well with the results reported by L.E.Cross [11]. Such micro inhomogeneity resulted into the small variation in potential energy of the ferroactive B-site atoms of oxygen octahedral responsible for temperature sensitive atomic displacement and variation in relaxation time. Analogously, inbuilt heterogeneity in composition with the unit cell due to variation in soft mode, which spread over the temperature region giving rise to DPT behaviour. The temperature compensation or flattening of temperature behaviour has been attributed to the presence of a chemical inhomogeneous “grain core - grain shell structure” [12]



**Fig.4: Variation of transition temperature ( $T_c$ ) Vs concentration of PS glass (1 to 3wt %) at 700 and 800°C sintered temperature**



**Fig.5: Dielectric constant and dielectric loss for different concentration of glass sample sintered at 700°C and 800°C, for 1 kHz frequency**

Non relaxor behaviour, high dielectric loss and low packing density hinder the applicability of PFN. Therefore, a solution was sought by using PS glasses as sintering agents. Here PS glass has lower melting point (< 600°C) with a view to soak the PFN in molten glass in low concentration so that liquid seeps through the pores and follow the pore filling model [13].

Fig.5 reveals the variation of dielectric constant and loss of PFN-glass sample at 1 kHz frequency. In case of the samples sintered at 700°C the dielectric constant increases from 1.5 to 2.5wt% and thereafter it decreases till 3wt%. However, the loss factor ( $\tan\delta$ ) decreases drastically when glass concentration changes from 2.5 to 3wt%.

The pellets sintered at 800°C exhibit quite different results. As the glass content increases from 0-1.5wt%, dielectric constant increases and loss  $\tan\delta$  follows the natural decrease. Beyond this, i.e. from 2 to 3wt% dielectric constant decreases and  $\tan\delta$  increases and then attains a constant value. This is because the diffusivity of the materials changes with the concentration of the wt% of glass, which is distinctly exhibited

from SEM micrographs (Fig. 2b, c). As the glass content increases beyond 1wt % volumetrically it exceeds the limit in which it has to be uniformly distributed, i.e. it starts capsulation of the grains, in turn, blocks the grain growth and thereby the decrement of dielectric constant.

#### **4. Conclusion**

The present study shows that there is highest dielectric constant of PFN obtain at 2wt% LS glass for 800<sup>0</sup>C, but for 700<sup>0</sup>C sintered sample maximum dielectric constant optimized at 3wt% LS-glass. Thus LS glasses are found to improve the properties of PFN for the multilayer ceramic capacitor application.

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