A Comparative Study of Dielectric Properties of PMN and 0.7PMN- 0.3PZN Ceramic

Band S. A.

Yeshwantrao Chavan College of Engineering ,
Wanadongari - 4441110,Nagpur (M.S.), *India*

Takarkhede M .V.

*J D College of Engineering ,
Nagpur-441501(M.S.)India*

Abstract

Lead magnesium niobate designated as PMN is a representative of ferroelectric relaxors, It exhibits unusually high relative permittivity 12000-20000 with Tc ≈ - 9 to 15°C. PMN is of special interest due to its wide technological applications such as MLCS , electrostrictive positioners , electro-optical valves , memory devices , pyroelectric bolometers etc. The dielectric properties (ϵ_r and $tan\delta$) of PMN can be tailored by forming solid solution with other ferroelectric materials such as normal ($BaTiO_3$, $PbTiO_3$), antiferroelectric ($PbZrO_3$), relaxor (PZN). PMN and   0.7PMN+ 0.3PZN ceramic is synthesized by precalcination route suggested by Swartz. XRD analysis confirmed major single phase pervoskite formation in both the ceramics. SEM analysis also revealed single phase formation. Dielectric measurements (ϵr and $tan\delta$) are taken in the temperature range from -50 to 100°C at four different frequencies 0.1,1 ,10 and 100kHz . Dielectric properties are compared and improvement in   the dielectric properties are reported with a focus on microstructure , density and perovskite phase .

Key words: ferroelectric relaxors   , perovskite , pyrochlore , microstructure ,dielectric properties .

Introduction

Lead magnesium niobate (PMN) and Lead Zinc niobate designated as PZN both   shows ferroelectric relaxor behavior with transition temperature T_c ≈ - 15°C and 140°C respectively[1-2]. Relaxors are ferroelectrics which show pronounced change in its permittivity with frequency at temperature near curie point and broad phase transition in the temperature dependence of permittivity**.** They are complex perovskites characterised by A(B B')O$_3$ structure

where A—mono or divalent , B is di or tri-valent   , B' is tetra or penta-valent .They exhibit diffuse phase transition and obey quadratic law in the certain temperature range above transition temperature. On the other hand   normal ferroelectrics   show sharp first order or second order transition and obeys Curie Weiss law above T_c . PMN and PMN based relaxors exhibit   excellent dielectric properties .However its commercial use is limited owing to its reproducibility problems due to inevitable formation of cubic type pyrochlore phase($Pb_3 Nb_4 O_{13}$ or $Pb_3 Nb_2 O_8$)   along with perovskite phase formation which dilutes its dielectric properties [3-7]. It is more difficult to produce PZN in single phase than PMN by conventional solid state route although   the intrinsic dielectric constant of PZN is also high[8]. In the present work   we have synthesized PMN   and 0.7PMN+ 0.3PZN   ceramic   and the dielectric properties are studied in the temperature range -50 to 100°C at four different frequencies. An attempt has been made to compare the dielectric properties with a focus on microstructure , perovskite phase and density .

Experimental Details

PMN and 0.7PMN+0.3PZN ceramic is synthesized by columbite two stage route suggested by Swartz etal[9,10]. The Initial ingradients PbO, MgO , Nb_2O_5 , ZnO   used have been of 99.9% purity (AG Fluka, Switzerland). All the constituents were well dried before weighing. Especiallly MgO being moisture sensitive is dried for prolonged period (24hrs) to ensure desired stoichiometry of the   starting compositions.

In the first stage   the columbite $MgNb_2O_6$ is synthesized by taking MgO and Nb_2O_5 in 1.02:1 molar ratio as per Eq. 1 and following flow chart Fig1. Due to high refractivity of MgO , 2 mole % of

excess MgO is taken . Similarly $ZnNb_2O_6$ is synthesised by taking ZnO and Nb_2O_5 in 1.:1 molar ratio as per Eq. (2) following flow chart Fig1
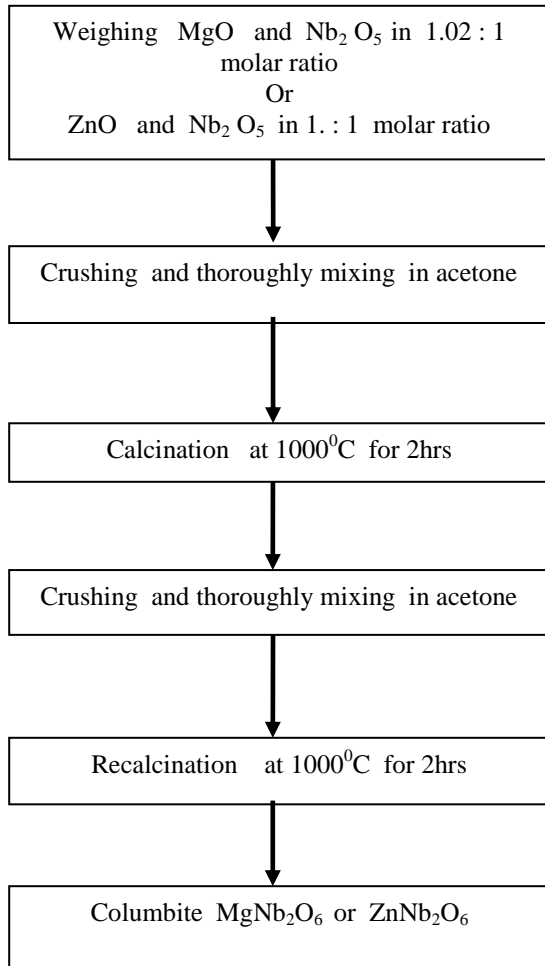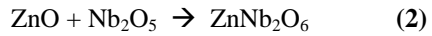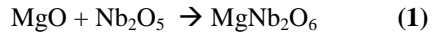
$$MgO + Nb_2O_5 \rightarrow MgNb_2O_6 \qquad (1)$$

$$ZnO + Nb_2O_5 \rightarrow ZnNb_2O_6 \qquad (2)$$

Weighing MgO and Nb_2O_5 in 1.02 : 1 molar ratio Or ZnO and Nb_2O_5 in 1. : 1 molar ratio

↓

Crushing and thoroughly mixing in acetone

↓

Calcination at 1000^0C for 2hrs

↓

Crushing and thoroughly mixing in acetone

↓

| Recalcination at 1000^0C for 2hrs |
|---|

↓

Columbite $MgNb_2O_6$ or $ZnNb_2O_6$

Fig1 : Flow chart of Material processing
of $MgNb_2O_6$ or $ZnNb_2O_6$

In the 2nd stage PMN ceramic is synthesised by taking PbO and $MgNb_2O_6$ in 3:1 molar ratio as per Eq 3 and following flow chart Fig2 .

$$3PbO + MgNb_2O_6 \rightarrow 3(PbMg_{1/3}Nb_{2/3}O_3) = 3PMN \qquad (3)$$
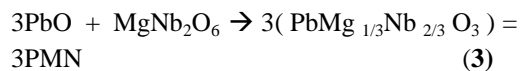
Similarly 0.7PMN - 0.3PZN is synthesized by taking PbO , $MgNb_2O_6$ and $ZnNb_2O_6$ in
3: 0.7: 0.3 molar ratio as per Eq 4. and following flow chart Fig 2 .

$$3PbO +(0.7)MgNb_2O_6 +(0.3) ZnNb_2O_6 \rightarrow$$
$$Pb_3Mg_{0.7}Zn_{0.3}Nb_2O_9 = 3(0.7PMN-0.3PZN) \qquad (4)$$
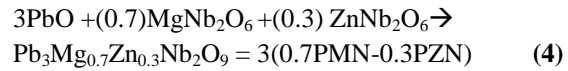
During sintering the pellets are coverd with the powder of the same composition to overcome the PbO losses .

Weighing PbO and $MgNb_2O_6$ in 3: 1 molar ratio **Or** PbO , MgNb2O6 and $ZnNb_2O_6$ in 3: 0.7: 0.3 molar ratio.

↓

Crushing and thoroughly mixing in acetone

↓

Calcinations at 800^oC for 3 hrs

↓

Crushing and thoroughly mixing in acetone

↓

Pelletisation using uniaxial pressure $\approx$ 1 ton

↓

Heating at 400^0C for 2hrs to remove organic binder binder

↓

Sintering at 1180^0C for 2hrs

↓

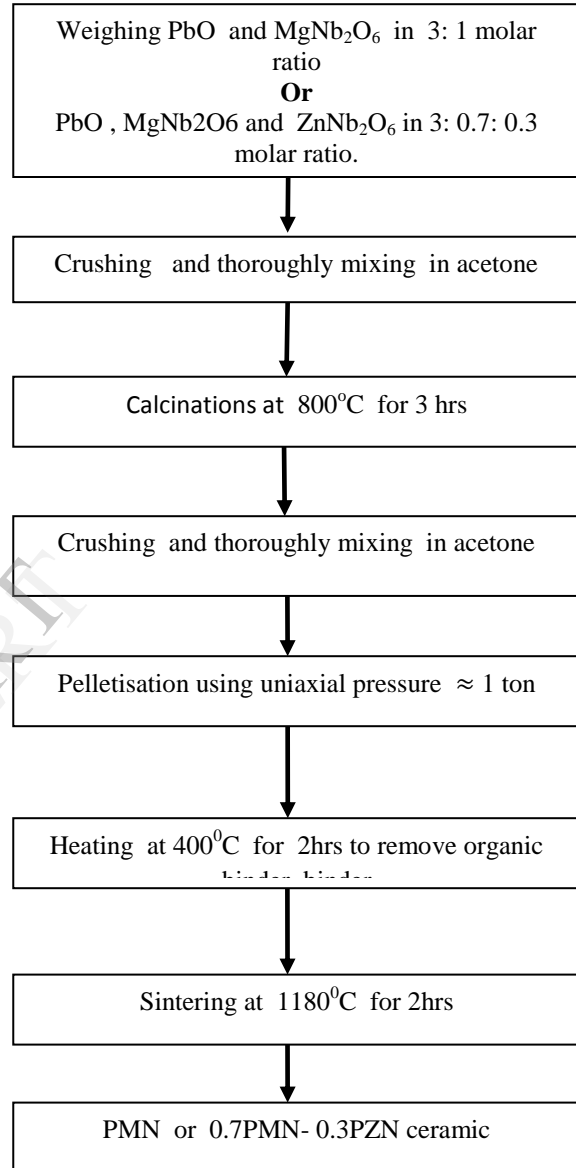| PMN or 0.7PMN- 0.3PZN ceramic |
|---|

Fig2: Flow chart of Material processing of PMN

XRD scans of powder of the sintered pellet were recorded using PW 1700 X-ray diffractometer with 1710 controlling unit , using Kα /Fα radiation ,scanning rate 2.4^o/min 2θ range 10-120°. The fractured surfaces of the sintered pallet has been examined by using 250 MK3 Cambridge UK , scanning electron microscope of high resolution

x20 to X800,000 at 10 mm at RSIC , Nagpur. The bulk density of the sintered pellet is measured by Archimedes principle. Dielectric measurements were taken (ε_r , tanδ) using HP4192A LF Impedence analyzer selected in parallel mode of operation in the temperature range -50 to 100° C at 0.1 ,1, 10 and 100 kHz .

Result and Discussion

X-ray diffraction patterns of PMN and 0.7PMN-0.3PZN are shown in Fig 1 & 2. The appearance of 9-10 major characteristics peaks due to perovskite phase ensures its formation in maximum percentage in both cases. In addition to perovskite phase few lines of weak intensity corresponding to pyrochlore phase are also observed . A critical analysis of XRD data reveals cubic symmetry with lattice constant of 4.053A^o for PMN and that for solid solution is 4.056A^o at room temperature. Almost same value of lattice constant confirm the solid solution formation in 0.7PMN – 0.3 PZN .
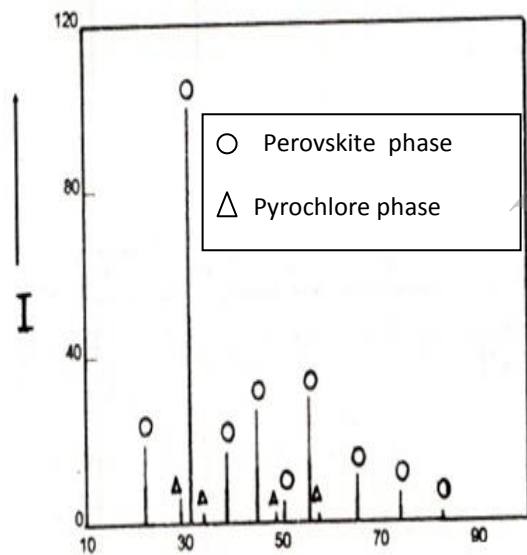

Fig 1. X-ray power diffraction patterns of PMN

The relative % of perovskite phase present in respective samples is quantitatively estimated using following equation similar to reported by Goo etal [11] and Chen etal [12]

$$\text{vol \% of perovskite phase} = \frac{100 \; x \; Iperov}{Iperov \; + \; Ipyro} \quad \textbf{(5)}$$

where I perv and I pyro are the intensities corresponding to major peaks of perovskite and pyrochlore phase respectively.
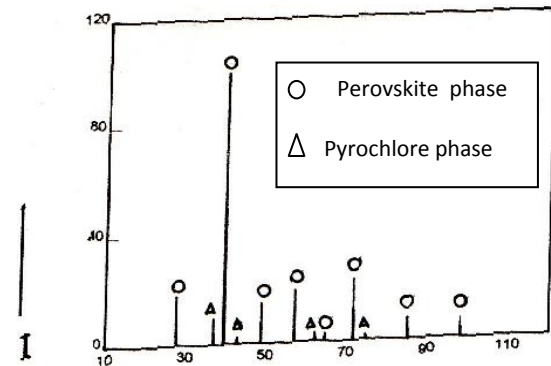

**Fig.2** X-ray diffraction pattern of 0.7 PMN-0.3 PZN

The estimated volume percent of perovskite phase is 94 % in PMN and 91 % for 0.7PMN – 0.3 PZN . The high value of perovskite phase observed in PMN mig ceramics . The tole PZN is 0.984 as reported by shrout etal [13] . For stable perovskite phase 't' should be between 0.88 to 1.09. Hence it is difficult to produce PZN than PMN in perovskite phase . The sintered density determined in both the samples is same = 96 % .

The microphotographs of both the samples are depicted in Fig 3 and 4 . A close look of microstructure reconfirms single major pervoskite phase formation. Few small angular grains of pyrochlore phase are also observed .
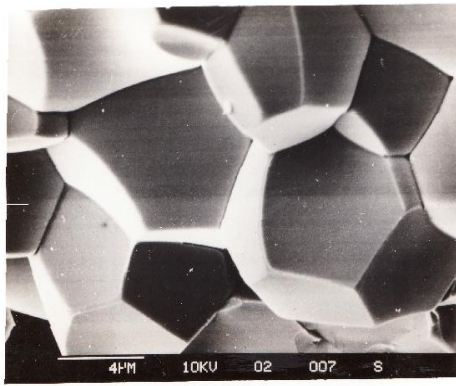
Fig.3 Scanning electron microphotographs of fractured surface of PMN ceramic
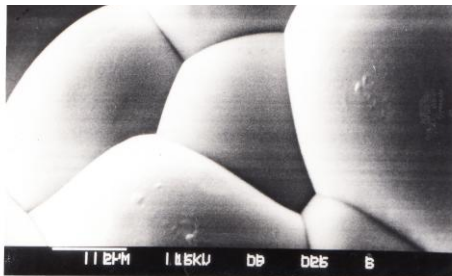
Fig.4 Scanning electron miicrophotographs of fractured surface of 0.7PMN-0.3PZN ceramic

The grain size calculated from microphotographs for PMN ceramic is 5.8 ± 0.2 μm and is that of solid solution 6.9 ± 0.6 μm.

The graphs of ϵ_r , tanδ versus temperature for four different frequencies are given in fig 5 and 6 respectively.The characteristic relaxor behavior ,broad phase transition,dispersion in maximum of ϵ_r and tanδ peak with frequency is observed in both the samples. The T_c and $\epsilon_{r\,max}$ values at four different frequencies for both samples are presented in table 1.
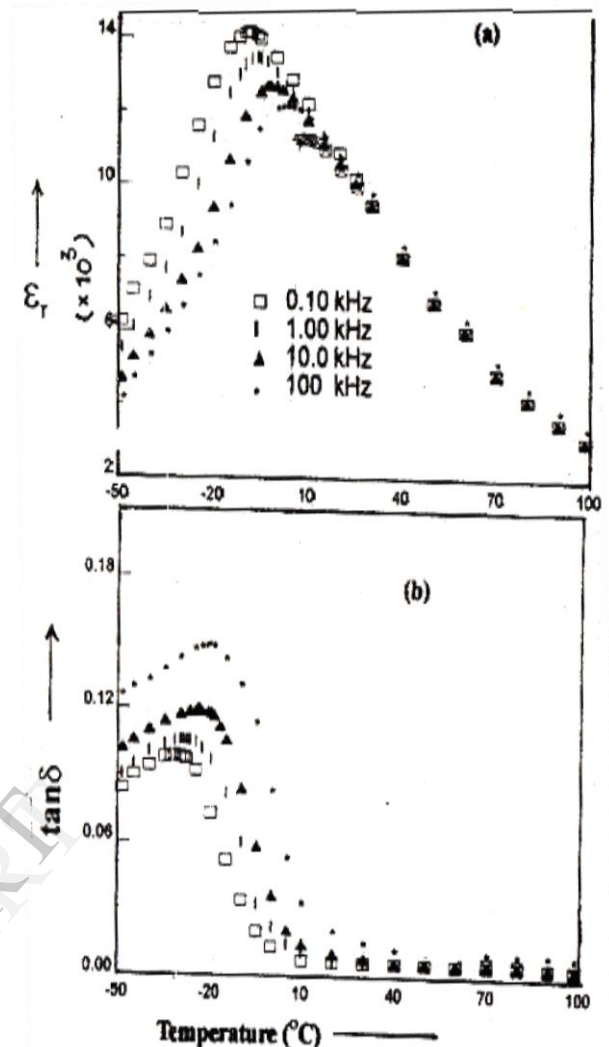
Fig 5 (a)Relative permittivity (ϵr)and (b)Dissipation factor(tanδ)) ,as a function of temperature and frequency for PMN ceramic

For PMN ceramic at 100 Hz $\epsilon_{r\,max}$ = 14200 at Tc =-9^0C and for 0.7PMN – 0.3 PZN $\epsilon_{r\,max}$ = 18200 at Tc =24^0C.

The high relative permittivity is observed in case of 0.7PMN – 0.3 PZN ceramic than PMN ceramic . This value obtained is also higher than reported value = 14400 by Landin etal [14] for the PMN-PZNceramic .
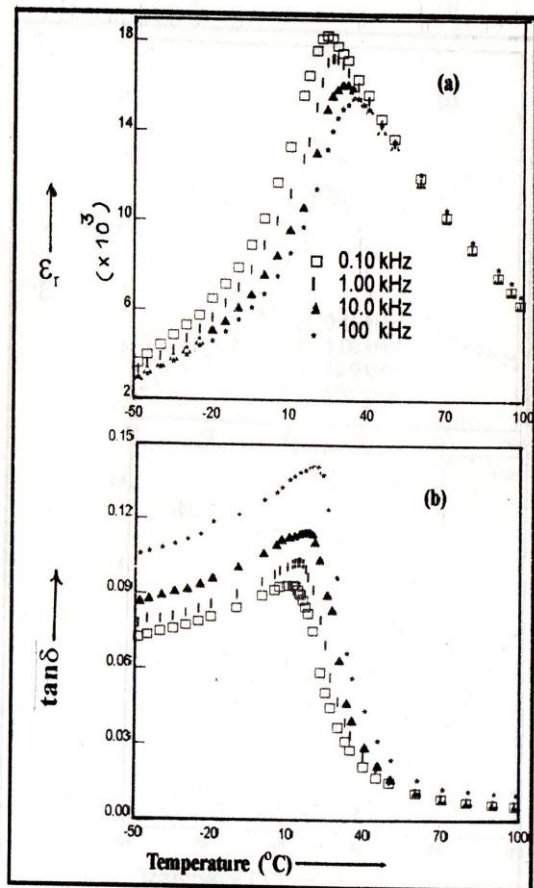
Fig 6 (a)Relative permittivity (Єr)and (b)Dissipation factor(tanδ)) ,as a function of temperature and frequency for 0.7 PMN-0.3 PZN

Table 1 : Relative permittivity (Є$_{rmax}$) and Curie temperature (T$_c$)
PMN and 0.7PMN – 0.3PZN ceramic at four different frequencies .

Frequency	Є$_{rmax}$ and Tc	
	PMN	**O.7PMN – 0.3PZN**
100Hz	14200 , -9°C	18270 , 24°C
1kHz	13500 , -6°C	17270 , 26.5^{o}C
10kHz	12730 , -2° C	16110 , 30°C
100kHz	11842 , 3°C	15130 , 35°C

Conclusion :

A high value of relative permittivity along with favourable shift of T$_c$ (= 24°c) near room temperature observed for 0.7PMN-.3 PZN solid solution than PMN ceramic is due to increased grain size and intrinsic high dielectric constant of PZN inspite of relatively low vol % of of perovskite phase.

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