High-pressure structural state of La-doped $PbSc_{0.5}Ta_{0.5}O_3$ and $PbSc_{0.5}Nb_{0.5}O_3$ relaxor ferroelectrics

B.J. Maier, R.J. Angel[1], B. Mihailova, J. Engel[2], A.-M. Welsch, C. Paulmann, M. Gospodinov[3], and U. Bismayer

Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, 20146 Hamburg, Germany

[1]Virginia Tech Crystallography Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24060, USA

[2]Institut für Werkstoffwissenschaften, Technische Universität Dresden, Helmholtzstr. 7, 01069 Dresden, Germany

[3]Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Tzarigradsko Chausse 72, 1784 Sofia, Bulgaria

Relaxor ferroelectric materials of the perovskite structure type (ABO_3) are key functional materials. Their structure is strongly inhomogeneous, with co-existing polar and non-polar spatial nano-regions, which give rise to remarkably high dielectric, piezoelectric, electro-elastic and electro-optic responses near room temperature. B-site complex relaxors are additionally characterized with a coexistence of B-site chemically ordered and disordered nanoregions, as the chemical order consists of 1:1 alternation of different types of B-cations along the pseudocubic $\langle 100 \rangle$ direction. Although relaxors have been extensively studied over last two decades, the interplay between the chemical disorder, the nanoscale structural features and, correspondingly, the relaxor macroproperties still remains an enigma. Pressure can help to elucidate the structural complexity of relaxors, because it is a much stronger driving force than temperature. Our recent studies on pure, Ba- and Bi doped $PbSc_{0.5}Ta_{0.5}O_3$ (PST) and $PbSc_{0.5}Na_{0.5}O_3$ (PSN) [1-3] demonstrated that pressure leads to a dynamical decoupling of Pb and B-site cations, thus promoting the B-cations in polar nanoregions to go back to the corresponding octahedral centres. At the same time, pressure induces long-range order of antiphase octahedral tilts. The pressure-induced phase transition is continuous. It is smeared out over a pressure range if the system of A-site cations with lone-pair electrons is disturbed. In order to complete our studies on A-site doped Pb(B', B")O_3-type we have analysed La-doped PST and PSN. Thus, the objective of this study was to probe the high-pressure structure of La-doped PST and PSN to check the effect of replacement of A-positioned Pb with heterovalent cations showing no affinity to form lone pairs.

Single crystals of La-doped PST and PSN were synthesized by the high-temperature solution crystal growth method. Backscattered electron images confirmed the chemical homogeneity of the single-crystal specimens. The actual chemical composition was determined using electron microprobe analysis, by averaging over 100 spatial points. The calculated chemical formula was $Pb_{0.86}La_{0.08}\square_{0.06}Sc_{0.53}Ta_{0.47}O_{2.93}$ for the tantalate compound and $Pb_{0.70}La_{0.23}\square_{0.07}Sc_{0.62}Nb_{0.38}O_{2.93}$ for the niobate compound, which can be approximated as $Pb_{1-x}La_xSc_{(1+x)/2}Ta_{(1-x)/2}O_3$, x = 0.08 (PST-La) and $Pb_{1-x}La_xSc_{(1+x)/2}Nb_{(1-x)/2}O_3$, x = 0.23 (PSN-La), respectively. High-pressure synchrotron single-crystal XRD experiments were performed at the F1 beamline of HASYLAB/DESY using a MarCCD 165 detector. Data on PST-Ba were collected with a radiation wavelength $\lambda = 0.5000$ Å, a sample-to-detector distance of 100 mm, stepwidth of 0.5° per frame and exposure times of 120 s. The in-situ pressure experiments were conducted in diamond anvil cells of Boehler-Almax and Ahsbahs design. The pressure values were determined from the pressure-induced shift of the R1 photoluminescence line of ruby. A mixture of methanol-ethanol in the ratio 4:1 was used as a pressure-transmitting medium, which restricted the pressure range of hydrostaticity up to 9.8 GPa. Synchrotron single-crystal XRD data were collected on pressure load at 0.65, 1.1, 2.3, 3.2, 4.3, and 6.0 GPa for PST-La and at 0.7, 1.8, 2.7, 3.6, 4.5, and 6.0 GPa for PSN-La. The final measurements were conducted after decompressing to 0.4 and 0.1 GPa for PST-La and PSN-La, respectively.

Two features accompany the pressure-induced phase transition in all Pb-based perovskite-type relaxors studied so far: the suppression of the X-ray diffuse scattering (XDS) along $\langle 110 \rangle$*, which arises from polar cation shifts, and the appearance of sharp Bragg reflections with *hkl*, all odd, as indexed in $Fm\bar{3}m$, which are accompanied by XDS along $\langle 100 \rangle$*. These Bragg peaks arise from long-range order of antiphase octahedral tilts. For PST-La the $\langle 110 \rangle$*-XDS seems to weaken above ~ 1.5 GPa, which is in accordance with the changes in the Raman scattering and dependence of the normalized pressure F on the Eulerian strain f. The analysis of the pressure induced odd-odd-odd diffraction peaks was however interfered by the presence of chemical B-site long-range order producing also Bragg peaks with *hkl*, all odd. For PSN-La the $\langle 110 \rangle$*-XDS is very weak even at ambient pressure and gradually disappears at high pressures. A very interesting result is that for PSN-La a long-range octahedral tilt order is observed at very low pressures and does not change substantially with pressure. The Raman spectra of PSN-La showed gradual changes in the local structure with pressure increase but without the appearance of a soft mode indicative of a phase transition. The *f-F* diagram also did not reveal any phase transition up to 8 GPa. The high degree of octahedral tilting is most probably due to the relatively small tolerance factor. Apparently, the existence of octahedral tilt order is not enough to drive the whole structure to a new phase upon pressure increase, because of the high dilution of the Pb system with La. This again underlines that correlated A-site cations with lone-pair electrons is the key governing factor for the development of ferroic long-range order.

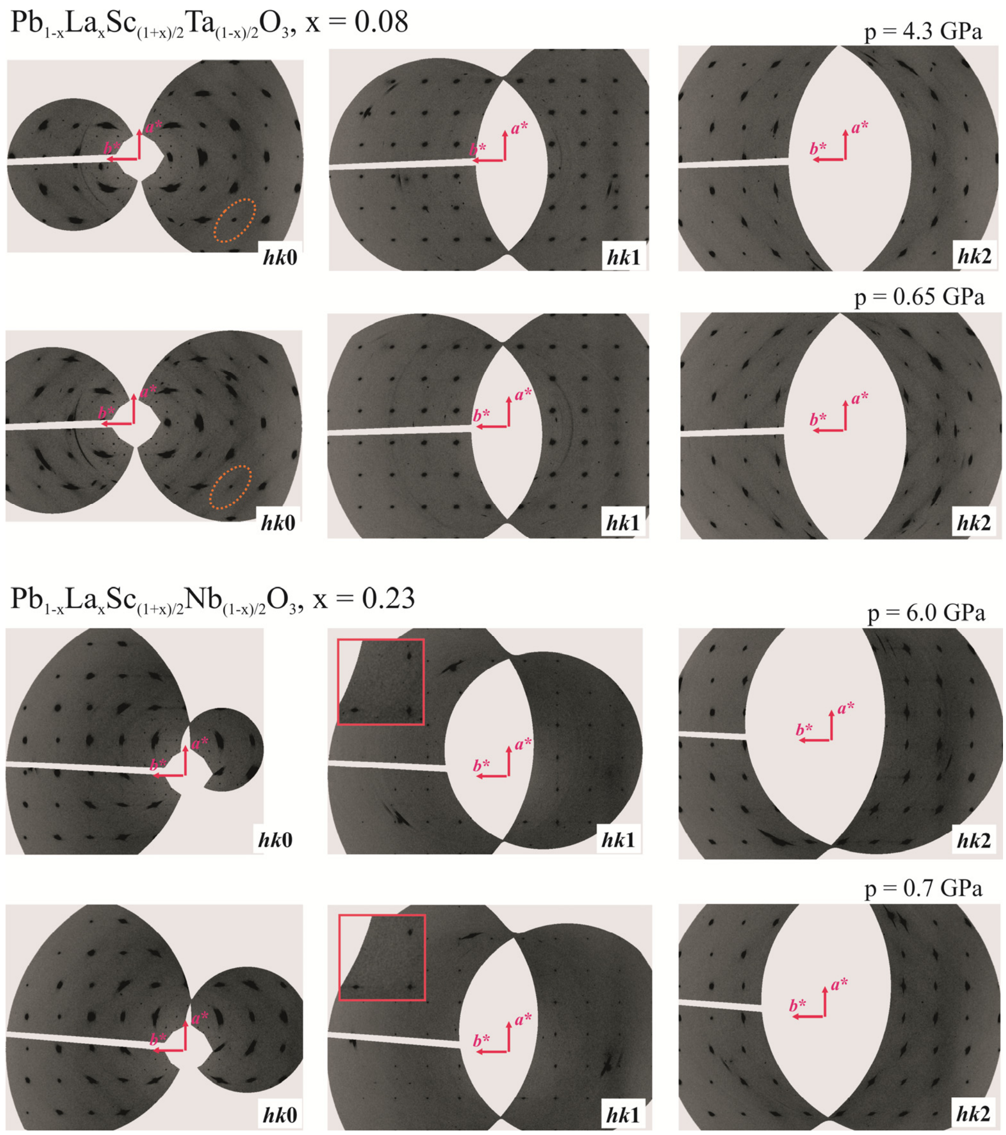

Figure 1: Reciprocal space layers of La-doped PST and PSN at two representative pressures showing the ⟨110⟩ *-XDS (in the *hk*0 and *hk*2 layers) at low pressures that is suppressed at high pressures while the odd-odd-odd peaks (in the *hk*1 layers) persist.

Acknowledgements: Financial support by the DFG and NSF is gratefully acknowledged.

References

[1] B. Mihailova, R. J. Angel, A.-M. Welsch, J. Zhao, J. Engel, C. Paulmann, M. Gospodinov, H. Ahsbahs, R. Stosch, B. Güttler, and U. Bismayer, Phys. Rev. Lett. **101**, 017602 (2008).

[2] A.-M. Welsch, B. J. Maier, J. M. Engel, B. Mihailova, R. J. Angel, C. Paulmann, M. Gospodinov, A. Friedrich, R. Stosch, B. Güttler, D. Petrova, and U. Bismayer, Phys. Rev. B, **80**, 104118 (2008).

[3] B. J. Maier, J. A.-M. Welsch, R. J. Angel, B. Mihailova, J. Zhao, M. Engel, L.A. Schmitt, C. Paulmann, M. Gospodinov, A. Friedrich, and U. Bismayer, submitted to Phys. Rev. B.