# Pressure-induced phase transitions in relaxors $PbSc_{0.5}Ta_{0.5}O_3$ and $PbSc_{0.5}Nb_{0.5}O_3$ up to 30 GPa

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Lead scandium tantalate (PST) and lead scandium niobate (PSN) belong to the class of relaxor-ferroelectric materials with the perovskite-type $ABO_3$ structure. Relaxors are of great interest to the scientific community due to their outstanding dielectric, electroelastic, and electrooptic properties, which are related to their complex local structure comprising dynamic polar nanoregions. Their superior performance is of great technological importance, e.g. for non-volatile memory devices, yet their structure-property relationships are still a matter of debate. High-pressure experiments are of particular importance for the better understanding of the atomistic origin of the unique relaxor properties, as pressure may enhance structural species present at ambient conditions which are not favoured by a temperature decrease. Our previous high-pressure studies on PSN and PST [1] showed that both compounds undergo a pressure-induced continuous cubic-to-rhombohedral phase transition associated with the development of anti-phase octahedral tilts. The critical pressure $p_{c1}$ = 1.9 GPa for PST and $p_{c1}$ = 4.1 GPa for PSN is preceded by an intermediate pressure $p^*$ at which the dynamic coupling between Pb and B-site cations is suppressed, long-range ordered $BO_6$ tilts become detectable by neutron diffraction, and the Pb atomic displacements parameters become anisotropic. For PST the displacement ellipsoids are elongated along the cubic body diagonal, whereas for PSN they are shaped like flattened disks parallel to the cubic {111} plane. The later indicates that the degree of local order of Pb off-centre displacements is higher in PST than in PSN. High-pressure synchrotron single-crystal X-ray diffraction (XRD) experiments were conducted at the beamline F1 of HASYLAB/DESY, using a radiation of wavelength λ = 0.5000 Å and a MarCCD 165 detector. Data were collected at a sample-to-detector distance of 100 mm with a step width of 0.5° and an exposure times per frame of 120 s for PST and 360 s for PSN. Pressure was generated using diamond-anvil cells of the Boehler-Almax design. The ruby-line luminescence method was used to determine the actual pressure values. Helium was used as a pressure-transmitting medium, ensuring hydrostaticity in the entire pressure range of measurements up to 30 GPa. Measurements on decompression verified the reversibility of the observed structural changes. Figure 1 shows reciprocal lattice sections reconstructed in $Fm\bar{3}m$ for PST at different pressures. At 5.0 GPa sharp reflections with *h,k,l*, all odd (*ooo*) (indexed in $Fm\bar{3}m$) arising from antiphase $BO_6$ tilts are superimposed on broad *ooo* reflections originating from nanodomains with 1:1 chemical ordering of the B cations on the octahedral sites. At 7.7 GPa new classes of superstructure reflections are observed, revealing a second pressure-induced phase transition at $p_{c2}$ between 5.0 and 7.7 GPa. The first class has Miller indices of type *h,k,l* with two odd and one even (*ooe*), which is associated with the *M*-point of the primitive cubic structure ($Pm\bar{3}m$). The second class has Miller indices of type *h,k,l* with one odd and two even (*oee*), which are associated with the *X*-point of the primitive cubic structure. The simultaneous appearance of *M*-point and *X*-point reflections may be explained by three types of structural transformations: (i) development of in-phase octahedral tilting (*M*-point mode), which along with the pre-existing anti-phase tilting (corresponding to an *R*-point mode in the primitive cubic cell) further lowers the symmetry and allows additional distortion that would give rise to weak *X*-point reflections; (ii) development of a pattern of anti-polar *A*-cation shifts consistent with an *X*-point mode (e.g. $X^{1+}$ or $X^{5+}$ in Miller-Love notation), which along with the pre-existing anti-phase tilts further lowers the symmetry and allows additional distortions that would produce weak *M*-point reflections; (iii) simultaneous development of both in-phase tilts and an *X*-point pattern of A-cation shifts which are consistent with each other. The intensities of the (*oee*) reflections are much stronger than the intensities of the (*ooe*) reflections. This unambiguously indicates the presence of long-range anti-polar order of the A-site Pb atoms in PST at 7.7 GPa and above. Off-beam Raman spectroscopy performed on the same specimen also indicates that the most pronounced structural change is a rearrangement of the Pb system. The existence of in-phase $BO_6$ tilts could only be confirmed or ruled out by structure refinements but we cannot refine the current dataset because of the oversaturation of the strongest Bragg peaks under experimental conditions needed for the detection of the new peaks. New classes of pressure-induced Bragg peaks were not detected for PSN over the entire pressure range studied (Fig. 2). Therefore, neither long-range order of A-cation antipolar shifts corresponding to X-point modes nor in-phase octahedral tilts are developed up to 28.9 GPa.

All reflections split above 10.1 GPa, which however could result solely from the increasing rhombohedral distortion of the unit cell and the development of the multidomain rhombohedral structure. On the other hand, off-beam Raman spectra of PSN suggest that above 10 GPa the magnitude of the anti-phase tilts along the cubic [100], [010], and [001] become unequal. If the symmetry of the average structure is lowered, reflections of type *e*00 (e.g. 0 10 0, in Fig. 2) would split along the *d*-spacing (the direction to the coordinate origin). Such a splitting of the 0 10 0 reflection may be present at 20.3 GPa (see Fig.2) but due to the insufficient experimental resolution, one cannot definitely state that the symmetry of the average structure is lowered from rhombohedral with a tilt system $a^-a^-a^-$ (Glazer notation) to monoclinic or triclinic, consistent with a tilt system $a^-b^-b^-$ or $a^-b^-c^-$. The difference between the structural states of PST and PSN at very high pressures is most probably related to the degree of local Pb-atom displacive order developed at *p**.

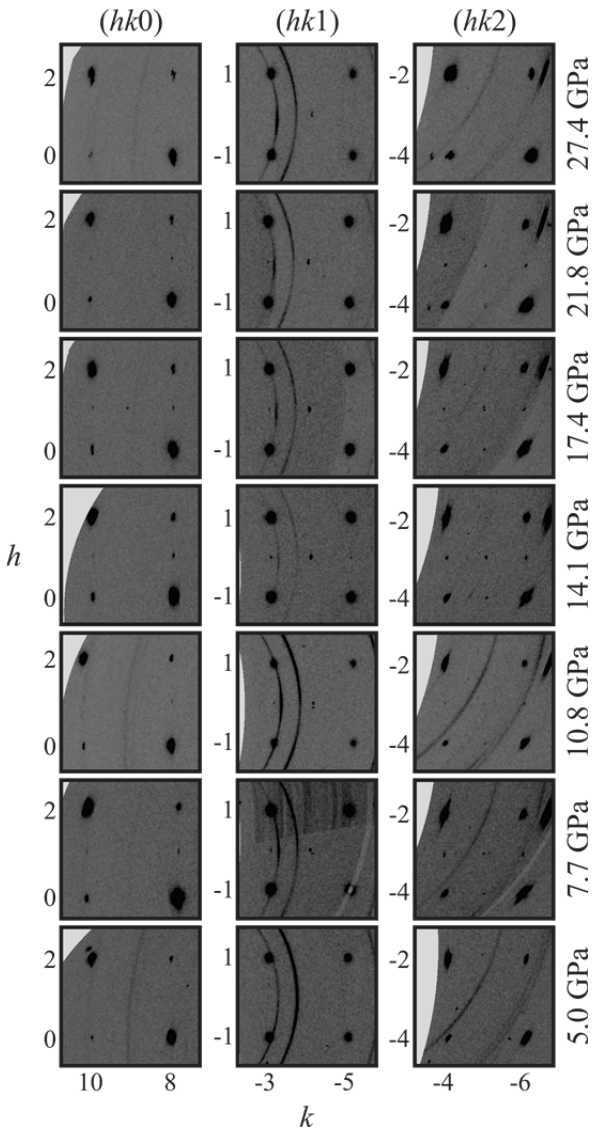


Fig. 1: Reciprocal space layer sections **reconstruc**ted in $Fm\bar{3}m$ from synchrotron XRD data on PST at different pressures.

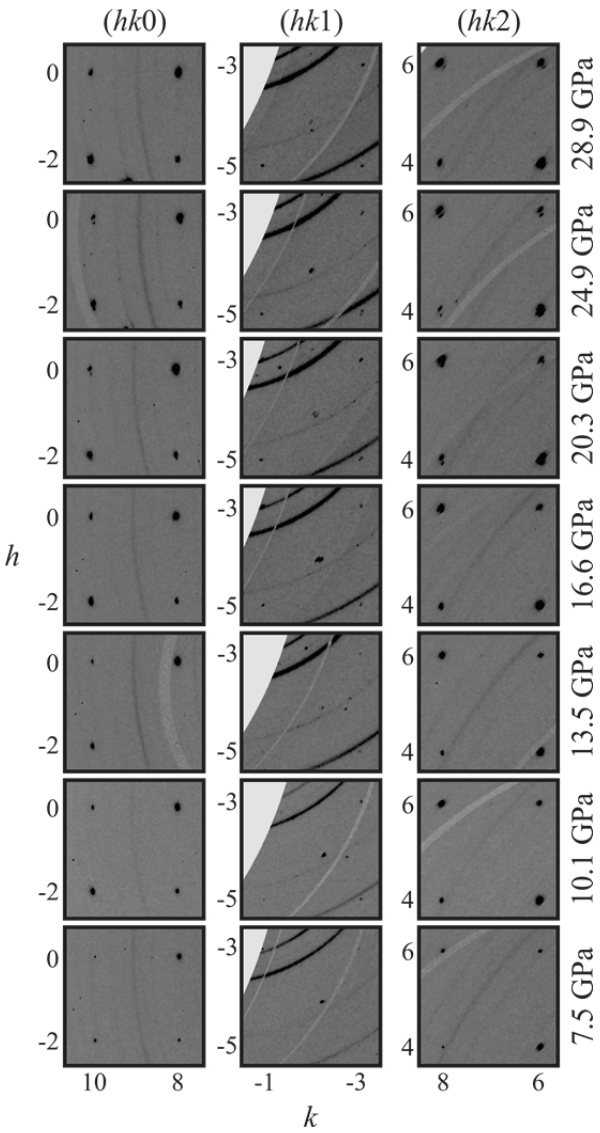


Fig. 2: Reciprocal space layer sections reconstructed in $Fm\bar{3}m$ from synchrotron XRD data on PSN at different pressures.

**Acknowledgements:** Financial support by the DFG (MI 1127/2-2, INST 152/526-1) and NSF (EAR-0738692) is gratefully acknowledged.

**References**

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