Evidence for $M_B$ and $M_C$ phases in the morphotropic phase boundary region of 
$(1 - x)[Pb(Mg_{1/3}Nb_{2/3})O_3] - xPbTiO_3$ : A Rietveld study

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March 22, 2022

Abstract

We present here the results of the room temperature dielectric constant measurements and Rietveld analysis of the powder x-ray diffraction data on $(1 - x)[Pb(Mg_{1/3}Nb_{2/3})O_3] - xPbTiO_3$ (PMN-xPT) in the composition range $0.20 \leq x \leq 0.45$ to show that the morphotropic phase boundary (MPB) region contains two monoclinic phases with space groups Cm (or $M_B$ type) and Pm (or $M_C$ type) stable in the composition ranges $0.27 \leq x \leq 0.30$ and $0.31 \leq x \leq 0.34$, respectively. The structure of PMN-xPT in the composition ranges $0 \leq x \leq 0.26$, and $0.35 \leq x \leq 1$ is found to be rhombohedral (R3m) and tetragonal (P4mm), respectively. These results are compared with the predictions of Vanderbilt & Cohen’s theory.

1 Introduction

Relaxor ferroelectric based morphotropic phase boundary (MPB) ceramics like $(1 - x)[Pb(Mg_{1/3}Nb_{2/3})O_3] - xPbTiO_3$ (PMN-xPT) \[\text{[1]}\] and $(1 -
show much higher electromechanical response about their MPBs in comparison to the well known Pb(ZrxTi1-x)O3 (PZT) system [3]. The reason why relaxor based MPB systems have much higher electromechanical response is still not very clear eventhough recent theoretical and experimental developments in PZT have improved our understanding of the phase stabilities in the vicinity of the MPB [4, 5, 6, 7, 8, 9, 10, 11, 12]. Noheda et al have discovered that the tetragonal phase of PZT with compositions (x = 0.50, 0.52) close to the MPB transforms to a monoclinic phase with space group Cm at low temperatures [4, 5]. Ragini et al [6] and Ranjan et al [7] have discovered yet another low temperature phase transition in which the Cm monoclinic phase transforms to another monoclinic phase with Cc space group [8]. The Cm to Cc phase transition is an antiferrodistortive (AFD) transition leading to superlattice reflections which are observable in the electron [6] and neutron [7] diffraction patterns only and not in the XRD patterns as a result of which Noheda et al missed the Cc phase in their high resolution XRD studies at low temperatures. The tetragonal to Cm, and Cm to Cc transitions are accompanied with pronounced anomalies in the elastic constant and dielectric constant [3]. It has been argued [4, 5, 11] that the monoclinic Cm phase provides the path for polarization rotation between tetragonal (P4mm) and rhombohedral (R3m) phases. X-ray Rietveld analysis by Ragini et al [12] has, however, revealed that the hitherto believed rhombohedral phase of PZT for 0.53 < x < 0.62 [13, 14] is indeed monoclinic (Cm) with very small domain size leading to composition dependent anomalous broadening of various reflections. Thus the MPB in the PZT system separates the stability fields of tetragonal and monoclinic Cm phases [12]. On application of DC field, these monoclinic domains get aligned and merged as a result of which some of the XRD peaks showing anomalous broadening in the unpoled state start exhibiting splittings characteristic of the Cm phase in the poled state. Thus, according to Ragini et al [12, 13], the field induced rhombohedral to Cm transition reported by Guo et al [11] is really a transition from a small-domain Cm phase to large-domain Cm phase. Based on Rietveld analysis of the XRD data, Ragini et al [12] have also shown that the tetragonal and monoclinic (Cm) phases coexist across the MPB in the composition range 0.520 ≤ x ≤ 0.525 due to nucleation barrier to the first order transition between the high temperature tetragonal and the low temperature monoclinic Cm phases [13]. These recent developments in PZT have been followed up by similar stud-
ies on the structure of MPB phases in the PMN-xPT \cite{16, 17, 18, 19, 20} and PZN-xPT \cite{21, 22} systems. In these systems also, the structure of the morphotropic phase in the unpoled state is monoclinic but with a space group Pm \cite{17, 17}, which is different from that in the PZT system. The Pm space group proposed by Singh and Pandey \cite{16} and Kiat et al \cite{17} in the MPB region of the PMN-xPT system has recently been confirmed in the high resolution powder XRD studies by Noheda et al \cite{23} contradicting an earlier report of Cm space group by the same workers for a similar composition \cite{21}. However in the PZN-xPT system, the possibility of monoclinic Pm \cite{17} or orthorhombic Bmm2 \cite{21} structures in the MPB region continues to be debated. More interestingly, Noheda et al \cite{24} and Ohwada, et al \cite{25} have observed a field-induced irreversible rhombohedral to Pm monoclinic phase transition in PZN-0.8PT through the Cm monoclinic phase.

Using eighth-order expansion of Devonshire theory, Vanderbilt and Cohen \cite{26} have predicted different regions of stability for the monoclinic Pm and Cm phases that are designated as \( M_C \) and \( M_A/M_B \), respectively, in their paper. Although both \( M_A \) and \( M_B \) phases belong to the Cm space group, the difference lies in the magnitudes of the components of the polarization \((P)\) corresponding to the pseudocubic cell. For the \( M_A \) phase \( P_X = P_Y \neq P_Z \) with \( P_Z > P_X \), while for the \( M_B \) phase, \( P_X = P_Y \neq P_Z \) with \( P_Z < P_X \). As per the phase diagram of Vanderbilt and Cohen \cite{26}, one expects a narrow stability field of the \( M_B \) phase between the rhombohedral and \( M_C \) phases. The present work was undertaken to verify the existence of the Cm (\( M_B \)) phase for compositions in between those for the rhombohedral and monoclinic (Pm) phases using Rietveld analysis of X-ray powder diffraction data on PMN-xPT samples with \( x \) varying from 0.26 to 0.39 at an interval of \( \Delta x = 0.01 \). From a careful study of the variation of the dielectric constant and crystal structure with composition \((x)\) on unpoled PMN-xPT ceramics, we show that the dominant phases in the composition ranges \( 0 \leq x \leq 0.26 \), \( 0.27 \leq x \leq 0.30 \), \( 0.31 \leq x \leq 0.34 \) and \( 0.35 \leq x \leq 1 \) are rhombohedral (R3m), monoclinic \( M_B \) (Cm), monoclinic \( M_C \) (Pm) and tetragonal (P4mm), respectively, in reasonable agreement with the predictions of the Vanderbilt and Cohen’s theory \cite{26}.
2 Experimental

Samples used in the present work were prepared by a modified solid state route \[27\]. One of the common problems associated with the solid state synthesis of PMN-\(x\)PT ceramics is the appearance of an unwanted pyrochlore phase \[28\]. To get rid of this unwanted phase, off-stoichiometric compositions, with excess of MgO and PbO, are used \[29\]. For example, Noheda et al \[23\] have used 15.5 and 2wt\% excess of MgO and PbO for getting pure perovskite phase. This naturally perturbs the phase stabilities in the vicinity of the MPB where the crystal structure is very sensitive to even small variations in the composition because of nearly degenerate nature of various phases. In order to bring out the intrinsic features of the PMN-\(x\)PT system, it is imperative to prepare pyrochlore phase free PMN-\(x\)PT ceramics in stoichiometric compositions (i.e., without using any excess of PbO and MgO). We have achieved this by using \(\text{PbCO}_3\) and \(\text{MgCO}_3.3\text{H}_2\text{O}\), instead of PbO and MgO, respectively, and introducing one more step in the reaction sequence for mixing of \(\text{TiO}_2\) \[27\]. In the present work, AR grade \(\text{Nb}_2\text{O}_5\) (99.95 \%) , \(\text{TiO}_2\) (99 \%), \(\text{Mg(NO}_3)_2.6\text{H}_2\text{O}\) (99\%), \(\text{Pb(NO}_3)_2\) (99 \%) and ammonium carbonate were used. \(\text{MgCO}_3.3\text{H}_2\text{O}\) and \(\text{PbCO}_3\) were prepared from \(\text{Mg(NO}_3)_2.6\text{H}_2\text{O}\) and \(\text{Pb(NO}_3)_2\) by precipitation. Mixing of various ingredients in stoichiometric proportions was carried out for 6 hours using a ball mill (Retsch, Japan) with zirconia jars and zirconia balls. AR grade acetone was used as the mixing media. Heat treatments for calcination were carried out in alumina crucibles using a globar furnace. The columbite precursor \(\text{MgNb}_2\text{O}_6\) (MN) \[28\] was prepared by calcining a stoichiometric mixture of \(\text{MgCO}_3.3\text{H}_2\text{O}\) and \(\text{Nb}_2\text{O}_5\) at 1050\(^\circ\)C for six hours. At the next stage, stoichiometric amount of \(\text{TiO}_2\) was mixed with \(\text{MgNb}_2\text{O}_6\) and the mixture was calcined at 1050\(^\circ\)C for six hours to obtain \([(1 - x)/3]\text{MgNb}_2\text{O}_6 - (x)\text{TiO}_2\) (MNT) precursor. This MNT precursor was then mixed with stoichiometric amount of \(\text{PbCO}_3\) and calcined at 750\(^\circ\)C for six hours. The powder obtained at this stage consists of pure perovskite phase of PMN-\(x\)PT free from the pyrochlore phase. Cold compaction of calcined powders was done using a steel die of 12-mm diameter and an uniaxial hydraulic press at an optimised load of 65 kN. 2 \% polyvinyl alcohol (PVA) solution in water was used as binder. The green pellets were kept at 500\(^\circ\)C for 10 hours to burn off the binder material and then sintered at 1150\(^\circ\)C for 6 hours in sealed crucibles with controlled PbO atmosphere. Density of the sintered pellets was higher than 98\% of the theoretical density. Sintered pellets were crushed into fine
powders and then annealed at 500°C for 10 hours to remove the strains introduced during crushing for x-ray characterizations. XRD measurements were carried out using a 12kW rotating anode (Cu) based Rigaku powder diffractometer operating in the Bragg-Brentano geometry and fitted with a graphite monochromator in the diffracted beam. Fired-on silver paste was used for electroding the sintered pellets. The dielectric measurements at 1kHz were carried out using a HIOKI 3532 LCR HiTester.

3 Details of the Rietveld refinement

Rietveld refinement was carried out using DBWS-9411 programme [30]. In all the refinements pseudo-Voigt function was used to define the peak profiles while a fifth order polynomial was used for describing the background. Except for the occupancy parameters of the ions, which were kept fixed at the nominal composition, all other parameters i.e., scale factor, zero correction, background, half width parameters along with mixing parameters, lattice parameters, positional coordinates and isotropic thermal parameters were refined. The isotropic thermal parameter values for Pb was invariably found to be high as reported by Kiat et al also [17]. Use of anisotropic thermal parameters for Pb did not lead to any improvement in the agreement factors.

In the tetragonal phase with P4mm space group, the $Pb^{2+}$ ion occupies 1(a) sites at (0, 0, z), $Ti^{4+}/Nb^{5+}/Mg^{2+}$ and $O^{2-}_I$ occupy 1(b) sites at (1/2, 1/2, z) and $O^{2-}_{II}$ occupy 2(c) sites at (1/2, 0, z). For the rhombohedral phase with R3mH space group, we used hexagonal axes with lattice parameters $a_H = b_H = \sqrt{2} a_R$ and $c_H = \sqrt{3} a_R$ where $a_R$ corresponds to the rhombohedral cell parameter. In the asymmetric unit of the structure of the rhombohedral phase with R3mH space group, Pb$^{2+}$ and Nb$^{5+}$ occupy 3(a) sites at (0, 0, z) and $O^{2-}$ at the 9(b) site at (x, 2x, z). In the monoclinic phase with space group Cm, there are four ions in the asymmetric unit with Pb$^{2+}$, Ti$^{4+}/Nb^{5+}/Mg^{2+}$ and O$^{2-}_I$ in 2(a) sites at (x, 0, z) and O$^{2-}_II$ in 4(b) sites at (x, y, z). The asymmetric unit of the monoclinic phase with space group Pm has got five ions with Pb$^{2+}$ and O$^{2-}_I$ in 1(a) site at (x, 0, z), Ti$^{4+}/Nb^{5+}/Mg^{2+}$, O$^{2-}_II$ and O$^{2-}_{III}$ in 1(b) sites at (x, 1/2, z). Following the established conventions, Pb$^{2+}$ was fixed at (0,0,0) for the tetragonal [31] and monoclinic [4, 10] structures. Following Megaw and Darlington [32], the z-coordinate of O$^{2-}$ was fixed at 1/6 for the rhombohedral structure. Additionally, space group Bmm2 was also taken into consideration for
a few compositions. For this space group, $Pb^{2+}$ ion occupies 2(b) sites at $(1/2, 1/2, z)$, $Nb^{5+}/Ti^{4+}/Mg^{2+}$ ions occupy 2(a) sites at $(0, 0, z)$, $O_1^{2+}$ in 4(d) sites at $(x, 0, z)$ and $O_2^{2-}$ in the 2(b) sites at $(0, 1/2, z)$. $Nb^{5+}/Ti^{4+}/Mg^{2+}$ ions were kept at the origin $(0,0,0)$ for the refinement [33].

4 Location of the morphotropic phase boundary

Lead magnesium niobate (PMN) is a relaxor ferroelectric with very high value of room temperature dielectric constant ($\approx 12000$ in ceramic form) [34]. With the addition of lead titanate (PT), whose dielectric constant is very low ($<400$)[3], it is expected that the dielectric constant of the resulting solid solution will decrease in comparison to PMN with increasing PT content. Fig.1 shows the variation of room temperature dielectric constant $\epsilon'$ with composition $(x)$ for the PMN-$x$PT ceramics in the composition range $0.20 \leq x \leq 0.45$. As expected, dielectric constant decreases with increasing value of $x$ upto $x = 0.26$. However, from $x = 0.27$, the $\epsilon' - x$ plot takes an upward trend marking the onset of the MPB region. This upward trend continues upto $x \approx 0.30$ and thereafter shows a plateau region for $0.30 < x < 0.34$. Kelly et al [35] have also observed a similar plateau region but in poled PMN-$x$PT samples. The dielectric constant again shows an upward trend leading to a peak around $x = 0.35$ and thereafter it decreases monotonically with increasing $x$. The results shown in this figure correspond to averaging over at least 5 samples for each composition. The sample to sample variation of dielectric constant for each composition was less than 1% for various PMN-$x$PT samples.

Fig.1 reveals the presence of four different regions. For correlating these regions with a corresponding change in the crystal structure as a function of composition $(x)$, we present in Fig.2 the powder XRD profiles of the 200, 220 and 222 pseudocubic reflections for various PMN-$x$PT composition. For the composition range $0.20 \leq x \leq 0.26$, the 200 is a singlet, while 220 and 222 are doublets with weaker reflections occurring on the lower $2\theta$ side. This characterizes a rhombohedral phase that is stable for $x \leq 0.26$. For $x > 0.26$, the width of the 200 profile increases eventually leading to an asymmetric tail on the higher $2\theta$ side which has become quite apparent for $x = 0.29$ and 0.30. As shown in the next section, Rietveld analysis of the XRD data reveals that
the structure of the dominant phase in the composition range $0.26 < x < 0.31$ is monoclinic ($M_B$ type) with Cm space group. The nature of the 200 profile again changes around $x = 0.31$ leading to the appearance of a shoulder on the higher $2\theta$ side which eventually becomes a distinct peak with increasing $x$ as can be seen from Fig. 2 for $0.31 \leq x \leq 0.34$. In this composition range, the dominant phase is monoclinic ($M_C$ type) with Pm space group. For $x \geq 0.35$, the profiles shown in Fig. 2 exhibit further changes. In particular, 200 pseudocubic reflection splits into 002 and 200/020 with nearly 1:2 intensity ratio. Further, the shoulder/peak on the lower $2\theta$ side of the 220 pseudocubic profile is replaced by a distinct peak on the higher $2\theta$ side. In addition, the 222 profile becomes a singlet. All these features correspond to the tetragonal structure and hence the dominant phase for $x \geq 0.35$ is tetragonal, as confirmed by the Rietveld analysis also, the results of which are presented in the next section. Thus the different regions shown in Fig. 1 correspond to four different crystallographic phases of PMN-xPT, which are stable over different range of composition.

5 Rietveld analysis of XRD data

5.1 Rhombohedral structure with space group R3mH ($0 \leq x \leq 0.26$)

Fig.3 depicts the observed, calculated and difference profiles obtained by Rietveld analysis of the XRD data for PMN-xPT with $x = 0.20$ and 0.26 using rhombohedral space group R3mH. The fit between the observed and calculated profiles is quite good confirming the rhombohedral structure of PMN-xPT for $x \leq 0.26$ in region I of Fig.1. The refined structural parameters and various agreement factors are given in Table1.

5.2 Monoclinic structure with space group Cm ($0.27 \leq x \leq 0.30$)

For compositions with $x \geq 0.27$, the 200 reflection becomes broader which can not be accounted for in terms of the rhombohedral structure for which 200 is a singlet. This anomalous broadening is similar to that reported in $Pb(Fc_{1/2}Nb_{2/3})O_3$ and PZT with $0.530 \leq x \leq 0.62$, where it has been attributed to the Cm phase. The anomalous broadening is absent for
$x \leq 0.26$ as can be seen from the excellent fit shown in the insets (b) to Fig. 3 for the 200 profile. To determine the true symmetry in the composition range $0.27 \leq x \leq 0.30$, we first carried out Rietveld refinements using various plausible space groups i.e., rhombohedral R3mH, monoclinic Cm, monoclinic Pm and orthorhombic Bmm2. Fig.4 shows the observed, calculated and difference profiles along with the various agreement factors for the pseudocubic 200, 220, 310 and 222 reflections using four different space groups for $x = 0.29$. For the R3mH space group [Fig. 4(a)], we see that the mismatch between the observed and calculated profiles is quite prominent for 200 and 310 pseudocubic reflections, which is also confirmed by highest value of the agreement factors. Thus R3mH space group is simply ruled out. For the space group Pm, the misfit between the observed and calculated profiles for the 220 and 222 pseudocubic reflections is very large. In particular, for the 222 pseudocubic profile, the observed and calculated peaks are appearing at different $2\theta$ values ruling out the possibility of the Pm phase. A similar misfit for the 220 and 222 profiles is observed for the Bmm2 space group also as can be seen from Fig. 4(c). The Cm space group gives the most satisfactory fit between the observed and calculated profiles for all the four reflections as can be seen from Fig. 4(d). This is corroborated by the lowest value of the agreement factors also. Fig. 5 depicts the observed, calculated and difference profiles in the $2\theta$ range 20 to 120 degrees for $x = 0.29$. The overall fit is quite satisfactory. The refined structural parameters are given in Table 2. From an analysis of the refined positional coordinates given in Table 2, it is found that the Cm phase of the PMN-$x$PT system is of $M_B$ type ($P_x = P_y > P_z$) in contrast to the PZT system where the Cm phase corresponds to the $M_A$ type ($P_x = P_y < P_z$) [26].

### 5.3 Monoclinic structure with space group Pm ($0.31 \leq x \leq 0.34$)

On increasing the PT content beyond $x = 0.30$, new features, like a shoulder in the 200 pseudocubic profile, appear. In order to determine the correct space group of PMN-$x$PT in this composition range, we considered Cm, Bmm2, and Pm space groups in our Rietveld analysis. Fig.6. depicts the observed, calculated and difference profiles of PMN-$x$PT with $x = 0.32$ for the pseudocubic 200, 220 and 310 reflections for the three space groups. It is evident from this figure that the best fit is obtained for the Pm space
group which corresponds to the $M_C$ phase in the notation of Vanderbilt and Cohen [26]. The agreement factors given in the last column of Fig. 6 are the lowest for the Pm space group. Fig. 7 depicts the observed, calculated and difference profiles in the 2$\theta$ range 20 to 120 degrees. The overall fit is quite satisfactory. Table 3 lists the refined structural parameters. It may be noted that the convention used for $\beta (> 90)$ in Table 2 is different from that $\beta (< 90)$ used in reference [16] as a result of which the positional coordinates also appear to be different.

5.4 Tetragonal structure with space group P4mm ($0.35 \leq x \leq 1$)

Rietveld analysis for $x \geq 0.35$ confirmed that the dominant phase of PMN-xPT for these compositions has got tetragonal structure. Very good fit between the observed and calculated profiles were obtained using tetragonal P4mm space group as can be seen from Fig. 8 for $x = 0.39$. The refined structural parameters are listed in Table 4 along with the agreement factors for this composition.

5.5 Phase coexistence

One often observes coexistence of neighbouring phases in the MPB region due to extrinsic factors like compositional fluctuations [37] and intrinsic factors like a first order phase transition between the low and high temperature phases [13, 15, 38]. The results of the previous section show that in the PMN-xPT system, there are three phase boundaries occurring around $0.26 \leq x \leq 0.27$, $0.30 \leq x \leq 0.31$ and $0.34 \leq x \leq 0.35$ separating the stability fields of rhombohedral and Cm, Cm and Pm, and Pm and tetragonal phases, respectively. In order to see if further improvements in the agreement factors can result from a consideration of the coexistence of a minority neighbouring phase, we carried out Rietveld refinements for the composition ranges $0.27 \leq x \leq 0.30$, $0.31 \leq x \leq 0.34$ and $0.35 \leq x \leq 0.39$ using various plausible coexisting phases. It was found that in the composition range $0.27 \leq x \leq 0.30$, consideration of a minority rhombohedral phase led to higher agreement factors while minority monoclinic Pm phase decreased the agreement factors. The fits between observed and calculated profiles have improved for the (Cm + Pm) model as can be seen from a comparison of Fig. 4 (e) with Fig. 4 (d). Similarly, for the composition range $0.31 \leq x \leq 0.34$, consideration
of a minority tetragonal phase decreased the agreement factors whereas the minority Cm phase increased the agreement factors. The presence of minority tetragonal phase improves the fit, especially on the lower 2θ side of the 200 pseudocubic profile, as can be seen from a comparison of Fig.6 (c) with 6(d). Further, monoclinic Pm phase was found to coexist as a minority phase in the tetragonal region $0.35 \leq x \leq 0.39$ in agreement with the results of Ref. [23].

The molar fractions of the minority and majority phases obtained by Rietveld refinement are plotted in Fig.9 as a function of PT content $(x)$. It is evident from this figure that pure R3m phase exists for $x < 0.27$. For $x = 0.27$, the structure corresponds to that of pure Cm phase. On increasing the PT content $(x)$, the Cm phase fraction decreases while the fraction of minority Pm phase increases.

However, on crossing the Cm-Pm phase boundary at $0.30 < x < 0.31$, the fraction of the Pm phase increases abruptly. For $x = 0.31$, the structure corresponds to pure Pm phase. On increasing $x$ further ($> 0.31$), the fraction of the majority Pm phase decreases while that of the minority P4mm phase increases with increasing $x$ in the composition range $0.31 < x < 0.35$. For compositions with $x > 0.34$, the P4mm phase becomes the majority phase whose fraction increases with $x$ while the fraction of the minority Pm phase continuously decreases.

### 5.6 Variation of lattice parameters with composition

Variation of lattice parameters with composition $(x)$ for the majority phase is plotted in Fig. 10 for $0.20 \leq x \leq 0.45$. The [100] and [010] directions of the tetragonal phase correspond to the [010] and [100] directions of the Pm phase respectively. The [001] direction of the Pm phase deviates slightly from [001] direction of the tetragonal phase towards the [100] direction of the Pm phase giving rise to a monoclinic cell with unique $b$-axis. The [100] and [010] directions of the Cm phase, on the otherhand, are along the $<110>$ directions of the Pm and tetragonal phases. The cell parameters $a_m, b_m$ of the Cm phase are related to the elementary perovskite cell parameters $a_p, b_p$ as: $a_p \approx a_m/\sqrt{2}$ and $b_p \approx b_m/\sqrt{2}$. For the sake of easy comparison with the corresponding cell parameters of the tetragonal and Pm phases, we have plotted $a_p$ and $b_p$ instead of $a_m, b_m$ for the Cm phase in Fig.10. In order to maintain the polarization rotation path [9, 26] in going from tetragonal to Pm to Cm phases for which $P_z \neq 0 (P_x, P_y = 0)$, $P_z \neq P_x \neq 0 (P_y = 0)$ and $P_x = P_y \neq 0, P_z \neq 0$, respectively, the $a, b, c$ axes of the Pm phase become $b_p, c_m, a_p$, respectively, of the Cm phase. It is evident from Fig.10 that for the
tetragonal compositions, the $a-$ parameter increases while the $c-$ parameter decreases continuously with decreasing $x$. Around $0.34 < x < 0.35$, the $a-$ parameter of the tetragonal phase matches with the $b-$ parameter of the monoclinic (Pm) phase while the $c-$ parameter of the tetragonal phase, which remains as the $c-$ parameter of the Pm phase, shows a discontinuous drop. The $a-$ and $c-$ parameters of the Pm phase are nearly independent of composition but the $b-$ parameter increases continuously with decreasing $x$. Further the monoclinic angle $\beta$ decreases continuously with decreasing $x$ in the Pm phase field. The $b, a$ and $c$ parameters of the Pm phase, which become $c_m, b_p$ and $a_p$ of the Cm phase, do not show any discontinuity at the Pm-Cm phase boundary. Similarly, there is no discontinuous change in the $b_p$ and $c_m$ cell parameters at the Cm-R3m phase boundary but $a_p$ drops discontinuously. Table 5 lists the lattice parameter values of the majority phases for all the compositions studied by us.

6 Concluding remarks

The phase diagram of Vanderbilt and Cohen [26] for an eight order expansion of the free energy predicts the stability regions of three types of monoclinic phases, $M_A, M_B, M_C$, in addition to the tetragonal(T), rhombohedral(R) and orthorhombic(O) phases (see Fig.11). The R-$M_A$-T sequence of phase transition observed in PZT as a function of composition has been attributed to the region near $\alpha = \pi/2, \beta = 0.102$ by Vanderbilt and Cohen. For the PMN-xPT system, we have shown that the stable phases in the composition ranges $x < 0.27, 0.26 < x < 0.31, 0.30 < x < 0.35$ and $x > 0.34$ correspond to R, $M_B, M_C$ and T phases, respectively. In the phase diagram shown in Fig.11, the R- phase region is followed by a narrow stability region of the $M_B$ phase in broad agreement with our observations. However, as per this phase diagram, the $M_B$ and $M_C$ regions should be separated by a very thin orthorhombic (O) phase region. According to our Rietveld analysis results, the $M_B - M_C$ phase boundary occurs around 0.30 < $x$ < 0.31. Interestingly, in the Rietveld refinement for $x = 0.30$, which is near this phase boundary, we found that $M_B$, $M_C$ and O phases give the same value of $R_{WP}$ (12.92) but the $R_B$ is the lowest for the O phase ($R_B = 12.84, 10.04, 9.92$ for the $M_B, M_C$ and O phases, respectively) raising the possibility of the existence of the O phase in between the $M_B$ and $M_C$ phase regions. Thus the phase transition sequence $R - M_B - O - M_C - T$ predicted by
Vanderbilt and Cohen for $3\pi/4 < \beta < 0.8\pi$ may indeed correspond to the PMN-xPT system. Obviously, the structure of the PMN-xPT system in the MPB region is much more complex as compared to that in the PZT system with a simple $R - M_A - T$ sequence of phase transitions. Although Vanderbilt and Cohen’s theory predicts that $R - M_B$ phase boundary to be of first order type, our Rietveld analysis does not reveal any coexistence of $R$ and $M_B$ phases. However, since the nature of the XRD profiles for the two phases are quite similar, except for the anomalous broadening of $h00$ and $hh0$ reflections for the $M_B$ phase, it may never be possible to settle the issue of coexistence of these two phases in a reliable fashion. The coexistence of $M_C$ and T phases revealed by our Rietveld analysis is not expected on the basis of the Vanderbilt and Cohen’s theory since the corresponding boundary is of second order type. This could be due to the limitations of the eight order truncation of the free energy expansion.

In the PZN-xPT system, there is some controversy about the structure of the MPB phase. According to Orauttapong et al. [17], the sequence of phase transition in unpoled samples is R-O-T which is expected for $\pi < \beta < 3\pi/2$ in the Vanderbilt and Cohen’s phase diagram. Kiat et al have [17], however, shown that the structure of PZN-xPT in the MPB region for $x = 0.09$ corresponds to the $M_C$ phase. If it is so, we suspect the existence of $M_B$ phase and possibly O phase also interposed between R and $M_C$ phases, similar to what we have observed in the present study on the PMN-xPT system. It is likely that the relaxor ferroelectric based MPB systems may have similar sequence of phase transitions. Further, we suspect that the higher electromechanical response of these relaxor based MPB systems may be linked with the ease of polarization rotation in the presence of $M_B$, $M_C$ and probably O phases in the morphotropic phase boundary region as compared to the presence of only one phase ($M_A$) in the PZT system.

7 Acknowledgement

AKS acknowledges the award of senior research fellowship of UGC-BHU.

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Figure Captions

Fig.1 Variation of the real part of the dielectric constant ($\epsilon'$) with composition ($x$) at room temperature for PMN-$x$PT ceramics.

Fig.2 Evolution of the X-ray diffraction profiles of the 200, 220 and 222 pseudocubic reflections with composition ($x$) for PMN-$x$PT ceramics.

Fig.3 Observed (dots), calculated (continuous line) and difference (bottom line) profiles obtained after the Rietveld refinement of PMN-$x$PT with $x=0.20$ and $x=0.26$ using rhombohedral space group R3m in the $2\theta$ range 20 to 60 degrees. Inset (a) shows the patterns in the $2\theta$ range 60 to 120 degrees while the inset (b) illustrates the quality of fit for the 200 reflection. Tick marks above the difference profile show peak positions for CuK\(\alpha_1\).

Fig.4 Observed (dots), calculated (continuous line) and difference (bottom line) profiles of the 200, 220, 310 and 222 pseudocubic reflections obtained after the Rietveld refinement of PMN-$x$PT with $x=0.29$ using different structural models (a) Rhombohedral R3m (b) Monoclinic Pm (c) Orthorhombic Bmm2 (d) Monoclinic Cm and (e) Monoclinic (Pm+Cm) coexistence model.

Fig.5 Observed (dots), calculated (continuous line) and difference (bottom line) profiles obtained after the Rietveld refinement of PMN-$x$PT with $x=0.29$ using monoclinic space group Cm in the $2\theta$ range 20 to 60 degrees. Inset shows the patterns in the $2\theta$ range 60 to 120 degrees. Tick marks above the difference profile show peak positions for CuK\(\alpha_1\).

Fig.6 Observed (dots), calculated (continuous line) and difference (bottom line) profiles of the 200, 220, and 310 pseudocubic reflections obtained after the Rietveld refinement of PMN-$x$PT with $x=0.32$ using different structural models (a) Monoclinic Cm (b) Orthorhombic Bmm2 (c) Monoclinic Pm and (e) Monoclinic and tetragonal (Pm+P4mm) coexistence model.

Fig.7 Observed (dots), calculated (continuous line) and difference (bottom line) profiles obtained after the Rietveld refinement of PMN-$x$PT with $x=0.32$ using monoclinic space group Pm in the $2\theta$ range 20 to 60 degrees. Inset shows the patterns in the $2\theta$ range 60 to 120 degrees. Tick marks above the difference profile show peak positions for CuK\(\alpha_1\).

Fig.8 Observed (dots), calculated (continuous line) and difference (bottom line) profiles obtained after the Rietveld refinement of PMN-$x$PT with $x=0.39$ using tetragonal space group P4mm in the $2\theta$ range 20 to 60 degrees. Inset shows the patterns in the $2\theta$ range 60 to 120 degrees. Tick marks above the difference profile show peak positions for CuK\(\alpha_1\).
**Fig. 9** Variation of molar fractions of different phases with composition (x) as obtained by Rietveld refinement.

**Fig. 10** Variation of lattice parameters with composition (x) for the majority phases of PMN-xPT.

**Fig. 11** Phase diagram for ferroelectric perovskites in the space of the dimensionless parameters $\alpha$ (vertical axis) and $\beta$ (horizontal axis) [after Ref. 26].
Table 1. Refined structural parameters of PMN-\(x\)PT for \(x=0.20\) and 0.26 using rhombohedral space group R3mH.

| composition (x) | Ions             | Positional coordinates | Thermal parameters |
|-----------------|------------------|------------------------|-------------------|
| 0.20            | \(Pb^{2+}\)      | X = 0.00, Y = 0.00, Z = 0.542(1) | B(\(Å^2\)) = 3.02(1) |
| 0.26            | \(Pb^{2+}\)      | X = 0.00, Y = 0.00, Z = 0.546(1) | B(\(Å^2\)) = 2.91(2) |
| 0.20            | \(Ti^{4+}/Nb^{5+}/Mg^{2+}\) | X = 0.00, Y = 0.00, Z = 0.02(2) | B(\(Å^2\)) = 0.61(7) |
| 0.26            | \(Ti^{4+}/Nb^{5+}/Mg^{2+}\) | X = 0.00, Y = 0.00, Z = 0.019(1) | B(\(Å^2\)) = 0.14(4) |
| 0.20            | \(O^{2-}\)      | X = 0.353(3), Y = 0.176(3), Z = 0.1667 | B(\(Å^2\)) = 0.0(1) |
| 0.26            | \(O^{2-}\)      | X = 0.325(3), Y = 0.162(3), Z = 0.1667 | B(\(Å^2\)) = 0.3(1) |

\(a = b = 5.6921(1)(\text{Å})\) \(c = 6.9882(2)\) (Å) \\
\(a = b = 5.6841(1)(\text{Å})\) \(c = 6.9800(1)\) (Å) \\

\(0.20\) \(R_{WP} = 14.76\) \(R_{exp} = 6.46\) \(R_B = 10.12\) \(\chi^2 = 5.06\) \\
\(0.26\) \(R_{WP} = 12.98\) \(R_{exp} = 7.45\) \(R_B = 9.93\) \(\chi^2 = 3.01\)

Table 2. Refined structural parameters of PMN-\(x\)PT for \(x=0.29\) using monoclinic space group Cm.

| Ions             | Positional coordinates | Thermal parameters |
|------------------|------------------------|-------------------|
| \(Pb^{2+}\)     | X = 0.00, Y = 0.00, Z = 0.00 | B(\(Å^2\)) = 3.08(2) |
| \(Ti^{4+}/Nb^{5+}/Mg^{2+}\) | X = 0.5250(8), Y = 0.00, Z = 0.498(2) | B(\(Å^2\)) = 0.73(4) |
| \(O^{2-}_I\)    | X = 0.54(1), Y = 0.00, Z = -0.01(2) | B(\(Å^2\)) = 0.2(3) |
| \(O^{2-}_{II}\) | X = 0.317(2), Y = 0.267(4), Z = 0.48(1) | B(\(Å^2\)) = 0.3(2) |

\(a = 5.6951(2)(\text{Å})\) \(b = 5.6813(2)(\text{Å})\) \(c = 4.0138(1)(\text{Å})\) \(\beta = 90.1363(3)^{\circ}\)

\(R_{WP} = 12.24\) \(R_{exp} = 6.46\) \(R_B = 7.10\) \(\chi^2 = 3.59\)
**Table 3.** Refined structural parameters of PMN-xPT for $x=0.32$ using monoclinic space group Pm.

| Ions       | Positional coordinates | Thermal parameters |
|------------|------------------------|--------------------|
| $Pb^{2+}$  | X=0.00 Y=0.00 Z=0.00   | B ($\text{Å}^2$)   |
| $Ti^{4+}/Nb^{5+}/Mg^{2+}$ | X=0.509(2) Y=0.50 Z=0.5479(7) | B=0.20(3) |
| $O_1^{2-}$ | X=0.47(1) Y=0.00 Z=0.57(1) | B=0.2(2) |
| $O_II^{2-}$ | X=0.417(8) Y=0.50 Z=0.059(6) | B=0.2(2) |
| $O_{III}^{2-}$ | X=-0.02(1) Y=0.50 Z=0.57(1) | B=0.0(3) |

$a=4.0183(2)(\text{Å})$  
$b=4.0046(1)(\text{Å})$  
$c=4.0276(2)(\text{Å})$  
$\beta=90.146(3)^{\circ}$

$R_{WP}=10.63$  
$R_{exp}=5.42$  
$R_B=9.56$  
$\chi^2=3.84$

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**Table 4.** Refined structural parameters of PMN-xPT for $x=0.39$ using tetragonal space group P4mm.

| Ions       | Positional coordinates | Thermal parameters |
|------------|------------------------|--------------------|
| $Pb^{2+}$  | X=0.00 Y=0.00 Z=0.00   | B ($\text{Å}^2$)   |
| $Ti^{4+}/Nb^{5+}/Mg^{2+}$ | X=0.50 Y=0.50 Z=0.532(1) | B=0.76(4) |
| $O_1^{2-}$ | X=0.50 Y=0.50 Z=0.054(4) | B=0.8(3) |
| $O_{II}^{2-}$ | X=0.50 Y=0.00 Z=0.601(2) | B=0.4(2) |

$a=3.9920(0)(\text{Å})$  
$c=4.0516(1)(\text{Å})$

$R_{WP}=13.85$  
$R_{exp}=6.75$  
$R_B=10.12$  
$\chi^2=4.21$
Table 5. Refined cell parameters of PMN-\(x\)PT for the majority phases in the composition range \(0.20 \leq x \leq 0.45\).

| Composition (x) | Cell parameters |
|-----------------|-----------------|
|                 | a(Å)            | b(Å)            | c(Å)            | β(deg.)          |
| 0.20            | 5.6921(1)       |                 | 6.9882(2)       |                 |
| 0.26            | 5.6841(1)       |                 | 6.9800(1)       |                 |
| 0.27            | 5.7001(2)       | 5.6852(2)       | 4.0186(1)       | 90.126(3)       |
| 0.28            | 5.6975(2)       | 5.6814(2)       | 4.0159(2)       | 90.133(3)       |
| 0.29            | 5.6953(2)       | 5.6813(2)       | 4.0138(1)       | 90.136(3)       |
| 0.30            | 5.6962(3)       | 5.6806(2)       | 4.0123(2)       | 90.131(3)       |
| 0.31            | 4.0193(2)       | 4.0082(2)       | 4.0288(2)       | 90.145(3)       |
| 0.32            | 4.0183(2)       | 4.0046(1)       | 4.0276(2)       | 90.146(3)       |
| 0.33            | 4.0185(2)       | 4.0026(1)       | 4.0274(1)       | 90.169(2)       |
| 0.34            | 4.0174(2)       | 4.0019(2)       | 4.0289(2)       | 90.177(3)       |
| 0.35            | 4.0004(1)       |                 |                 | 4.0464(1)       |
| 0.36            | 3.9970(1)       |                 |                 | 4.0468(1)       |
| 0.37            | 3.9953(1)       |                 |                 | 4.0492(1)       |
| 0.38            | 3.9933(0)       |                 |                 | 4.0495(1)       |
| 0.39            | 3.9920(0)       |                 |                 | 4.0516(1)       |
| 0.45            | 3.9832(1)       |                 |                 | 4.0579(1)       |