

Article



Structure and Dynamics of Ferroelectric Domains in Polycrystalline Pb(Fe1/2Nb1/2)O3

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Supplementary Material

Supplement S1. Microstructural Characterisation of PFN Ceramic Samples

The FE-SEM images of the polished and fractured surface reveal dense, homogeneous, and uniform microstructure as shown in Figure S1. No secondary phases were observed, which was additionally confirmed also by STEM/EDXS analysis (Figure S2).



Figure S1. FE-SEM micrographs of (a) polished and (b) fractured surface.



Figure S2. STEM image of grains in PFN sample, sintered at 1000 °C with the corresponding EDXS elemental maps showing chemically homogenous polycrystalline sample without secondary phases.

Supplement S2. Determination of the Phase Composition by Rietveld Refinement

At room temperature, PFN adopts the monoclinic phase with the space group Cm [1–5]. However, some reports also suggest a rhombohedral phase with the space group R3m [6, 7]. One study [8] even considered a tetragonal structure. To clarify which space group PFN prepared in this study adopts, the prepared PFN sample was analysed by Rietveld refinement of the room-temperature XRD data. Along with the monoclinic Cm (ICSD 88357), rhombohedral R3mR (ICSD 90490) and tetragonal P4mm (ICSD 88356) space groups were also considered for the fit.

Rietveld refinement analysis of the diffraction data of our samples was performed with Topas (version 6, Bruker, AXS, Karlsruhe, Germany) software. The fundamental parameters approach [9] was used to describe the peak profiles, while the background was estimated using a 5th order Chebychev polynomial. The sample displacement, lattice parameters, scale factor, background, strain, asymmetry [10], thermal displacement parameters, and atomic coordinates were stepwise refined to obtain a calculated diffraction profile that best-fit the experimental pattern. All the occupancies were fixed at nominal composition and kept constant during refinement. Finally, the quality of the fit was assessed from the fit parameters such as R_{wp} , R_p , R_{exp} , R_B , and G.O.F. [11]. The agreement factors of the Rietveld analysis along with the cell parameters are given in table S1, while the Rietveld fits plotted for the (200), (220), and (222) pseudocubic profiles are shown in Figure S3.

Space Group	Unit Cell Parameters	R_{wp}	Rexp	R_p	G.O.F. (χ²)	RB
Ст	a (Å) = 5.67920(8)					
	b (Å) = 5.67239(9)	6.012	5.528	4.535	1.087	1.373
	c (Å) = 4.01556(5)					
	β (°) = 89.8830(11)					
R3mR	a (Å) = 4.013879(16)	6.933	5.531	5.197	1.253	3 152
	α (°) = 89.9241(3)					5.152
P4mm	a (Å) = 4.01333(2)	7.921	5.530	5.813	1.432	3.751
	c (Å) = 4.01552(7)					

Table S1. Refined structural parameters for PFN using different space groups: Cm, R3mR, and P4mm.



Figure S3. XRD profiles of the (200), (220), and (222) pseudocubic reflections (corresponding only to Cu K α_1) for PFN obtained after Rietveld refinement of the room-temperature XRD data, considering

the (a) Cm, (b) R3mR, and (c) P4mm space groups. The black dots represent the observed data, the red line is the calculated profile, and the grey bottom line is the difference between the calculated and experimental (observed) profiles. The marked 2θ positions show the allowed Bragg peaks.

Looking at Figure S3, it is very easy to exclude the *P4mm* space group since the pseudocubic (222) reflection has to be a singlet for this space group, but in this case it is a doublet. The best agreement factors and matching between the observed and calculated profile were obtained with a monoclinic *Cm* phase with the unit-cell parameters: *a* = 5.67920(8) Å, *b* = 5.67239(9) Å, *c* = 4.01556(5) Å, and β = 89.8830(11)°. The Rietveld refined value for the thermal displacement parameter of Pb was anomalously large (3.03 Å²), but comparable to the values reported by other researchers [3–5]. The reason is probably the presence of displacive disorder on the Pb-site. The whole observed (dots), calculated (red line), and difference (grey bottom line) profiles obtained after Rietveld refinement of PFN using the monoclinic *Cm* space group are shown in Figure S4. A very satisfactory Rietveld fit was also obtained when considering the R3mR space group (Table S1). As shown in Figure S3, it is hard to discern between the Cm and R3mR space groups based only on the Bragg reflections. The only notable difference between the two structures is the (200) reflection, which is a doublet for the *Cm* space group, but a singlet for the *R*3*mR* space group. No obvious splitting of this peak is observed here, but a careful examination of the full width at half maximum (FWHM) of this peak revealed a higher peak width than the (220) and the (222) peaks. This result is not supporting the assumption of (200) being a singlet since the FHWM of this peak does not follow the Caglioti relationship for the 2θ dependence of the peak width [3,12]. Therefore, the unusual broadening of the (200) peak can only be explained by a splitting of two reflections, which is consistent with the Cm space group and excludes the *R*3*mR* space group.



Figure S4. The observed (dots), calculated (red line), and difference (grey bottom line) profiles obtained after Rietveld refinement of PFN using the monoclinic Cm space group. The marked 2θ positions below the profile show the allowed Bragg peaks for Cu K α_1 .

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