

Pressure-induced transformation processes in $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ heavily doped with Nb and Sn

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Perovskite-type (ABO_3) relaxor ferroelectrics and related materials are multifunctional materials due to their remarkably large dielectric permittivity as well as extremely strong piezoelectric, pyroelectric and electro-optic responses near room temperature. The unique properties of relaxors are related to the nanoscale structural inhomogeneities associated in most cases with the presence of substitutional disorder. At ambient conditions, the average structure of relaxors is pseudocubic but rich in dynamical ferroic nanoregions flipping between the possible orientational states. The small size and relatively short live time of these ferroic nanoregions makes it difficult to study the relaxor structure by conventional diffraction analysis. However, synchrotron X-ray diffraction (XRD), in-situ at varying temperatures and pressures, can help to resolve the structural complexity of relaxors, since the variation of these two thermodynamic parameters can reveal the energetically preferred structural nanoclusters existing at ambient conditions. In this regard, *high-pressure* experiments are vital for understanding the nanoscale structure of relaxors.

The objective of this study was to analyse the effect of a third type of B-cation on the pressure-induced structural changes in relaxors by in-situ synchrotron X-ray diffraction applied to heavily Nb- and Sn-doped $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST). The incorporation of Nb into the PST matrix represents the case of isovalent substitution of the ferroelectrically active B-site cation (Nb^{5+} for Ta^{5+}). The

tolerance factor $t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)}$ remains the same ($t = 0.977$) because in 6-fold coordination

$r(\text{Nb}^{5+}) = r(\text{Ta}^{5+}) = 0.64 \text{ \AA}$ and only the effective B^{5+} -cation mass and B^{5+} -O interactions are changed. The incorporation of Sn^{4+} into the PST matrix represents the case of aliovalent B-site substitution, as the Sn^{4+} cations are expected to replace pairs of Sc^{3+} and Ta^{5+} to preserve the overall charge balance. Again, there is no change in tolerance factor because the ionic radius of Sn^{4+} (0.69 Å) is the average of those of Sc^{3+} (0.745 Å) and Ta^{5+} (0.64 Å).

Single crystals of PST heavily doped with Nb and Sn were synthesized by the high temperature solution growth method. Electron microprobe analysis (Cameca microbeam SX100 SEM system) carried out over 100 spatial points yielded chemical compositions of $\text{PbSc}_{0.5}\text{Ta}_{0.36}\text{Nb}_{0.14}\text{O}_3$ and $\text{PbSc}_{0.39}\text{Ta}_{0.39}\text{Sn}_{0.22}\text{O}_3$. The high level of doping allowed us to consider the studied compounds as solid solution members $0.72\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ - $0.28\text{PbSc}_{0.5}\text{Nb}_{0.5}\text{O}_3$ (PSTN) and $0.78\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ - 0.22PbSnO_3 (PSTS), respectively. Synchrotron single-crystal XRD experiments were conducted at the DESY/HASYLAB F1 beamline, using a MarCCD 165 detector, $\lambda = 0.5000 \text{ \AA}$, a sample-to-detector distance of 100 mm, a step width of 0.5° per frame and an exposure time of 120 s. The in-situ high-pressure experiments were carried out with Boehler-Almax diamond anvil cells in a 4:1 methanol-ethanol mixture that ensures hydrostatic conditions up to 9.8 GPa. The ruby photoluminescence line was used to measure the pressure. According to precise p - V data sets previously measured in the laboratory with a Huber four-circle single-crystal diffractometer using by the method of eight-position diffraction beam centring [1], PSTN undergoes a continuous pressure-induced phase transition at $p_c = 2.5 \text{ GPa}$ (0.6 GPa higher than p_c for pure PST), whereas for PSTS the phase transition occurs at 1.3 GPa (0.6 GPa lower than p_c for pure PST). Combined neutron and X-ray diffraction studies on pure PST revealed that the phase transition is associated with a suppression of the intermediate polar order (revealed by the disappearance of X-ray diffuse scattering along $\langle 110 \rangle^*$) and a development of a long-range order of antiphase octahedral tilts, lowering the symmetry of the average structure from cubic to rhombohedral [2], as revealed by the appearance of sharp odd-odd-odd Bragg peaks (indexed in $Fm\bar{3}m$). The synchrotron XRD data (Fig.1.) show that for PSTN the same structural changes occur exactly at p_c , where the cubic metric

is broken. However, the incorporation of Sn^{4+} into the structure of PST shifts the pressure at which long-range octahedral tilt order is detected by XRD to 4.3 GPa, i.e. approximately 3 GPa higher than p_c as determined from the change in the volume compressibility. This is due to the disturbance of the local structure by the incorporation of an aliovalent B-cation [1]. In addition, the XRD patterns of PSTS show that the pressure-induced $\langle 100 \rangle^*$ -XDS (detected also in other B-site chemically disordered relaxors [3]) appears before the odd-odd-odd Bragg peaks and at higher pressures the $\langle 100 \rangle^*$ -XDS weakens while the Bragg reflections become stronger. This result indicates that the pressure-induced $\langle 100 \rangle^*$ -XDS arises from medium-range order of octahedral tilts.

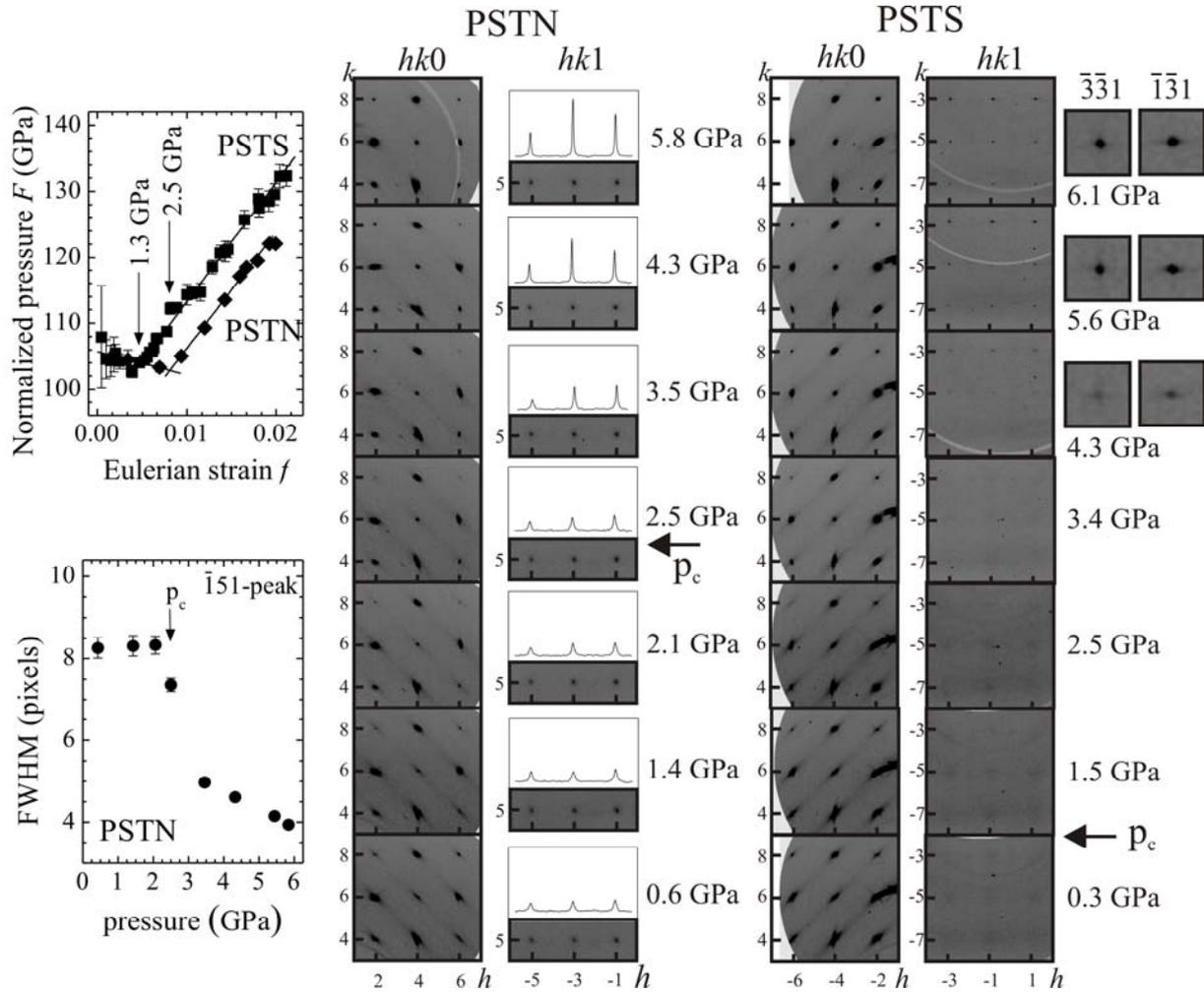


Figure 1: f - F plots [1] and reciprocal-space layers for PSTN and PSTS; for PSTN the pressure dependence of the FWHM of a representative Bragg peak determined by fitting the line profiles with pseudo-Voigt functions is also shown to better demonstrate the development of octahedral tilt order; the broad odd-odd-odd peaks in PSTN below p_c are due to partial 1:1 B-site chemical order, while above p_c they overlap with the sharp peaks arising from the pressure-induced antiphase octahedral tilts

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References

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