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## Evolution of short-range to long-range monoclinic order of $M_B$ type with decreasing temperature in $0.75[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-0.25\text{PbTiO}_3$

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Results of Rietveld analysis of powder neutron diffraction data on  $0.75[\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3]-0.25\text{PbTiO}_3$  (PMN-0.25PT) at room temperature and 80 K are presented. It is shown that the currently believed structural model based on average rhombohedral structure (space group  $R3m$ ) with local  $\langle 110 \rangle$  disordered Pb atoms cannot account for the structure of PMN-0.25PT at 80 K. The low temperature structure of PMN-0.25PT is best refined using  $Cm$  space group of  $M_B$  type. It is argued that with decreasing temperature the short-range monoclinic order at 300 K grows into a truly long-range ordered monoclinic structure at 80 K. © 2006 American Institute of Physics.  
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$(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})-x\text{PbTiO}_3$  (PMN- $x$ PT) and  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})-x\text{PbTiO}_3$  (PZN- $x$ PT) are next generation morphotropic phase boundary (MPB) materials whose piezoelectric response is far superior to the well known  $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$  (PZT) ceramics.<sup>1,2</sup> Until recently, the origin of large piezoelectric response for the MPB compositions was attributed to the coexistence of rhombohedral and tetragonal phases<sup>2</sup> or a phase transition between these two phases near room temperature.<sup>3</sup> Recently it has been proposed that the high piezoelectric response of these ceramics is linked with the presence of monoclinic phase(s) in the MPB region because the polarization vector of these phases can undergo continuous rotation in response to the poling field.<sup>4-10</sup> Such a rotation of polarization vector is not possible in the tetragonal and rhombohedral phases.<sup>5</sup> There is therefore a renewed interest in understanding the correct structure of these materials as it can provide clue to the high piezoelectric response.

Following the discovery of the monoclinic phases in these MPB systems, the structure of the rhombohedral compositions has also been revisited.<sup>6,8,9,11</sup> Many workers have refined the structure of the so-called rhombohedral compositions of PZT (Ref. 12) and PMN- $x$ PT (Ref. 13) using rhombohedral  $R3m$  space group and local off-center displacements of Pb along the  $\langle 110 \rangle$  pseudocubic direction which correspond to average rhombohedral structure with short-range monoclinic order. More recently Glazer *et al.*<sup>14</sup> have proposed that the local structural order of the so-called rhombohedral compositions of PZT is monoclinic which progressively increases from short range to long range with increasing Ti concentration. In the MPB region, the structural order becomes truly long-range monoclinic, as has been shown earlier by Ragini *et al.*<sup>6</sup> for PZT and Singh and Pandey<sup>8</sup> and Singh *et al.*<sup>9</sup> for PMN- $x$ PT. Besides Ti content, external electric field<sup>15,16</sup> and hydrostatic pressure<sup>17</sup> have been shown to be the other variables, which can induce a short-range to

long-range monoclinic order. In the present work, we show that the lowering of temperature is yet another way of inducing short-range to long-range monoclinic order in a so-called rhombohedral composition of PMN- $x$ PT with  $x=0.25$ .

Highly homogeneous and stoichiometric samples of PMN-0.25PT free from pyrochlore phase were prepared by a modified columbite precursor method<sup>7,8</sup> without using any excess amount of MgO or PbO. High-resolution neutron powder diffraction patterns were recorded on a high-resolution powder diffractometer for thermal neutrons (HRPT) at SINQ, Switzerland with a wavelength of 1.154 Å. Rietveld analysis of the neutron powder diffraction data was carried out using FULLPROF program.<sup>18</sup>

Figure 1 depicts the powder neutron diffraction patterns of the 400, 440, and 620 pseudocubic profiles of PMN-0.25PT recorded at 300 and 80 K. Using Rietveld analysis of powder XRD data it was earlier reported that the structure of PMN-0.25PT is rhombohedral with space group  $R3m$  at 300 K.<sup>8</sup> However, Rietveld refinement of the structure using powder neutron diffraction data at 300 K using  $R3m$  space group gives unsatisfactory  $R$  factors ( $R_{\text{WP}}=8.09$  and  $R_{\text{expt}}=3.14$ ), very poor fit between observed and calculated profiles and extremely large isotropic thermal parameter of Pb [ $3.08(4) \text{ \AA}^2$ ]. Such a large value of thermal parameter for Pb indicates disorder in Pb position. It has been earlier shown in the PZT context that Pb position is disordered over three possible sites along pseudocubic  $\langle 110 \rangle$  directions.<sup>12</sup> In view of this, we also refined the structure of PMN-0.25PT at 300 K using off-center displacements of Pb along  $\langle 110 \rangle$  pseudocubic directions which gave reasonable value of isotropic thermal parameter [ $0.94(6) \text{ \AA}^2$ ] and satisfactory fit between observed and calculated profiles as shown in Fig. 1(a) with lower  $R$  factor ( $R_{\text{WP}}=7.23$ ). Thus, the room temperature data can be fitted with the  $R3m$  space group and local Pb shift in the  $\langle 110 \rangle$  pseudocubic direction.

It is worth mentioning here that following our earlier work,<sup>8</sup> where the stability regions of the rhombohedral and

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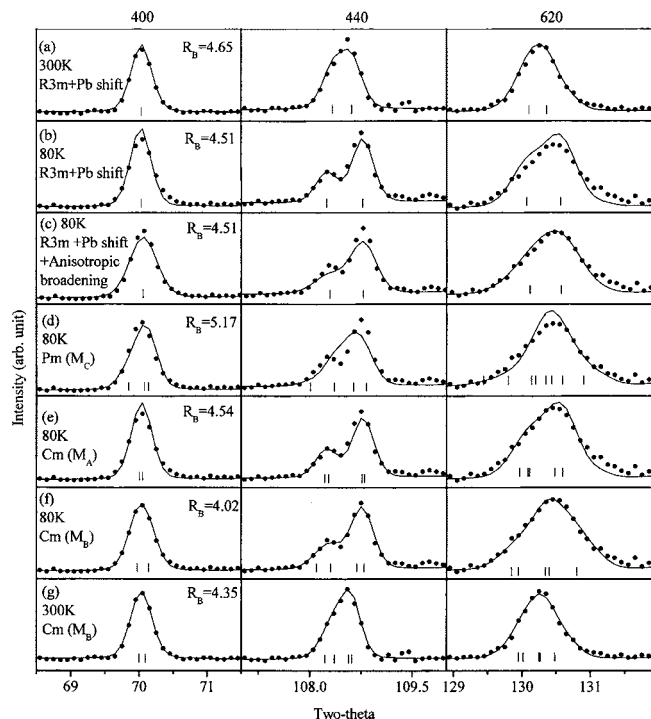


FIG. 1. The observed (dots) and calculated (continuous line) powder neutron diffraction profiles of pseudocubic 400, 440, and 620 reflections of PMN-0.25PT at 300 and 80 K using different structural models. Vertical tick marks show the positions of various Bragg reflections.

the monoclinic  $M_B$  phases were shown to be  $x < 0.27$  and  $0.27 \leq x \leq 0.30$  at, respectively, 300 K, Li *et al.*<sup>19</sup> have recently proposed that the  $M_B$  phase stability can extend up to  $x = 0.23$  at room temperature. However, the Rietveld fits given by these workers for  $x = 0.25$  are equally bad for both the rhombohedral and the monoclinic  $M_B$  phases as can be seen from the difference plots for the 220 pseudocubic profile given by these workers. Furthermore, the assumption of these workers that the thermal parameters of the so-called  $M_B$  phase at 300 K would be same as those of the  $M_C$  phase given by Kiat *et al.*<sup>10</sup> at 90 K is highly questionable. Even if one accepts their refinements as they are, the nonstoichiometric nature of their samples because of the presence of 2 wt % excess PbO, in contrast to our stoichiometric samples with no PbO excess, is sufficient to change the phase stabilities as also the unit cell parameters. In fact, their unit cell parameters are quite different from those reported earlier by Singh and Pandey<sup>8</sup> for stoichiometric samples for all the compositions.

On decreasing the temperature, the 620 profile (6 2 0 and  $6 0 \bar{2}$  of rhombohedral phase) in Fig. 1(b) becomes anomalously broad which, at first instance, indicates increased rhombohedral distortion leading to additional broadening. This is clearly seen for the 440 pseudocubic profile where at 80 K it has become a clear doublet as compared to nearly singlet like appearance at 300 K. We therefore, refined the structure of PMN-0.25PT at 80 K using  $R3m$  space group with local Pb shift, as was done for the refinement at 300 K. However, in contrast to room temperature data, the fit between observed and calculated profiles is not very satisfactory as can be seen from Fig. 1(b). In all refinements until

now, we have assumed isotropic peak broadening function. At the next stage of refinement, we considered anisotropic profile shape functions<sup>20</sup> to see if the large broadening of the 620 profile can be accounted for. Both the  $S_{HKL}$  parameters in the anisotropic profile shape functions and  $U$ ,  $V$ , and  $X$  parameters are due to the strain contributions.<sup>20</sup> When  $U$ ,  $V$ , and  $X$  parameters were refined along with  $S_{HKL}$ , it led to oscillatory  $R$  factors without convergence. The values of  $U$ ,  $V$ , and  $X$  parameters were therefore set to zero during subsequent refinement as the strain contributions are already taken care of by the  $S_{HKL}$  parameters, as shown by Stephens<sup>20</sup> in his original model. The fit for the 620 profile in fact improves dramatically after using anisotropic peak broadening functions but the fits for the other reflections such as 440 and 400 profiles deteriorates. As a result, the overall Bragg  $R$  factor ( $R_B$ ) does not show any improvement even after considering anisotropic peak broadening. The anisotropic peak broadening function was therefore not considered further.

It is evident from the foregoing that the observed neutron powder diffraction data for PMN-0.25PT at 80 K cannot be explained using rhombohedral structure and consideration of a lower symmetry structure is necessary. Landau-Devonshire free energy expansion up to the eighth order by Vanderbilt and Cohen<sup>21</sup> has shown that monoclinic phases with space groups  $Pm$  and  $Cm$  may appear in ferroelectric perovskites. Furthermore, the monoclinic  $Cm$  phase may be of two types: (i)  $M_A$  type with the component of polarization vector in the pseudocubic cell as  $\mathbf{P}_X = \mathbf{P}_Y < \mathbf{P}_Z$  and (ii)  $M_B$  type with  $\mathbf{P}_X = \mathbf{P}_Y > \mathbf{P}_Z$ . The  $M_A$  type monoclinic  $Cm$  phase was discovered by Noheda *et al.*<sup>5</sup> in the PZT system at low temperatures while the  $M_B$  type was reported by Singh and Pandey<sup>8</sup> and Singh *et al.*<sup>9</sup> in PMN- $x$ PT at room temperature. In view of the predictions of the Landau-Devonshire theory,<sup>21</sup> we considered monoclinic  $Pm$  and  $Cm$  space groups for refining the structure of PMN-0.25PT at 80 K. For the  $Cm$  space group, both  $M_A$  and  $M_B$  types were considered. It is evident from Fig. 1(d) that the monoclinic  $Pm$  space group gives very bad fit between the observed and calculated profiles and the resulting  $R_B$  (5.17) is much higher than even that for the pseudorhombohedral structural model shown in Fig. 1(b). Thus the monoclinic  $Pm$  phase can be easily ruled out. The monoclinic  $Cm$  phase of  $M_B$  type gives the lowest  $R$  factors and very good fit between observed and calculated profiles [see Fig. 1(f)]. A comparison of Fig. 1(e) with Fig. 1(f) suggests that the fits for the monoclinic  $Cm$  phase of  $M_A$  type are inferior to that for  $M_B$  phase and the  $R$  factor is also significantly higher, even though the number of refinable parameters are identical for both the models. Hence the monoclinic  $M_B$  phase is favored over  $M_A$  phase and the rhombohedral structure or pseudorhombohedral structure with local monoclinic order is ruled out. After successfully refining the structure of PMN-0.25PT at 80 K using monoclinic  $M_B$  phase, we considered the refinement of the structure at 300 K also using monoclinic phase of  $M_B$  type. As shown in Fig. 1(g), consideration of  $Cm$  space group of  $M_B$  type gives very good fit between observed and calculated profiles at 300 K also. Since the monoclinic distortion is small at 300 K and the monoclinic order is short ranged a pseudorhombohedral phase with local  $\langle 110 \rangle$  displacement of

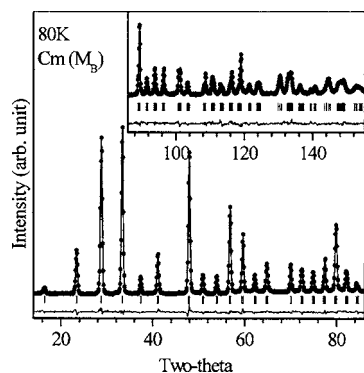


FIG. 2. Observed (dots), calculated (continuous line), and difference (bottom line) profiles obtained after the Rietveld analysis of the powder neutron diffraction data for PMN-0.25PT at 80 K using monoclinic  $Cm$  space group of  $M_B$  type in the  $2\theta$  range of  $14^\circ$ – $150^\circ$ . Vertical tick marks above the difference profile show peak positions.

Pb also gives reasonable fit. The structure of PMN-0.25PT at room temperature can therefore be also termed as pseudorhombohedral with short-range monoclinic-type correlated displacements of Pb atom. However, with increasing Ti concentration at a fixed temperature or decreasing temperature for fixed Ti content or increasing external electric field at a fixed temperature and composition, such a short-range ordered monoclinic phase can indeed grow into a truly long-range ordered monoclinic phase, as we have shown in the present work using temperature as a variable. Figure 2 depicts the observed, calculated, and difference profiles in the  $2\theta$  range of  $14^\circ$ – $150^\circ$  for the  $M_B$  phase with  $Cm$  space group using 80 K data. The overall fit is quite satisfactory. Table I lists the refined structural parameters for PMN-0.25PT at 80 K using  $Cm$  space group. The refined cell parameters for  $x=0.25$  at 80 K reveals that  $a_m/\sqrt{2} > b_m/\sqrt{2} > c_m$  in agreement with our earlier report for the  $M_B$  phase for  $0.27 \leq x \leq 0.30$  at 300 K.<sup>8</sup> Cao *et al.*,<sup>22</sup> on the other hand, have reported that  $b_m/\sqrt{2} < c_m$  even though  $a_m/\sqrt{2} > c_m$  for a single crystal of  $x=0.30$  but after applying electric field the cell parameters change such that  $a_m/\sqrt{2} > b_m/\sqrt{2} > c_m$  in agreement with our earlier<sup>8</sup> and present result for the  $M_B$  phase. Using density functional calculations, Grinberg and Rappe<sup>23</sup> have distinguished between Mg shift from the shift for Nb/Ti. In general, all the three cations ( $Mg^{2+}/Nb^{5+}/Ti^{4+}$ ) at the B site could be locally displaced by different amounts. It should in principle be possible to capture the difference in the  $Ti^{4+}$  displacement on one hand and the other two cations on the other using neutron diffraction data since the scatter-

TABLE I. Refined structural parameters of PMN-0.25PT at 80 K using monoclinic  $Cm$  space group of  $M_B$  type.  $a=5.7022(3)$  Å,  $b=5.6815(4)$  Å,  $c=4.0167(3)$  Å, and  $\beta=90.248(5)^\circ$ .  $R_{wp}=7.46$ ,  $R_{expt}=3.02$ , and  $\chi^2=6.10$ .

Atoms	X	Y	Z	$B(\text{Å}^2)$
Pb	0.00	0.00	0.00	$\beta_{11}=0.007(1)$ $\beta_{22}=0.027(1)$ $\beta_{33}=0.038(2)$ $\beta_{13}=0.009(1)$
Ti/Nb/Mg	0.532(1)	0.00	0.474(2)	$B_{iso}=0.37(3)$
O <sub>I</sub>	0.5714(9)	0.00	-0.037(2)	$B_{iso}=0.73(4)$
O <sub>II</sub>	0.272(1)	0.2530(6)	0.495(2)	$B_{iso}=0.85(2)$

ing length for Ti has a negative sign whereas it has positive sign for the other two. We considered this possibility in our refinements but the difference was found to be within the standard deviations. Probably still higher resolution neutron data in conjunction with pair distribution function analysis is required to capture the small differences in the local displacements for each of these three cations.<sup>24</sup>

To summarize, the short-range monoclinic order in the so-called pseudorhombohedral compositions of PMN- $x$ PT can be converted into a long-range monoclinic order not only by increasing Ti concentration or external electric field at room temperature but also by lowering the temperature at a fixed composition. The present study calls for more work on low Ti concentrations in the PMN- $x$ PT system to determine the limiting composition up to which the long-range monoclinic order can be established at low temperatures.

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