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Effect of Poling on Dielectric Properties of PMN-PT Ceramics

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Abstract
This article presents the phase transition analysis of $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ ceramics. The ceramics were prepared by a conventional solid-state reaction method in two steps. Structural analysis confirms the single phase formation without any impurity phases. Temperature dependent dielectric properties were measured on unpoled and poled ceramics. It is observed that poling process helps to identify diffuse phase transitions.

Keywords- Piezoelectric; Relaxor; Phase transition; Dielectric; Poling.

1. Introduction
In order to substitute lead-based materials, research into the creation of lead–free piezoelectric ceramics has lately been a priority (Banerjee et al., 2021; Wei et al., 2018; Zhang et al., 2021). A number of nations have recently committed substantial human and financial resources to the research of lead-free ceramics, with some major successes (Banerjee et al., 2021; Wei et al., 2018; Zhang et al., 2021). Although much effort has gone into developing lead alternatives, none have yet achieved attributes that are equivalent to those of lead (Hu et al., 2020; Rajput et al., 2020). To solve this challenge, the source of high piezoelectricity in lead-based materials (PZT, PMN-PT, etc.) as well as lead-free systems must be discovered, which is still a mystery due to their structural complexity. Although there has been some research on the structural complexity of both lead-based and lead-free systems (Fang et al., 2019; Rajput et al., 2020; Sharma et al., 2017).

During this development of research on piezo-ceramics, one concept has been usually recognized that the morphotropic phase boundary (MPB) and polymorphic phase boundary (PPB) are the crucial for the large piezoelectric response in solid solution systems. Typically, there are two types of approaches to attain high piezoelectric properties in the piezoelectric ceramic. One is to design a morphotropic phase boundary (MPB), as in the case for $PbZrO_3$–$PbTiO_3$ (PZT) (Fang et al., 2019; Sharma et al., 2017), $PbMg_{1/3}Nb_{2/3}O_3$-$PbTiO_3$ (PMN-PT) (Rajput et al., 2020) and $BaTi_{0.8}Zr_{0.2}O_3$-$Ba_{0.7}Ca_{0.3}TiO_3$ (BZT-BCT) (Liu and Ren, 2009). Alternative technique to acquire high piezoelectric properties is to design polymorphic phase transition (PPT) in a composition system such as $K_{0.5}Na_{0.5}NbO_3$ (KNN) solid solution (Wu et al., 2015). Relaxor ferroelectrics are a kind of disordered material with a large and substantially frequency-dependent dielectric permittivity as well as a variety of odd characteristic temperatures (Cowley et al., 2011; Hajra et al., 2019; Shvartsman and Lupascu, 2012). Relaxor ferroelectrics are identified by their very broad dielectric constant peak identified as T_{m} (the temperature of dielectric constant maximum). For relaxor ferroelectric, there is another characteristic temperature, the depolarization temperature (T_{d}) which lies lower that of T_{m}. To explain physical properties in relaxors, different models such as super para electric model, spherical random-bond-random-field model and random field model were proposed. Despite extensive foundational research and sophisticated applications of relaxor ferroelectrics in recent years, the basis of their remarkable capabilities remains a mystery, and the mechanism for the appearance of relaxor properties seems to be still controversial (Li et al., 2020; Li et al., 2018; Wang et al., 2019). The ratio of monoclinic to tetragonal phases may be changed by applying a poling electric field, and the extent of this shift is depending on the field intensity.

In this work, we study the dielectric behavior of poled and unpoled PMN-*x*PT ceramics. The ceramics are prepared standard solid state reaction method in two steps.

2. Experiment

Polycrystalline samples of PMN-*x*PT (x = 0.20-0.40) were synthesized by columbite precursor method. Firstly, reagent grade MgO (99.99%) and $\mathrm{Nb_2O_5}$ (99.99%) were reacted to form columbite structure $\mathrm{MgNb_2O_6}$. In second step, columbite precursor powder was reacted with PbO (99.99%) and $\mathrm{TiO_2}$ (99.985%), according to $\mathrm{PbO} + x\mathrm{TiO} + [(1-x)/3]\mathrm{MgNb_2O_6} \rightarrow \mathrm{Pb}[(\mathrm{Mg_{1/3}Nb_{2/3}})_{(1-x)}\mathrm{Ti}_x\mathrm{O_3}$. Extra amount of PbO (2 wt% excess) was added to compensate for evaporation of Pb during subsequent calcination and sintering processes. Green pellets were sintered at 1230-1250°C for 4 hours after being compressed (isobaric pressure of 20 MPa) from well-prepared powders with a 5% PVA binder. To maintain a PbO-rich environment during sintering, a combination of $\mathrm{PbZrO_3}$+5 wt.%$\mathrm{ZrO_2}$ was utilised as a lead source. Sintered pellets were crushed into fine powders and annealed at 500°C for 10 h to remove the strains introduced by crushing. The X-ray diffraction (XRD) analysis was performed at room temperature using a Bruker D8 Advance X-ray Diffractometer. Data were taken for the range 20˚≤2θ≤80˚ with step size of 0.02. The samples were poled in silicon oil at 160°C for 5 minutes with a DC electric field of 0.5 to 4.5 kV/mm and then cooled in the same bias field (field cooling, i.e., an FC run). After poling for 24 hours, the samples were aged. In a thermal cycling chamber, dielectric characteristics were measured using an LCR metre (HIOKI3532) at various frequencies (100 Hz to 1 MHz) with a heating and cooling rate of 0.5°C/min (0-250°C). For each mixture, two samples were generated, and each sample was tested at least three times to acquire experimental data.

3. Results and Discussion

Figure 1 demonstrates the XRD patterns of PMN-*x*PT ($x = 0.27$, 0.275, and 0.28) ceramics. Preliminary examination of XRD data confirms the single phase formation without any impurity phases. Detailed XRD analysis confirms that the average structure for compositions ($x \leq 0.34$) is rhombohedral at room temperature. For compositions $0.34 \leq x \leq 0.35$, the average structure is mixture of rhombohedral, orthorhombic/monoclinic and tetragonal phases. However, the average structure for compositions ($x \geq 0.35$) is tetragonal at room temperature. We want to clarify here that the average structure in the MPB region is complicated, hence, different types of methods were employed to predict the average structure in the MPB region of PMN-PT ceramics (Li et al., 2018; Li et al., 2020).

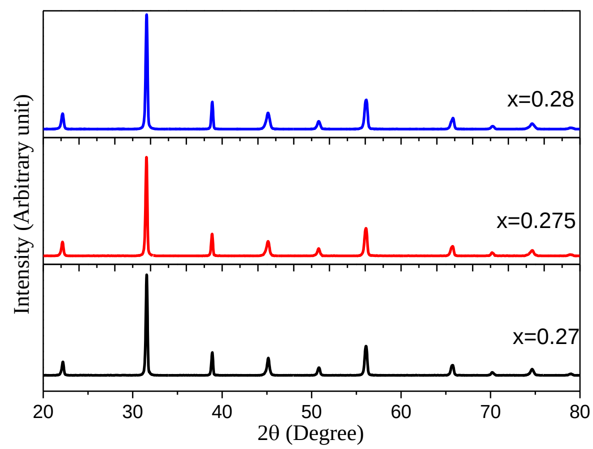

Figure 1. XRD patterns of PMN-*x*PT ($x = 0.27$, 0.275, and 0.28) ceramics.

The temperature dependence of dielectric permittivity ($\varepsilon - T$) at various frequencies (100Hz-1MHz) for PMN-*x*PT ceramics can be found in our previous article (Rajput et al., 2020). The $\varepsilon - T$ curves clearly indicate that the PMN rich samples show relaxor behavior with broad peak and significant frequency dispersion, while samples of $x \geq 0.30$ show sharp peaks at transition temperature (Rajput et al., 2020). Figure 2 illustrates the permittivity values at room temperature (25°C) and transition temperatures for PMN-*x*PT ceramics. It can be seen that room temperature permittivity value is maximum for $x = 0.34$, which is MPB composition. However, permittivity value is maximum for $x = 0.275$ at transition temperature as compared to other compositions. This composition is defined as the tricritical point (TCP). Previously, we have shown that the TCP displays both the highest dielectric susceptibility and the greatest degree of elastic softening at the transition temperature, in comparison to surrounding compositions, based on the preceding findings (Rajput et al., 2020). In general, it means that the triple point composition has a weaker first-order ferroelectric transition and that the lattice instability is higher at the ferroelectric transition than in neighboring compositions (Rajput et al., 2020). For $BaTi_{1-x}Hf_xO_3$ ceramics, it was found that the electrostrain is maximum in single rhombohedral phase region at the TCP (Hu et al., 2020).

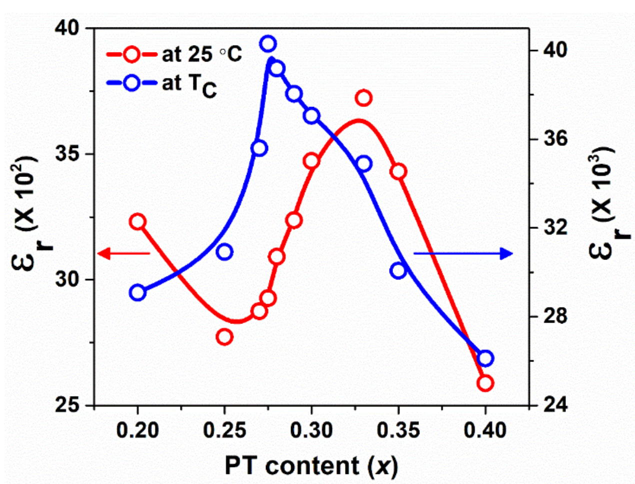

Figure 2. Permittivity values at room temperature (25°C) and transition temperatures for PMN-*x*PT ceramics.

However, it is very difficult to detect T_{R-T} (rhombohedral to tetragonal) phase transition for other compositions. Due to involvement of numerous diffused processes, it is significantly difficult to recognize different phase transition for nearby triple point compositions. In such cases, ε-T curve of poled ceramics is helpful to identify diffuse phase transitions. Before T_m or T_C, the poling process creates ferroelectric phases and promotes long-range order, resulting in further dielectric anomalies (Liu et al., 2015; Sahoo et al., 2018). The $\varepsilon(T)$ curve at 100 kHz for the non-poled and poled ceramics is shown in Figure 3. We have considered/assigned intermediate phase as O-phase rather than M-phase appear in between T and R phase. It was argued that intermediate phase has M-phase with different space group or O-phase (Singh and Pandey, 2001; Singh et al., 2006). Previously, Guo et al. (2002a) did a series of work on PMN-PT system and claimed that O-phase have strong influence on dielectric and piezoelectric properties (Guo et al., 2002a; Guo et al., 2002b; Guo et al., 2002c; Singh and Pandey, 2001). They observed that a single domain orthorhombic state could be achieved by applying an electric field along the direction <110>cub. Observed domain structure proved that a small poling field can induced a polydomain M or O phase but a poling with higher field can induce a monodomain O-phase. We believe that this is similar to our PMN-PT system. One of possibility is that the M-phase phase can be considered as pseudo O-phase with specific crystallographic arrangement.

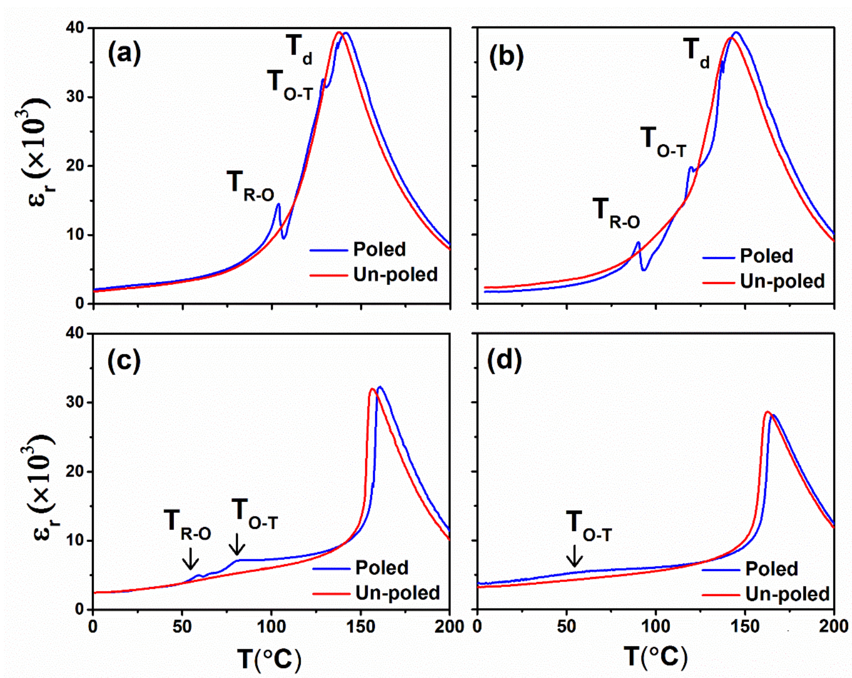

Figure 3. Temperature dependence of dielectric permittivity of poled and un-poled samples, (a) 28.5PT, (b) 29PT, (c) 33PT and (d) 34PT.

Figure 4 shows the phase diagram of the PMN-PT system. It is very difficult to distinguish between distinct phase transitions for close quadruple point compositions due to the participation of several scattered processes. In such cases, $\varepsilon - T$ curve of poled ceramics is helpful to identify diffuse phase transitions. Dielectric measurements on unpoled samples under heating were used to identify the transition temperatures between ferroelectric and paraelectric cubic phases, whereas dielectric measurements on poled samples were used to determine the second transition from tetragonal to rhombohedral phase.

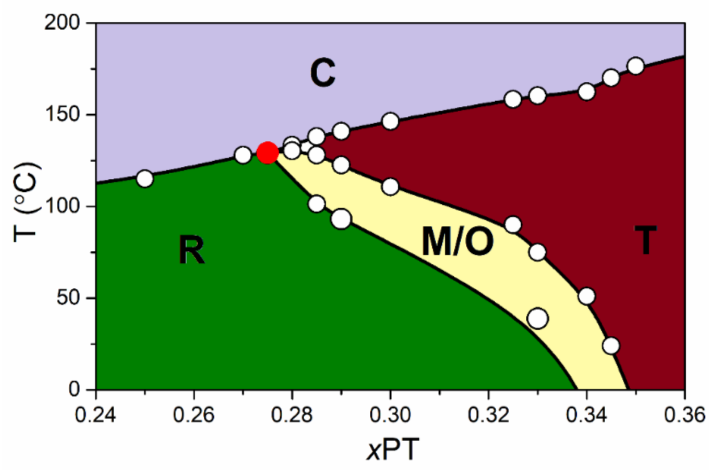

Figure 4. Phase diagram of the PMN-*x*PT system (adapted with permission from (Rajput et al., 2020)).

The monoclinic phase with the space group Pm was found in 86% of the non-poled ceramics, whereas the tetragonal phase with the space group $P4mm$ was found in 14% of the non-poled ceramics. The ceramics poled at 2.5 kV/mm, on the other hand, had 99% monoclinic phase while the remainder was tetragonal phase (Uršič et al., 2011). Because lead volatilization is a bigger issue during sintering than it is during calcination, an atmospheric powder is required. Other important parameters, including as impurities, heating rate, sintering duration, grain size, grain boundary structure, perovskite phase stoichiometry, and pyrochlore distribution, all have a role in defining the dielectric response of the final sintered products.

4. Conclusion

In summary, we have successfully prepared the PMN-*x*PT ceramics using solid state reaction. The XRD analysis validate that the grown ceramics do not have impurity phases. We have shown that the poling process can help to identify diffuse phase transitions.

Conflict of Interest

The authors declare no conflict of interest.

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