Dielectric and electrostrictive properties of PMNT near MPB

Pawan Kumar\textsuperscript{a,*,} Chandra Prakash\textsuperscript{b}, T.C. Goel\textsuperscript{c}

\textsuperscript{a}Department of Physics, National Institute of Technology, Rourkela 769008, India
\textsuperscript{b}Directorate of ER & IPR DRDO, DRDO Bhawan, Rajaji Marg, New Delhi 110011, India
\textsuperscript{c}BITS Pilani-Goa Campus, Goa 403720, India

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Abstract
The dielectric constant ($\varepsilon_r$), dielectric loss ($\tan\delta$) and strain induced by electric field in lead magnesium niobate–lead titanate (PMN-PT/PMNT) solid solutions in the morphotropic phase boundary (MPB) region at different sintering temperatures have been studied. $\varepsilon_r$ and $\tan\delta$ increase, whereas Curie phase transition range decreases with the increase in sintering temperature. Strain levels in the range of 0.07–0.2% were obtained. A high saturated strain\% of 0.19, a high $d_{33}$ coefficient of 320 pm/V and a low strain hysteresis\% of 3.5 in PMNT 68/32 composition sintered at 1200$^\circ$C indicate its suitability for actuator applications.

Keywords: Relaxor; PMNT; MPB; $T_c$; Strain%; Hysteresis%

1. Introduction
Ferroelectric ceramics are used in a variety of sensor and actuator applications. They are one of the basic building blocks of smart structures, which have been successfully used for active damping and damage detection [1]. Recent developments in the relaxor perovskite-type ferroelectric materials have attracted much attention due to their greatly enhanced piezoelectric performance and strain levels compared with normal ferroelectric ceramic solid solutions. As a result, the piezoelectric, electromechanical and strain level performance of complex relaxor ferroelectrics, such as lead magnesium niobate titanate (PMNT) or PZNT, is superior to that of PZT [2]. Therefore, these complex relaxor ferroelectrics are considered promising candidates for the new generation of transducers and actuator materials [3].

Lead magnesium niobate (PMN) is a relaxor perovskite material, which possesses a high $\varepsilon_r$ (\textasciitilde 20,000), high electrostrictive strain at room temperature and a diffuse phase transition (\textasciitilde 10$^\circ$C) [4]. High $\varepsilon_r$ of this material is useful for multiplayer capacitors, pyroelectric bolometers and dynamic random memory applications, and high electric field-induced strain is useful for electrostrictive actuator applications [5]. But, its low transition temperature (\textasciitilde 10$^\circ$C) inhibits its applications in various devices. PMN forms a solid solution with lead titanate (PT), denoted as (1\textendash x)PMN\textendash xPT/PMNT [6]. In this system, the MPB exists between PMNT 70/30 and 65/35 compositions [7]. The compositions within this MPB region have been reported to possess ultrahigh piezoelectric response and large electric field-induced strain\% values with low strain hysteresis\% [8\textendash 11]. The high piezoelectric and strain levels in the PMNT compositions in the MPB region are related to the co-existence of mixed structures (tetragonal and rhombohedral) [12]. This MPB region of PMNT system is not clearly marked and different researchers have studied different compositions. Also, the development of perovskite phase and structures in the MPB region are affected by sintering temperature, which in turn affects the material properties. Hence, there is a need to study different compositions of PMNT system and the sintering temperature effects on their properties in the MPB region. In the present study, different compositions of PMNT system,
namely PMNT 70/30, 68/32 and 66/34 in the MPB region, have been synthesized by Columbite technique. The surface morphology, dielectric and strain induced by electric field in these compositions, sintered at different temperatures, have been discussed.

2. Experimental procedure

PMNT compositions in the MPB region were prepared by Columbite technique. The details of the processing steps have been described elsewhere [13]. Phase-formation studies were performed on a PW 3020 Philips type X-ray diffractometer using CuKα (λ = 1.5405 Å) radiation. The surface morphology was studied using the scanning electron microscope (SEM, Cambridge Stereo scan 360) technique. εr and tanδ were measured at different frequencies (0.1–100 kHz) as a function of temperature using a computer-interfaced 4284A HP LCR meter. The samples were poled under corona discharge. Here, first the samples were preheated at a temperature of about 100 °C (below Tc) and then subjected to corona discharge by applying a voltage of 6 kV for 15 min, after which the heater was turned off while maintaining the corona voltage. Strain% versus electric field (S–E) loops were taken using the SS-50 strain measurement system (Sensor Tec. Ltd., Canada), shown in Fig. 1. An electric field as high as 4.5 MV/cm was applied using an amplified triangle waveform at a drive frequency of 50 Hz. All strain curves were obtained after the third cycle. During testing, the samples were submerged in silicon oil to prevent arcing.

3. Results and discussions

Fig. 2 shows the evolution of X-ray diffraction patterns of PMNT 70/30, 68/32 and 66/34 compositions, each sintered at 1200 °C. The absence of the pyrochlore phase peak (at 2θ = 29.5°) in all these compositions confirms the formation of pure perovskite phase and the significance of using Columbite technique [14]. Sharp and distinct diffraction peaks are obtained for all the samples and the intensity of diffraction peaks increases with the increase in sintering temperature. XRD peak intensities in polycrystalline ceramics increase with the increase in grain size and density of the ceramic [15]. Therefore, the increase in peak intensities with the increase in sintering temperatures of PMNT compositions in the MPB region can be attributed to the increase in crystalline and homogeneous nature of the materials [16].

The surface morphology of PMNT 70/30, 68/32 and 66/34 compositions, each sintered at different temperatures, is studied using SEM. The average grain size is calculated using the linear intercept method. For different PMNT compositions in the MPB region, grain size is found in the range of ~1–5 μm. Porosity in the samples decreases and grain size increases with the increase in sintering temperature. As can be seen from Figs. 3(i–iii), grain size of ~1.5, 2 and 4.3 μm for PMNT 70/30, whereas ~2, 3.6 and 4.3 μm for PMNT 68/32 and ~3.3, 4 and 4.5 μm for PMNT 66/34 compositions, each sintered at 1150, 1200 and 1250 °C, respectively, are obtained.

Variation of εr and tanδ at 1 kHz frequency of PMNT 70/30, 68/32 and 66/34 compositions at different sintering temperatures has been studied. Fig. 4 shows the typical dielectric variations of PMNT 68/32 composition, sintered at 1150, 1200 and 1250 °C, respectively. In all compositions, near Tc, εr increases with the increase in sintering temperature, whereas Tc corresponding to the peak of εr at 1 kHz of PMNT 68/32 and 66/34 compositions is found to be decreasing. The increase in εr with the increase in sintering temperature can be attributed to the decrease in porosity and increase in crystallinity, homogeneity and density of the ceramics [16]. The decrease in Tc with the increase in sintering temperature can be attributed to the increase in internal stress in the system. Here, we can consider a relationship to be present between internal stress and pores because pores can relieve internal stress, which do not constrain the grains. As shown in SEM microstructures, with the increase in sintering temperature the porosity of the samples decreases and grain size increases, which leads to an increase in internal stress in the PMNT 68/32 and 66/34 compositions [17]. Also, the phase
transformation temperature is inversely proportional to the internal stress [18]. Consequently, the decrease in $T_c$ with the increase in sintering temperature in PMNT 68/32 and PMNT 66/34 compositions seems to be the result of increase in internal stress due to decrease in porosity [19].

Curie transition temperature ($T_c$) increases with the increase in PT content in PMNT system and follows the relation [20]:

$$T_c = 5x - 10,$$

where $x$ (mol%) is the PT content and the Curie range is calculated using the relation

Curie range = Temperature of $(1/2\epsilon_{\text{emax}})$ in paraelectric region – Temperature of $(1/2\epsilon_{\text{emax}})$ in the ferroelectric region.

This Curie range is found to be maximum for PMNT 70/30 composition sintered at 1150 °C and decreases with the increase in sintering temperature and PT content in all the PMNT compositions in the MPB region. The dielectric broadening at the paraelectric–ferroelectric phase transition in PMNT system is due to compositional fluctuations and microscopic inhomogeneity [21–23]. Therefore, decrease in dielectric broadening with the increase in sintering temperature and increase in PT content suggests the decrease in compositional fluctuations and microscopic inhomogeneity. The $\epsilon_r$ vs. temperature plots of PMNT 68/32 and 66/34 compositions sintered at 1150, 1200 and 1250 °C temperatures display two major anomalies. As can be seen in Fig. 4(i), in $\epsilon_r$ vs. temperature plots of PMNT 68/32 composition, sintered at different temperatures, there is a dielectric hump near 110 and 150 °C. The existence of
two dielectric anomalies in PMNT 68/32 and 66/34 compositions is related to their MPB nature. PMNT 68/32 and 66/34 compositions belong to MPB region; therefore, at room temperature, there can exist mixed structures (tetragonal + rhombohedral). Near 110 °C, this mixed structure (tetragonal + rhombohedral) is transforming into a single tetragonal structure and gives rise to a dielectric hump, whereas the second dielectric anomaly is related to the ferroelectric to paraelectric phase transition. Therefore, appearance of double dielectric anomaly in PMNT 68/32 and 66/34 compositions, sintered at different temperatures, confirms their MPB nature [24]. From room temperature to 225 °C, tan δ is in the range of 0.008–0.075 for all PMNT compositions, sintered at different temperatures. Except in PMNT 68/32 composition, sintered at 1150 °C, as shown in Fig. 4(ii), tan δ increases with the increase in sintering temperature. High tan δ at room temperature in PMNT 68/32 composition, sintered at 1150 °C, may be attributed to the presence of intergranular layers of a Pb-rich atmosphere, which has been successfully described by brick–wall dielectric mixing laws [25–28]. On the contrary, the increase in tan δ with the increase in sintering temperature can be explained on the basis of increase in space charge conduction in the system. These space charges increases with the increase in sintering temperature due to high volatility of PbO, which can produce Pb or O site vacancies in the PMNT compositions [29]. Temperature of maximum tan δ of all MPB compositions is different from the temperature of maximum εr, which is a characteristic of relaxor ferroelectric [30] materials, and the Kramers–Kronig relation indicates that this can be the consequence of temperature-dependent relaxation near Curie temperature [31].

Longitudinal strain induced as a function of unipolar electric field for different PMNT compositions, in the MPB region, sintered at different temperatures, is shown in Figs. 5(i)–(iii). Here, the longitudinal strain vs. unipolar electric field measurements are taken because it is realistic to apply unipolar driving in actuator devices in order to avoid inverting the remnant polarization (Pr) or depoling of the material [32]. Strain% in the range of 0.07–0.2 is obtained. The strain hysteresis% is calculated using the relation [33]

\[
\text{Strain hysteresis%} = (\text{hysteresis in strain% at half of the maximum electric field/strain% at the maximum electric field}) \times 100
\]

and the strain hysteresis% of ~6, 6.6 and 8.9 in PMNT 70/30, 3.2, 3.5 and 6.5 in PMNT 68/32 and 6.5, 3.9 and 1 are found in PMNT 66/34 compositions, each sintered at 1150, 1200 and 1250 °C, respectively (also shown in Table 1). It can be seen from Figs. 5(i) and (ii) that saturated strain% and strain hysteresis% increase with the increase in sintering temperature in PMNT 70/30 and 68/32 compositions, and from Fig. 5(iii) that saturated strain% increases and strain hysteresis% decreases with the increase in sintering temperature in PMNT 66/34 composition. Generally, the electric field-induced strain takes place through micro-domain transformations, domain reorientation and phase transitions [34]. The electric field-induced phase transition and domain motion can be accompanied by high hysteresis and high strain [20,34]. The decrease in saturated strain% and strain hysteresis% in PMNT 70/30 and 68/32 compositions with the decrease in sintering temperature can be explained on the basis of decrease in grain size. In general, the domain wall size decreases with decreasing grain size. And with decreasing grain size, it becomes difficult to form domain walls in the grains and hence the domain rotation contribution to the strain% and strain hysteresis% becomes smaller [33]. Also, the presence of residual stresses in the ceramics prevents domain reversal under external field. This effect decreases with the increase in grain size and the decrease in porosity in the ceramic [31]. The increase in saturated strain% with the increase in sintering temperature in PMNT compositions, in the MPB region, can be explained on the basis of predominance of electric field-induced phase transition and domain wall motion. There can exist mixed structures in PMNT 70/30, 68/32 and 66/34 compositions, since they are in the MPB region [24]. As can be seen from Fig. 5(i), the presence of the two anomalies in the variation of εr with
Fig. 5. Strain% vs. unipolar electric field behavior of (i) PMNT 70/30, (ii) PMNT 68/32 and (iii) PMNT 66/34 compositions, each sintered at (a) 1150, (b) 1200 and (c) 1250 °C.
temperature of PMNT 68/32 composition, which indicates its MPB nature. Also, the hump nature in the plot of $\varepsilon_r$ variation with temperature is increasing with the increase in sintering temperature of PMNT 68/32 composition, shown in Fig. 5(i). This gives us the hint that with the increase in sintering temperature of PMNT compositions, the mixed phase nature is increasing. And, from Devonshire theory, a little discrepancy of the free energy exists in the mixed structures near MPB of these types of systems. Therefore, domain wall motion and ferroelectric phase transitions are prone to be induced by electric field [35], whereas the decrease in strain hysteresis% in PMNT 66/34 compositions with the increase in sintering temperature can be attributed to the increase in engineered domain stability [35].

The piezoelectric coefficient, $d_{33}$, is calculated from the slope of strain% vs. electric field ($S$–$E$) behavior in the higher electric field region, using the relation

$$d_{33} = \frac{\Delta \text{strain} (\%) \times 10^6 \text{ pm/V}}{\Delta E}.$$ 

$d_{33}$ for different compositions is given in Table 2. The development of high $d_{33}$ and high induced saturated strain% (~0.19) with low strain hysteresis% (~3.2) in PMNT 68/32 composition sintered at 1200 °C suggests its suitability for actuator application.

### 4. Conclusions

The effect of sintering temperature on the dielectric and strain induced by electric field behaviors of PMNT compositions, in the MPB region, has been studied. $\varepsilon_r$ and $\tan \delta$ increase and Curie transition range decreases with the increase in sintering temperature. Strain levels in the range of 0.07–0.2% were obtained. High $d_{33}$~320 pm/V and saturated strain% ~0.19 with low strain hysteresis% (~3.5) in PMNT 68/32 ceramics sintered at 1200 °C indicates its suitability for actuator applications.

### Table 1

| Sintering temperature (°C) | Strain hysteresis % |
|---------------------------|---------------------|
|                           | PMNT 70/30 | PMNT 68/32 | PMNT 66/34 |
| 1150                      | 6          | 3.2        | 6.5        |
| 1200                      | 6.6        | 3.5        | 3.9        |
| 1250                      | 8.9        | 6.5        | 1          |

### Table 2

Piezoelectric coefficient $d_{33}$, from the slope of the (S–E) behavior in the higher electric field region

| PMNT compositions | $70/70/70$ | $68/68/68$ | $66/66/66$ |
|-------------------|------------|------------|------------|
| Sintered at (°C)  | 1150 1200 1250 | 1150 1200 1250 | 1150 1200 1250 |
| $d_{33}$ (pm/V)   | 205 195 235 | 320 235 190 | 300 230 190 |

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