

Temperature-dependent evolution of X-ray diffuse scattering in the vicinity of T^* for the canonical relaxor $\text{Pb}_{0.78}\text{Ba}_{0.22}\text{Sc}_{0.5}\text{Ta}_{0.5}\text{O}_3$

B.J. Maier¹, T. Prüßmann¹, B. Mihailova¹, R.J. Angel^{1,2}, C. Paulmann¹,
M. Gospodinov³, and U. Bismayer

¹*Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, 20146 Hamburg, Germany*

²*Virginia Tech Crystallography Laboratory, Department of Geosciences, Virginia Tech, Blacksburg, VA 24060, USA*

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

Lead-based perovskite-type (ABO_3) relaxor ferroelectrics possess exceptional piezoelectric, electro-elastic and electro-optic properties, in particular a remarkably high dielectric permittivity, which exhibits as a function of temperature a broad and frequency-dispersive maximum. Hence, relaxors play an important role in a number of technological applications and therefore have been challenging the scientific community over the past decades to better understand the atomistic origin of their unique properties. Although the theoretical approach is still controversial, it is experimentally established that their properties are related to the complex local structure, i.e. dynamic polar nanoregions (PNRs) which flip between different states of polarization in the microsecond regime. These dynamic PNRs nucleate at the Burns temperature T_B by coupling of randomly off-centred cation shifts, which is several hundred kelvins above the frequency-dependent temperature of the dielectric permittivity maximum T_m . At T^* , a recently established intermediate temperature in relaxors, they couple into larger polar clusters with slower dynamics. Below T_m , the PNRs become static at the freezing temperature T_f for canonical relaxors or they develop into normal ferroelectric domains exhibiting a very weak ferroic distortion of the unit cell.

X-ray diffuse scattering (XDS) along $\langle 110 \rangle^*$ is typical of Pb-based perovskite-type relaxors and it arises from Pb- and B-site cation shifts in PNRs correlated in the cubic $\{110\}$ planes. Hence, the temperature evolution of the XDS reflects the development of PNRs in terms of size and fraction. Recently, acoustic emission measurements on $\text{Pb}_{0.78}\text{Ba}_{0.22}\text{Sc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PBST) revealed that the transformation process near T^* exhibits a temperature hysteresis of 15 K, with $T^* = 491$ K on heating and 476 K on cooling [1]. In order to get deeper insight into the nature of the transformation processes occurring at T^* we measured the XDS as a function of temperature for PBST.

Synchrotron single-crystal X-ray diffraction experiments were conducted at the beamline F1 of HASYLAB/DESY, using a radiation of wavelength $\lambda = 0.4000$ 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 time of 150 s per frame. The low-temperature experiments were performed using a liquid- N_2 cryostat Oxford Cryosystems 600, whereas high-temperature measurements were performed on heating using a beam-line developed gas-stream heating device. Reciprocal lattice sections were reconstructed using the beam-line developed software RASTM. Line profiles along the $\langle 110 \rangle^*$ directions were taken at three symmetry equivalent reflections of $\{240\}$ (see solid red lines in Fig. 1). The background was determined by a second perpendicular line profile (dashed red line in Fig. 1) and subtracted. A subsequent profile fit was carried out using a Voigt profile for the Bragg reflection and a Gaussian profile for the XDS (see Fig. 2).

Figure 3 shows the temperature evolution of the intensity ratio $\eta = I_{\text{diff}}/I_{\text{Bragg}}$ averaged over three equivalent $\{240\}$ reflections. As can be seen, the diffuse scattering is strongly enhanced below 400 K. A fit to the data using the growth function $\eta = (I_{\text{max}} - I_{\text{min}})/(1 + \exp((T - T_0)/dT) + I_{\text{min}})$ reveals that the diffuse scattering intensity starts to increase near 475 K, slightly below T^* . This supports the idea that PNRs couple and grow into larger polar nanodomains at T^* .

In addition, we checked if the application of the Landau theory could reveal a first-order character of the transformation process near T^* since the temperature hysteresis suggests such a behaviour. However, $\eta(T)$ shows no discontinuity. Assuming η as the order parameter of the phase transformation we fitted the data with the function $\eta = A(T_C - T)^{1/x}$, where $2 \leq x \leq 4$. The best fit revealed a tricritical behaviour ($x \sim 4$) with T_C near 400 K.

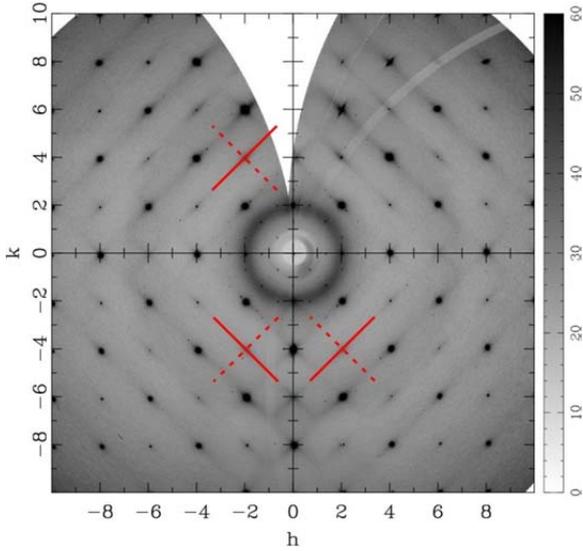


Fig. 1: Reciprocal space layer ($hk0$) reconstructed in $Fm\bar{3}m$ from synchrotron XRD data on PBST at 465 K. Line profiles were taken along the solid red lines, which were subsequently baseline corrected using the average level of the background across the dashed lines.

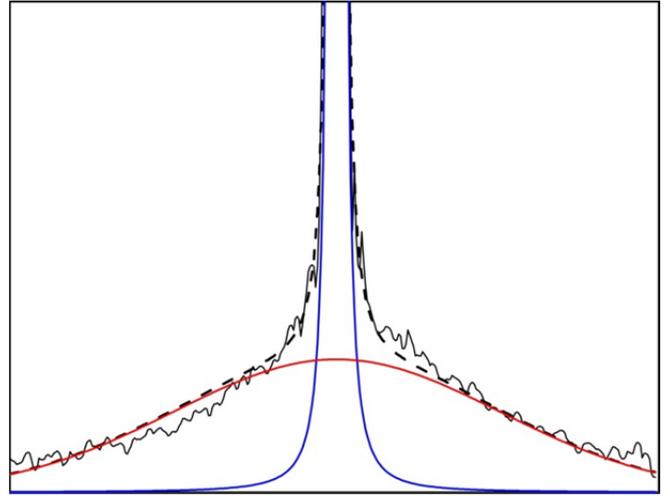


Fig. 2: Sample fit to the line profile along $(110)^*$ of the 240 reflection of PBST at 465 K. The blue line represents a Voigt profile fitted to the Bragg peak, whereas the red line represents a Gaussian profile fitted to the X-ray diffuse scattering, both adding up to the dashed black line representing the fitted curve.

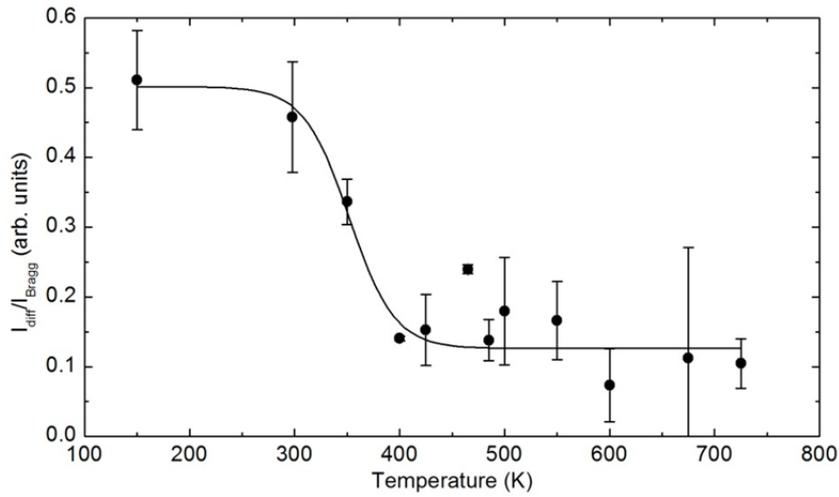


Fig. 3: Temperature dependence of the intensity ratio I_{diff}/I_{Bragg} averaged over the three equivalent $\{240\}$ reflections. The solid line represents a fit using the growth function.

$$I_{diff}/I_{Bragg} = (I_{max} - I_{min}) / (1 + \exp((T - T_0)/dT)) + I_{min}$$

Acknowledgements

Financial support by the DFG (MI 1127/5-1) is gratefully acknowledged.

References

- [1] E. Dul'kin, B. Mihailova, M. Gospodinov, E. Mojaev, and M. Roth;
J. Phys.: Condens. Matter **22** (2010) 222201