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## Combined use of Mössbauer spectroscopy, XPS, HRTEM, dielectric and anelastic spectroscopy for estimating incipient phase separation in lead titanate-based multiferroics

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- XRD pattern and SEM image of the as-calcined powder
- SEM images of the materials microstructures
- An example of the fitting of the XRD patterns
- A typical TEM image of domain boundaries
- Tables listing lattice plane distances obtained from HRTEM and XRD for the PNTF-4 and PNTF-

5 materials



**Fig. S1.** a) Typical XRD patterns showing the effect of calcination time on the phase composition for the sample PNTF-3. The arrows indicate the reduction of the secondary phase amount with increasing calcination time; b) a SEM image of the powder. The white segment represents  $2 \,\mu m$ .



**Fig. S2.** a) SEM image of sample PNT; b)-d) SEM images of samples PNTF-3, PNTF-4 and PNTF-5, respectively. On all images the white segment (approximately of the same length) represents 5 µm.



**Fig. S3.** An example of fitting of the XRD pattern for PNTF-5 material by using Rigaku PDXL software connected to ICDD PDF-2 database (PDF card-01-070-4258). The curve displayed on the bottom graph represents the difference between the experimental and the calculated pattern.



**Fig. S4** a) A typical image of  $90^{0}$  a-a domain boundaries revealed on PNTF-4 material. The inset shows a SAED image taken on this area (the viewing direction is [100]); b) two adjacent grains showing ferroelectric domains with 90 a-a domain boundaries (region A) and  $90^{0}$  a-c domain boundaries (region B).

Table S1. Comparison between the lattice plane distances obtained from HRTEM and XRD for the PNTF-4 material.

	d (200) (Å)	d (110) (Å)	d (111) (Å)
HRTEM	1.92	2.76	2.22
XRD	1.9538	2.7632	2.2881
Diff (%)	1.76	0.1	3.07

Table S2. Comparison between the lattice plane distances obtained from HRTEM and XRD for the PNTF-5 material.

	d (001) (Å)	d (110) (Å)	d (111) (Å)
HRTEM	4.13	2.76	2.29
XRD	4.083	2.7633	2.2884
Diff (%)	1.15	0.1	0.06