Effect of processing parameters on microstructural properties of lead magnesium niobates

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The synchrotron powder X-ray diffraction (XRD) and subsequent detailed Rietveld analysis of lead magnesium niobate (PMN) samples were performed to study the microstructural properties of polar nanoregions (PNRs) of the $R3m$ phase. PMN samples were synthesized under different sample processing conditions. The line profile broadening analysis of room-temperature synchrotron powder XRD patterns was performed using the multi-phase Rietveld refinement method for isotropic microstructural evaluation of different PMN samples. The two phases of perovskite PMN considered in the Rietveld refinement approach for satisfactorily fitting the XRD patterns are the paraelectric cubic phase ($Pm\bar{3}m$) and the local rhombohedral phase ($R3m$) which corresponds to the PNRs. It is observed that the contributions of the Gaussian component of size broadening of the polar rhombohedral phase ($R3m$) and the Lorentzian component of strain broadening of the paraelectric cubic phase ($Pm\bar{3}m$) are apposite for satisfactory Rietveld refinement of the synchrotron XRD data for all PMN samples. The volume-average crystallite size of PNRs ($R3m$ phase) is almost invariant (approximately 12 nm) with increasing processing temperature while their weight percentage increases. The values of the apparent microstrain in the paraelectric cubic phase ($Pm\bar{3}m$) are larger for hot-pressed samples.

1. Introduction

Lead magnesium niobate ($\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$) (PMN) belongs to the family of relaxors. The technical importance of relaxors is due to their outstanding dielectric, electrostriction (electromechanical) and opto-electronic properties which are very useful in making capacitors, actuators, ultrasonic devices, transducers, micro-positioners, ferroelectric random access memories, etc. (Uchino, 2000; Wadhawan *et al.*, 2005; Scott, 2007). These physical properties are attributed mainly to the existence of complex polar nanoregions (PNRs) in relaxors. However, the origin of their occurrence is not completely understood (Bokov & Ye, 2006; Welberry, 2008; Fu *et al.*, 2009; Bokov *et al.*, 2011; Cowley *et al.*, 2011).

The existence of PNRs has been proposed as the reason for the relaxor behaviour of PMN (Burns & Dacol, 1983; Yoshida *et al.*, 1998; Dkhil *et al.*, 2001; Ma & Cross, 2001; Hirota *et al.*, 2002; Xu *et al.*, 2004; Welberry, 2008; Gehring *et al.*, 2009; Stock *et al.*, 2010; Cowley *et al.*, 2011; Paściak *et al.*, 2007, 2012). The local crystal symmetry of these PNRs is different from the average crystal symmetry of PMN (de Mathan, Husson, Calvarin & Morell, 1991; de Mathan, Husson, Calvarin, Gavarrin *et al.* 1991; Verbaere *et al.*, 1992; Vakhrushev *et al.*, 1997; Thomas *et al.*, 1999; Takesue *et al.*, 2001; Svitelskiy *et al.*,

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2003; Ye *et al.*, 2003; Jeong *et al.*, 2005; Taniguchi *et al.*, 2011; Hu *et al.*, 2014; Bhakar *et al.*, 2016). The physical properties of PMN (dielectric constant, grain size, electrostrictive strain *etc.*) are strongly influenced by the sample preparation and processing conditions (Swartz & Shrout, 1982; Swartz *et al.*, 1984; Uchino *et al.*, 1985; Gupta & Kulkarni, 1994, 1995, 1996; Gupta *et al.*, 1997; Guha, 1999, 2001; Samara, 2003; Bokov & Ye, 2006; Wongmaneerung *et al.*, 2006; Zhao *et al.*, 2009). Thus, quantification of the phase percentage of PNRs, their crystallite size and the lattice strain present in PMN are important factors for understanding the effect of processing parameters [such as sintering temperature, sintering time and sintering at atmospheric pressure or high pressure (hot-pressing) conditions] on these properties. The crystal structure of PMN is inhomogeneous at the local scale due to the existence of PNRs and chemical ordered regions (CORs). Transmission electron microscopy (TEM) is widely used to determine the phase percentage and domain size of these local/nanoregions (Husson *et al.*, 1988; Chen *et al.*, 1989; Hilton *et al.*, 1990; Boulesteix *et al.*, 1994; Yoshida *et al.*, 1998; Xu *et al.*, 2000; Davies & Akbas, 2000; Fu *et al.*, 2009, 2012). X-ray diffraction (XRD) is an alternative, non-destructive technique which is used to estimate the average crystallite size and phase percentage of PNRs in PMN. Additionally, XRD gives information on microstrain in the sample (Cullity & Stock, 2001; Balzar *et al.*, 2004; Rai *et al.*, 2004). Most examples in the literature are of investigations of the structural (atomic) arrangements of relaxors, with few reports on the microstructural properties of these materials using diffraction techniques. The motivation of the present study is to carry out microstructural analysis of PMN samples using the XRD technique and subsequent multi-phase Rietveld analysis.

The diffraction line broadening arises due to (i) instrumental effects and (ii) microstructural effects of the sample under investigation. For extracting the sample effects (crystallite size and microstrain due to lattice imperfections) the analysis and quantification of XRD line broadening due to the sample are essential. The accuracy of size-strain parameters (sample effects) is strongly dependent on the correction applied for instrumental effects. To deconvolve these two effects, it is necessary to have proper knowledge/details of the instrumental peak profile function such as the peak shape and its tails (Langford, 1992). The Rietveld refinement method is commonly used for size-strain analysis of materials as a non-destructive technique (Balzar *et al.*, 2004; Rai *et al.*, 2004). In this work line profile analysis (peak shapes and tails) of different samples is used to explain the origin of size-strain values obtained from the Rietveld refinement. To reduce the possible systematic errors and their propagation during the deconvolution process, the Rietveld method is used and instrument effects are corrected with caution (Balzar *et al.*, 2004; Rodríguez-Carvajal & Roisnel, 2004). The origin of profile parameters of microstructural importance obtained by the Rietveld refinement process of PMN samples is explained by physical parameters of interest. In the Rietveld method XRD peak positions are constrained by lattice constants and relative peak intensity ratios (RIRs) are obtained by atom

types and their positions in the unit cell. Thus, for a multi-phase system with a severe degree of overlap of XRD peaks, as in the present situation, the most appropriate choice for microstructural analysis is the Rietveld method for reliable results. The synchrotron XRD data are extremely useful in this case due to enhanced signal-to-noise ratio (Bhakar *et al.*, 2016).

The Rietveld method is used for the quantification of the polar $R3m$ and paraelectric cubic $Pm\bar{3}m$ phases in PMN samples prepared under different processing conditions. The sample processing parameters chosen in this study are hot-pressing and sintering of calcined powder at different temperatures followed by grinding and post-annealing. These parameters strongly influence the XRD peak profile of PMN samples. Thus isotropic microstructural analysis is combined with the Rietveld refinement approach to extract the processing-parameter-dependent size-strain information from these PMN samples. In the present study the line profile broadening analysis is used to explicitly prove that the polar $R3m$ phase consists of nano-sized crystalline domains (PNRs). The XRD peaks corresponding to the unit-cell doubling due to CORs (Husson *et al.*, 1988; Chen *et al.*, 1989; Hilton *et al.*, 1990; Boulesteix *et al.*, 1994; Yoshida *et al.*, 1998; Xu *et al.*, 2000) are not discernible within the detection limit of synchrotron XRD measurement of different PMN samples; thus the $Fm\bar{3}m$ phase corresponding to CORs is excluded in this study.

2. Experimental

2.1. Sample preparation and characterization methods

The PMN sample in powder form was prepared using the columbite method at 800°C (Swartz & Shrout, 1982), using high-purity (>99.9%) Alfa Aesar chemicals. This calcined powder was hot-pressed at 110 MPa to form pellets at 800 and 1000°C for 2 h. The small amount of calcined powder and small pieces of hot-pressed pellets were ground gently in an agate mortar-pestle to form uniform powder samples. Ground samples were annealed at 600°C for 4 h to remove the strain generated during grinding. These samples are abbreviated as 800CP for PMN powder calcined at 800°C, 800HP and 1000HP for PMN samples hot-pressed at 800 and 1000°C, respectively. These powder samples were filled in capillaries of 0.1 mm diameter (boron glass, Charles Supper, USA) and rotated during XRD measurements. The powder XRD measurements were carried out at $\lambda \sim 0.695 \text{ \AA}$ on a two-dimensional MAR345dtb image plate installed at the angle-dispersive X-ray diffraction beamline of the Indus-2 synchrotron source (Sinha *et al.*, 2013). Details of the diffraction geometry, image-plate calibration strategy using NIST SRM LaB₆ 660b and the *Fit2D* program (Hammersley *et al.*, 1995), polarization and absorption correction were reported earlier (Bhakar *et al.*, 2016).

2.2. Rietveld refinement approach/strategy for microstructural analysis

The line widths of Bragg peaks of an XRD pattern have contributions from the measuring instrument and the sample. For microstructural analysis of a sample, it is essential to deconvolute the effect of instrumental (intrinsic) broadening from the observed XRD peak profile of the sample. *FullProf* software (Rodríguez-Carvajal, 1993) was used for the Rietveld refinement of synchrotron powder XRD data of all PMN samples using the Thompson–Cox–Hastings (TCH) peak profile function (Thompson *et al.*, 1987; Finger *et al.*, 1994). It is imperative to use an external instrument resolution file (IRF) for extracting microstructural information from a sample. For this purpose an IRF was prepared by fitting the XRD data of NIST SRM LaB₆ 660b. The methodologies of extracting microstructural (size–strain) parameters of a sample using the Rietveld method by *FullProf* software are reported by Rodríguez-Carvajal & Roisnel (2004). The expressions for Gaussian (H_G) and Lorentzian (H_L) contributions to the full width at half-maxima (FWHM) of the observed line profile are

$$H_G^2 = U \tan^2 \theta + V \tan \theta + W + \frac{I_G}{\cos^2 \theta} \quad (1a)$$

$$H_L = X \tan \theta + \frac{Y}{\cos \theta}. \quad (1b)$$

Here U , V , W , I_G , X and Y are refinable parameters of FWHM. The parameters I_G and Y describe the Gaussian and Lorentzian contributions of isotropic size broadening, and the parameters U and X describe the Gaussian and Lorentzian contributions of isotropic microstrain broadening, respectively. The brief mathematical procedure for isotropic size–strain analysis is given in Appendix A. Because of the different angular dependence of microstructural parameters (*i.e.* $1/\cos \theta$ for isotropic size and $\tan \theta$ for microstrain) on the FWHM of diffraction peaks, it is possible to separate the size and strain contributions. Fig. 1 shows the angular dependence of size and strain parameters on the variation of FWHM, from which it is clear that the size contribution to peak widths is almost

Figure 1

Angular dependency of FWHM on size and strain parameters also known as a Williamson–Hall plot. For better visualization the size parameter is multiplied by a constant 0.1 to have an equal value of the FWHM contribution from both size and strain parameters at $\sim 6^\circ$.

constant while the strain contribution to peak widths increases sharply with increasing angle.

For IRF construction, the occupancy of La and B in LaB₆ is kept fixed at nominal composition values and all other parameters, *i.e.* scale factor, instrument zero correction, peak profile half-width parameters (U , V , W , X and Y), asymmetry parameters, atomic positional coordinate of boron and isotropic atomic displacement parameters (ADPs), are refined. The details of the procedure adopted for the Rietveld refinement and the Wyckoff positions considered for two phases of all PMN samples are the same as reported earlier (Bhakar *et al.*, 2016). Except for ‘ z ’ positions of Pb²⁺ ions of the $R3m$ phase, all other atomic positions of these two phases ($Pm\bar{3}m$ and $R3m$) are kept fixed as reported in earlier work. During multi-phase Rietveld refinement of all PMN samples using external IRF, asymmetry parameter values are kept fixed and are the same as those obtained by refining SRM LaB₆ XRD data; all other parameters are refined. For estimating the size and/or strain contribution of PMN samples

Figure 2

FWHM comparison of the (331) Bragg peak of SRM LaB₆ 660b with the pseudo-cubic (330)–(411)_c Bragg peak of different PMN samples. The subscript ‘ c ’ specifies that the indexing of Bragg peaks of PMN is carried out using cubic symmetry.

prepared under different processing conditions, all microstructural parameters (Gaussian: U , I_G ; Lorentzian: X , Y) of the two phases ($Pm\bar{3}m$ and $R3m$) are refined independently and their possible combinations are tried simultaneously as advised by Balzar *et al.* (2004). The ADP (B_{iso}) values of Mg^{2+} / Nb^{5+} and O^{2-} ions are constrained to be equal for the two phases ($Pm\bar{3}m$ and $R3m$), respectively, because their values are not significantly different for XRD data (de Mathan, Husson, Calvarn, Gavarrì *et al.*, 1991; Bhakar *et al.*, 2016).

3. Results

3.1. X-ray diffraction line profile

The line shape broadening of room-temperature synchrotron powder XRD patterns of all PMN samples are compared with LaB_6 (660b) standard sample measured under similar conditions. The Bragg peak position of the (331) peak of LaB_6 standard almost coincides with the pseudo-cubic (330)–(411)_c

Figure 3
FWHM comparison of various Bragg peaks of PMN 800CP and PMN 800HP samples.

Bragg peak of PMN samples and is shown in Figs. 2(a)–2(c). The PMN sample that has already been reported by Bhakar *et al.* (2016) (here abbreviated as 1200SP for a PMN sample sintered at 1200°C) is included in Fig. 2(d) for the purpose of comparison. It is clear from Fig. 2 that the Bragg peaks of PMN samples are broader than those of LaB_6 and their difference is called additional peak broadening due to the microstructural effects of the sample. The XRD peak profile broadening of PMN samples strongly depends on the processing conditions. This shows that the processing parameters dependent microstructural contribution is present in all samples. In order to account for the difference in line profile shape/broadening of PMN samples arising due to sample preparation conditions, comparison of three Bragg peaks of two PMN samples 800CP and 800HP across the XRD

Figure 4
Three-phase Rietveld refinement fitting of PMN XRD data of 800CP, 800HP and 1000HP samples with (a), (b), (c) IRF for three phases. Insets show the fitting of (110)_c, (321)_c and (420)_c Bragg peaks. Here, red circles represent the synchrotron powder XRD data, black and blue lines represent the fitted curve and difference curve, respectively. The upper, middle and lower green vertical ticks correspond to the Bragg positions of the $Pm\bar{3}m$, $R3m$ and pyrochlore ($Fd\bar{3}m$) phases, respectively.

pattern is shown in Fig. 3 for convenience. The intensities of XRD patterns of these two samples are normalized with respect to their 100% Bragg peak $(110)_c$. It is observed that the FWHM values of these two samples are nearly the same at lower 2θ values, whereas the FWHM of the 800HP sample increases with increasing scattering angle. The RIRs of both samples are almost the same, whereas the relative peak height of the 800HP sample decreases compared with the 800CP sample with increasing angle.

3.2. Microstructural parameter determination using the Rietveld method

The pseudo-cubic Bragg peaks $(320)_c$, $(322)_c$ – $(410)_c$, $(331)_c$ and $(421)_c$ of PMN XRD patterns which are reported to be extinct up to -268°C in laboratory sources by Bonneau *et al.*

(1989, 1991) are clearly discernible in the room-temperature synchrotron XRD data of all PMN samples. This gives assurance that the quality of the synchrotron powder XRD patterns of these PMN samples is better than that of laboratory-source X-ray data (Bhakar *et al.*, 2016). Thus, these XRD patterns are suitable for multi-phase Rietveld refinement and reliable atomic and microstructural analysis.

Now, it is well established that at room temperature both polar rhombohedral ($R3m$) and paraelectric cubic ($Pm\bar{3}m$) phases coexist in perovskite PMN. Initially all FWHM parameters of both phases are kept at zero to check the difference between the IRF and observed XRD data of PMN samples, and fitted patterns are shown in Figs. 4(a)–4(c). The insets of

Figure 5
Three-phase Rietveld refinement fitting of PMN XRD data of 800CP, 800HP and 1000HP samples with (a), (b), (c) the Gaussian size contribution to the $R3m$ phase only and IRF for the $Pm\bar{3}m$ and $Fd\bar{3}m$ phases. Insets show the fitting of $(110)_c$, $(321)_c$ and $(420)_c$ Bragg peaks. Here, red circles represent the synchrotron powder XRD data, black and blue lines represent the fitted curve and difference curve, respectively. The upper, middle and lower green vertical ticks correspond to the Bragg positions of the $Pm\bar{3}m$, $R3m$ and pyrochlore ($Fd\bar{3}m$) phases, respectively.

Figure 6
Three-phase Rietveld refinement fitting of PMN XRD data of 800CP, 800HP and 1000HP samples with (a), (b), (c) the Gaussian size contribution to the $R3m$ phase, strain contribution to the $Pm\bar{3}m$ phase and IRF for the $Fd\bar{3}m$ phase. Insets show the fitting of $(110)_c$, $(321)_c$ and $(420)_c$ Bragg peaks. Here, red circles represent the synchrotron powder XRD data, black and blue lines represent the fitted curve and difference curve, respectively. The upper, middle and lower green vertical ticks correspond to the Bragg positions of the $Pm\bar{3}m$, $R3m$ and pyrochlore ($Fd\bar{3}m$) phases, respectively.

Table 1

Rietveld refinement parameters obtained with multi-phase fitting of PMN samples.

Numbers in parentheses show the standard uncertainty of refinement. Parameters without parentheses are optimized and kept fixed during final refinement.

Parameters	PMN 800CP	PMN 800HP	PMN 1000HP
<i>Pm</i> $\bar{3}m$ phase			
Lattice constant ($\text{\AA}$)	4.04774 (13)	4.04809 (16)	4.04776 (13)
ADP of Pb^{2+} ($\text{\AA}^2$) ions	4.22 (3)	4.23 (5)	4.44 (3)
ADP of $\text{Mg}^{2+}/\text{Nb}^{5+}$ ($\text{\AA}^2$) ions†	1.21 (6)	1.21 (8)	1.19 (4)
ADP of O^{2-} ($\text{\AA}^2$) ions†	2.8 (1)	2.9 (2)	3.1 (9)
X , U	0.058 (2), 0	0.145 (3), 0.02	0.180 (2), 0.01
Average maximum strain (%)	0.04	0.14	0.145
<i>R</i> 3 <i>m</i> phase			
Lattice constant ($\text{\AA}$)	5.72, 7.027	5.72, 7.03	5.72, 7.026
ADP of Pb^{2+} ($\text{\AA}^2$) ions‡	2.90	2.55	2.72
Fractional coordinate of Pb^{2+} ions	−0.035 (7)	−0.029 (9)	−0.035 (4)
I_G	0.08979	0.09838	0.1025
D_V (nm)	~12.5	~12	~11.7
Wt% of phase	8–10	9–12	11–16
Pyrochlore (<i>Fd</i> $\bar{3}m$) phase			
Wt% of phase	~1.4	~1.4	~0.3
Conventional Rietveld			
R factors			
R_p (%), R_{wp} (%), χ^2	5.47, 3.88, 0.195	6.85, 5.27, 0.207	6.78, 5.65, 0.837

† These ADP values are constrained to be the same for *Pm* $\bar{3}m$ and *R*3*m* phases. ‡ During the Rietveld refinement the ADP values of Pb^{2+} ions of the *R*3*m* phase are found to oscillate between 2.4 and 2.9.

Fig. 4 show the three Bragg peaks across the XRD patterns for clarity. The mismatch between the observed and instrument peak profile patterns [blue line at the bottom of Figs. 4(a)–4(c)] indicates the microstructural contribution arising due to PMN samples. From the literature, it is clear that the two-phase Rietveld refinement of PMN samples gives a significantly larger value of FWHM parameters for the *R*3*m* phase than for the *Pm* $\bar{3}m$ phase (de Mathan, Husson, Calvarin, Gavarrri *et al.*, 1991; Bhakar *et al.*, 2016), which is relevant in the present study too. It seems that the size and/or strain broadening are primarily associated with the *R*3*m* phase, because the larger values of the FWHM parameters are associated with this phase. Therefore, the microstructural parameters of the *R*3*m* phase are refined first.

3.2.1. Microstructural parameters of the *R*3*m* phase. As per the literature the PNRs of the *R*3*m* phase are dispersed in the paraelectric *Pm* $\bar{3}m$ phase of PMN (de Mathan, Husson, Calvarin & Morell, 1991; de Mathan, Husson, Calvarin, Gavarrri *et al.*, 1991; Yoshida *et al.*, 1998; Jeong *et al.*, 2005; Fu *et al.*, 2009, 2012). Thus isotropic size parameters of the polar *R*3*m* phase are refined first. It is found that independent refinement of either the Gaussian (I_G) or Lorentzian (Y) isotropic size broadening parameter gives an apparent volume-average crystallite size (D_V) of ~12 nm for all PMN samples. Varying both size parameters (I_G and Y) simultaneously leads to little reduction in crystallite size but the value of Y is ~0. Likewise, when all size–strain parameters of the

*R*3*m* phase are refined simultaneously, the Lorentzian size (Y) and strain (X) parameter values are close to zero and the Gaussian strain (U) parameter value is negative for all PMN samples. Thus only the Gaussian component (I_G) of the isotropic size parameter is refined and other parameters are fixed at zero [*i.e.* instrument values as per Rodríguez-Carvajal & Roisnel (2004)] as advised by Balzar *et al.* (2004). This implies that the microstrain components associated with the rhombohedral phase are negligible, which is consistent with earlier results (Carpenter *et al.*, 2012). It is also evident from Figs. 5(a)–5(c) that the microstructural (size) contribution of the *R*3*m* phase alone is inadequate to fit the observed XRD patterns satisfactorily and additional peak broadening is not accounted for properly. This is probably due to the smaller weight% of the *R*3*m* phase in PMN samples and it contributes mainly to improving the XRD peak shape near the tails. Therefore microstructural parameters of the *Pm* $\bar{3}m$ phase are also refined with the Gaussian size parameter of the *R*3*m* phase.

3.2.2. Microstructural parameters of the *Pm* $\bar{3}m$ phase. Initially, the Gaussian (I_G , U) and Lorentzian (Y , X) components of the size and strain parameters of the *Pm* $\bar{3}m$ phase are refined independently. It is observed that refining only the Lorentzian component ' X ' of the microstrain broadening gives far better fitting to the observed XRD patterns of all PMN samples compared with the individual refinement of the other microstructural components and leads to a significant reduction in the χ^2 value. This indicates that a major contribution to XRD line broadening in the *Pm* $\bar{3}m$ phase is due to Lorentzian strain. When a combination of microstructural parameters is tried it is found that isotropic size parameters (I_G , Y) are close to zero and have an insignificant effect on improvement of refinement for all PMN samples. Therefore these parameters are kept at zero. It is possible only to refine strain parameters in the *Pm* $\bar{3}m$ phase and the results of final refinements are shown in Figs. 6(a)–6(c). In the case of PMN 800CP, it is not possible to refine the Gaussian component of isotropic strain parameters (U), whereas in the case of PMN 800HP and 1000HP this parameter is also required to be refined for better fitting. This process influences the I_G parameter of the *R*3*m* phase. Therefore this parameter value is constrained to be fixed (I_G) as per §3.2.1, while refining the microstructural parameters of the *Pm* $\bar{3}m$ phase. A small fraction of pyrochlore phase ($\text{Pb}_{1.86}\text{Mg}_{0.24}\text{Nb}_{1.76}\text{O}_{6.5}$) is also observed in the three samples of PMN, which is also fitted using the IRF with the *Fd* $\bar{3}m$ phase (Wakiya *et al.*, 1993) during the Rietveld refinement to have a reliable estimate of its phase fraction. The estimated volume-average crystallite size and phase fraction of the *R*3*m* phase, apparent strain (maximum) of the *Pm* $\bar{3}m$ phase as well as the phase fraction of the pyrochlore phase along with important structural parameters are listed in Table 1 for all PMN samples. The size–strain error estimation procedure and other details are given in Appendix A. Similarly, the microstructural analysis of PMN 1200SP is carried out, which gives an average maximum microstrain of 0.085% and estimated average coherently diffracting crystallite size (D_V) of ~13.4 nm.

4. Discussion

The comparison of observed XRD data with the only IRF contribution of the two phases ($Pm\bar{3}m$ and $R3m$) of perovskite PMN shows that the values of the agreement factor R_{wp} for hot-pressed samples are almost double those of the calcined sample, indicating smaller additional peak broadening due to microstructural effects and hence better fitting for the 800CP sample. This is obvious because the FWHM of the 800CP sample is close to that of the SRM LaB_6 sample compared with the hot-pressed samples (800HP and 1000HP), clearly visible from Fig. 2 and the insets of Figs. 4(a)–4(c).

The average apparent crystallite size (D_v) of the polar $R3m$ phase is estimated in the nanometre range ($\sim 12 \pm 1.4$ nm) using synchrotron powder XRD data and the Rietveld method, which gives unequivocal evidence that this polar $R3m$ phase consists of PNRs. This result is consistent with earlier reports (Yoshida *et al.*, 1998; Fu *et al.*, 2009, 2012), which also estimate the domain size of PNRs ($R3m$ phase) to be ~ 10 nm at room temperature, using TEM. Balzar *et al.* (2004) have performed a round-robin test on ceria samples using various X-ray and neutron diffractometers having wide variation in their IRF. It is found that the estimation of coherently diffracting domains of size (D_v) up to ~ 25 nm is independent of IRF, which assures us that the present results are reliable. As listed in Table 1, the average apparent crystallite size (D_v) of the $R3m$ phase is approximately the same for all PMN samples. This can be explained by using the angle-independent behaviour of the size parameter of the FWHM shown in Fig. 1, as the FWHM values of Bragg peaks at the lower 2θ angles for all PMN samples are nearly the same as seen from the $(110)_c$ peak in Fig. 3 for PMN 800CP and 800HP samples. Thus the apparent crystallite sizes for these samples are quite close within the evaluation limit of XRD data (Cullity & Stock, 2001).

During the Rietveld refinement, it is possible to refine mainly the Gaussian component (I_G) of size broadening of the $R3m$ phase. This can be understood as follows: at room temperature the PNRs of the $R3m$ phase of PMN are reported to be predominantly spherical in shape with a narrow size distribution (de Mathan, Husson, Calvarin, Gavarrri *et al.*, 1991; Yoshida *et al.*, 1998; Jeong *et al.*, 2005; Fu *et al.*, 2009, 2012). The spherical crystallites yield isotropic (direction-independent) line broadening of diffraction peaks and their narrow size distribution leads to a Gaussian contribution, which is found to be reasonable in the present study (Langford, 1992; Balzar *et al.*, 2004). For tungsten filings Langford (1992) has demonstrated that the line profile due to crystallite size is largely Gaussian in character and is purely Lorentzian for lattice distortion using a Voigt model. The weight percentage of PNRs increases from ~ 8 –10% for PMN 800CP, to ~ 9 –12% for PMN 800HP and ~ 11 –16% for PMN 1000HP samples. The change in phase percentage of PNRs at room temperature with processing parameters is consistent with reported results, where single crystals and ceramics are analysed using different experimental techniques (Jeong *et al.*, 2005; Fu *et al.*, 2009, 2012; Bhakar *et al.*, 2016).

During Rietveld fitting, it is observed that only strain parameters of the $Pm\bar{3}m$ phase are sufficient to account for the additional peak broadening of all XRD patterns. This indicates that in the $Pm\bar{3}m$ phase the major contribution to XRD line broadening is due to strain, as expected. From Figs. 4(a)–4(c) and 5(a)–5(c), it is clear that the FWHMs of these PMN samples increase with increasing scattering angle compared with the IRF, which is consistent with the effect of strain from Fig. 1. Thus, on refinement of strain parameters of the $Pm\bar{3}m$ phase significant improvement in the fitting of XRD patterns of PMN samples is observed as shown in Figs. 6(a), 6(b) and 6(c). In the case of the calcined sample of PMN (800CP) a relatively smaller additional broadening of XRD peaks is observed compared with intrinsic (LaB_6) broadening as seen from Fig. 2(a) and the insets of Figs. 4(a) and 5(a). This broadening lies only at the tails, *i.e.* is Lorentzian in nature. This explains why only a Lorentzian strain value is sufficient to account for this broadening for the 800CP sample. Similarly, from Figs. 2(b)–2(d), Fig. 3 and the insets of Figs. 4(b), 5(b), 4(c), 5(c) it is clear that larger values of strain for hot-pressed samples and intermediate strain values for sintered samples are expected compared with the calcined one (see Table 1).

From Fig. 3, it is clear that broadening (Lorentzian) of the FWHM of XRD peaks of the PMN 800HP sample is a dominant feature, which implies this feature is associated at least with the major phase ($Pm\bar{3}m$) of PMN, which is clearly evident from the findings of the present study. The refined isotropic size broadening parameters of the $Pm\bar{3}m$ phase are almost zero (insignificant), indicating that no size broadening effect is associated with this phase. It is obvious, as the size effects of $Pm\bar{3}m$ as the major phase (85–90%) would have significantly broadened the lower 2θ angle XRD peak of PMN samples compared with the IRF as per Fig. 1, which is not the case as seen from the $(110)_c$ XRD peak of the insets of Figs. 4(a)–4(c).

The values of the ADPs of the two phases ($Pm\bar{3}m$ and $R3m$) of all PMN samples are fairly similar, indicating that the RIRs of their XRD peaks are similar and almost independent of sample processing conditions. This is consistent with the observed RIR trend for PMN 800CP and PMN 800HP samples, as discussed in §3.1. This is expected also because RIRs in an XRD pattern are temperature dependent (Kittel, 2008), whereas all the XRD measurements are carried out at the same (room) temperature. The lattice parameters and ADPs of all atoms of both the phases of PMN samples match well the values in the literature (Bonneau *et al.*, 1989, 1991; Verbaere *et al.*, 1992; Thomas *et al.*, 1999; Ye *et al.*, 2003; Jeong *et al.*, 2005; Paściak *et al.*, 2012; Bhakar *et al.*, 2016). A little scatter in the ADP and 'z' parameter values (within standard uncertainty values) of Pb^{2+} ions of the $R3m$ phase in all the PMN samples is observed. This is probably due to strongly overlapping Bragg peaks of the two phases where RIRs are dominated by the major phase (cubic). The smaller phase fraction and correlation between 'z' positions and the ADP of Pb^{2+} ions of the $R3m$ phase further complicate their estimation. For such an exacting situation synchrotron data are necessary. The weight percentage of the pyrochlore phase

vanishes with increasing temperature. An attempt to constrain the same values of isotropic microstrain parameters for both phases ($Pm\bar{3}m$ and $R3m$) of perovskite PMN does not lead to any observable change in the Rietveld fitting of XRD patterns of PMN samples. Thus it could be convincingly concluded that the processing parameters (hot-pressing and sintering of calcined powder at different temperatures followed by grinding and post-annealing) of PMN mainly affect the microstrain of the major phase ($Pm\bar{3}m$) and weight percentage of minor phases.

5. Conclusions

The isotropic size-strain line broadening of synchrotron powder XRD patterns of PMN samples are analysed using the Rietveld method. The results of the Rietveld refinements are explained by using the simple angular dependence of the FWHM on size and strain parameters. It is demonstrated that the $R3m$ phase consists of PNRs and their coherently diffracting domain size is nearly the same for all the samples synthesized using different processing conditions. The average weight percentage of PNRs shows an increasing trend with the temperature of synthesis. The value of the apparent maximum strain of the paraelectric phase ($Pm\bar{3}m$) is found to be strongly dependent on the processing conditions. In conclusion, it has been demonstrated that a simple tool of XRD with an isotropic size-strain model combined with the Rietveld method is good enough to determine/estimate the apparent crystallite size of PNRs in relaxor PMN samples having a significant degree of overlapping Bragg peaks.

APPENDIX A

Mathematical procedure for isotropic size-strain analysis and error estimation

In *FullProf* the integral breadth method is employed to deal with the microstructural effects and the pseudo-Voigt (pV) peak profile function is used as an approximation to mimic the Voigt function (*FullProf* Manual, July 2001, <https://www.psi.ch/sinq/dmc/ManualsEN/fullprof.pdf>). A pseudo-Voigt function is defined as a linear combination of Lorentzian (L) and Gaussian (G) functions with the same FWHM (H). The integral breadth (degrees) of a normalized pV function is

$$\beta_{pV} = \frac{\Pi H/2}{\eta + (1 - \eta)(\Pi \ln 2)^{1/2}}, \quad (2)$$

where η represents the fraction of the Lorentzian contribution and $0 \leq \eta \leq 1$. Instead of using η and H in the refinement procedure, it is advantageous to use the TCH pseudo-Voigt peak profile function, i.e. H_G and H_L as per equations (1a) and (1b) because the latter can be simply related to parameters (size-strain) of physical importance (Thompson *et al.*, 1987). The numerical approximations relating the pairs (η , H) and (H_G , H_L) given by Thompson *et al.* (1987) are

$$H^5 = H_G^5 + 2.69269H_G^4H_L + 2.42843H_G^3H_L^2 + 4.47163H_G^2H_L^3 + 0.07842H_GH_L^4 + H_L^5 \quad (3)$$

$$\eta = 1.36603 \frac{H_L}{H} - 0.47719 \left(\frac{H_L}{H} \right)^2 + 0.11116 \left(\frac{H_L}{H} \right)^3. \quad (4)$$

From the Scherrer formula the expression for estimation of apparent crystallite size D_V considering both Lorentzian and Gaussian contributions is

$$D_V = \frac{\lambda}{\beta_{pV}(sz) \cos \theta} \frac{180}{\Pi} = \frac{\eta + (1 - \eta)(\Pi \ln 2)^{1/2}}{\Pi H_{sz}/2} \frac{180\lambda}{\Pi \cos \theta}. \quad (5a)$$

A factor of $\Pi/180$ is used to transform degrees to radians and 'sz' stands for size contribution. If only Gaussian size broadening is present (as found in the $R3m$ phase of PMN of the present study) then $H_{L(sZ)} = 0$ ($\eta = 0$) and equation (3) becomes $H_{sz} = H_G = (I_G)^{1/2} / \cos \theta$; substituting this value in equation (5a) gives for the apparent Gaussian size

$$D_{VG} = \left(\frac{\Pi \ln 2}{I_G} \right)^{1/2} \frac{360\lambda}{\Pi^2} \quad (5b)$$

and for $H_{G(sZ)} = 0$ ($\eta = 1$) the apparent Lorentzian size is

$$D_{VL} = \frac{360\lambda}{Y\Pi^2}. \quad (5c)$$

Similarly, the expression for the so-called maximum strain ε [defined as $\frac{1}{4}$ of the apparent strain 'eta' defined by Stokes & Wilson (1944)] considering both Lorentzian and Gaussian contributions is

$$\varepsilon = \frac{1}{4 \tan \theta} \beta_{pV}(st) = \frac{1}{4 \tan \theta} \frac{\Pi H_{st}/2}{\eta + (1 - \eta)(\Pi \ln 2)^{1/2}} \frac{\Pi}{180}, \quad (6a)$$

where 'st' stands for microstrain contribution and a factor of $\Pi/180$ is used to transform degrees to radians. Under two extreme conditions ($\eta = 0, 1$) equation (6a) reduces to

$$\varepsilon_G = \frac{1}{4} \left(\frac{\Pi U}{\ln 2} \right)^{1/2} \frac{\Pi}{360} \quad (6b)$$

and

$$\varepsilon_L = \frac{1}{4} \frac{\Pi^2 X}{360}. \quad (6c)$$

From equations (5b), (5c) and (6b), (6c), it is clear that I_G , Y , U and X are directly related to microstructural parameters.

The apparent crystallite size and average maximum microstrain values are obtained with standard deviations in the microstructural file using the *FullProf* package. This standard deviation is a measure of the degree of anisotropy, not of the estimated errors (*FullProf* Manual, July 2001, <https://www.psi.ch/sinq/dmc/ManualsEN/fullprof.pdf>). Thus, the standard deviation in I_G (Y) is used to estimate the error in apparent crystallite size (average microstrain) of the $R3m$ ($Pm\bar{3}m$) phase of PMN. Using equations (5b) and (6c) the error estimations in apparent Gaussian size and average maximum microstrain are given as follows:

$$\frac{\Delta D_{VG}}{D_{VG}} = \pm \left| \frac{1}{2} \frac{\Delta I_G}{I_G} \right| \quad (7)$$

and

$$\Delta \varepsilon_L = \pm \left| \frac{1}{4} \frac{\Pi^2 \Delta X}{360} \right|. \quad (8)$$

As the value of I_G is kept fixed in the final steps while refining microstrain components of the $Pm\bar{3}m$ phase of PMN, the quoted error estimation in apparent size is based on the standard deviation in I_G ($\Delta I_G \sim 0.02$) obtained in the final refinement of the $R3m$ phase. This will lead to an average apparent crystallite size variation of $\sim(12 \pm 1.4)$ nm. Similarly, using values of X and ΔX from Table 1, equations (6c) and (8) lead to an average microstrain value $\sim 4 \times 10^{-4}$ and estimated error value $\sim 1.3 \times 10^{-5}$ for PMN 800CP, which is one order of magnitude smaller than the microstrain itself for calcined samples and two orders of magnitude smaller for hot-pressed samples.

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