

Ba-induced changes in the structure of $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$

C. Paulmann, T. Malcherek, B. Mihailova, M. Gospodinov¹ and U. Bismayer

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

¹ Institute of Solid State Physics, Bulgarian Academy of Sciences, Blvd. Tzarigradsko Chausse 72, 1784 Sofia, Bulgaria

Relaxor ferroelectrics are multi-functional, technologically important materials with a complex nano-scale structure. The structure-property relationship in these materials are not yet well understood. Occurrence of dynamical polar nanoclusters far above the temperature of the dielectric-permittivity maximum T_m as well as the suppression or even no development of long-range ordered ferroelectric domains below T_m is typical of relaxors. The low-temperature structure of canonical relaxors is pseudo-cubic and the system is in the so-called non-ergodic state consisting of static polar-nanoclusters in a paraelectric matrix. Most of relaxors are Pb-based perovskite-type relaxors with the general formula ABO_3 , having two types of cations that occupy the B-site. Often, the absence/occurrence of long-range ferroelectric ordering is attributed to a high/low degree of long-range chemical B-site disorder. However, our studies on A- and B-site doped $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST) as well as PST with different degree of oxygen deficiency showed that defects in the lead and oxygen system have also an important role for the development of relaxor state [1,2]. Further, dielectric measurements on PST and $\text{Pb}_{0.78}\text{Ba}_{0.22}\text{Sc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PBST) revealed that the partial substitution of Ba for Pb strongly suppresses the formation of proper ferroelectric state and enhances the non-ergodic state, regardless of the degree of B-site compositional order [3]. To gain deeper insights into relaxor structure we applied X-ray diffraction and inelastic light scattering analyses to PST and PBST as model representatives for Pb-based perovskite-type relaxors; PST is known to develop a proper ferroelectric state, while PBST shows canonical relaxor behaviour. Thus the goal of our synchrotron-based single-crystal X-ray diffraction (XRD) study was two fold: (i) to verify the absence of ferroelectric long-range ordering in PBST, and (ii) to follow the temperature evolution of the X-ray diffuse scattering in the two compounds.

Single crystals of PST and PBST were grown by the high-temperature solution growth method. Synchrotron single-crystal XRD experiments were conducted at the F1 beamline of HASYLAB/DESY, using a high-energy radiation of wavelength $\lambda = 0.4000 \text{ \AA}$ and a MarCCD 165 detector. Data were collected at a sample-to-detector distance of 50 mm with a stepwidth of 1° per frame with exposure times between 60 and 160 s. The experiments were performed at three different temperatures using an in-house developed heating device and a liquid- N_2 cryostat (Oxford Cryosystems, Series 600).

Representative (hkl) reciprocal-space sections of PST and PBST are shown in Figure 1. As can be seen from the well-pronounced ($hk1$) Bragg reflections at high temperatures, both compounds possess compositional B-site long-range ordering. The average size of the B-site ordered spatial regions as determined from the full-width-at-half-maximum of the superlattice Bragg reflections in the powder XRD patterns is approximately 6 and 33 nm for PST and PBST, respectively. The temperature evolution of the Bragg reflections and diffuse x-ray scattering reveals the structural changes occurring upon cooling. For PST, on cooling from 700 to 300 K, when the system approaches $T_m \sim 280 \text{ K}$, strong diffuse scattering along $\langle 110 \rangle$ develops. This diffuse scattering is typical of relaxors and originates from the polar nanoclusters existing in the paraelectric matrix. The direction of diffuse scattering shows that the atomic ferroic shifts correlate within $\{110\}$ planes of the real space. At $T = 150 \text{ K}$, which is below T_m , diffuse scattering for PST is gathered in additional Bragg reflections, thus revealing the development of proper ferroelectric state. The temperature dependence of the (hkl)-layers for PBST is different from that of PST. On cooling the diffuse scattering gradually increases in intensity and it is strongest at low temperatures. As an estimate, the ratio $I_{DS}/(I_{BR}+I_{DS})$ calculated for the (660) reciprocal-space point is approximately zero at 748 K, 0.98×10^{-3} at 300 K and 6.41×10^{-3} at 150 K; I_{BR} is the Bragg intensity determined from the fitted Voigt-profile along $[110]$, while I_{DS} is the diffuse scattering determined as the difference between the average intensity of a parallel but off-peak profile and the baseline of the Bragg peak fitting. Similar tendency was found for other ($hk0$) points with $h+k = 4n$, i.e., with nominally additive scattering contributions from both A- and B-cations. No appearance of additional Bragg reflections due to a ferroic phase is observed at 150 K, which confirms the

suppression of ferroelectric long-range ordering and the enhancement of non-ergodic relaxor state [3]. The Bragg reflections in the $(hk1)$ -layer, which are related to chemically B-site ordered regions, become weaker and poorly resolved when the temperature decreases. This phenomenon is due to the loss of periodicity in the B-cation system resulting from a massive formation of small-sized polar regions comprising B-cation off-centre shifts. Because of the small coherence length of correlated B-cation off-centre displacements, those spatial regions contribute much stronger to the diffuse scattering rather than to the Bragg reflections, i.e., chemical B-site ordering and B-cation off-centre displacements compete. A strong weakening of the reflections stemming from $\{h00\}$ -planes, $h = 6$, and $\{hh2\}$ -planes, $h = 4$, is observed for PBST. At $T = 748$ K neither the corresponding Bragg signal nor diffuse scattering exists, at $T = 300$ K mostly diffuse scattering along $\langle 110 \rangle$ -directions is seen, whereas at $T = 150$ K a Bragg spot with diffuse scattering is clearly observed. The observed intensity alterations are most probably due to Ba-doping-induced changes in the medium-range ordering of the Pb-system.

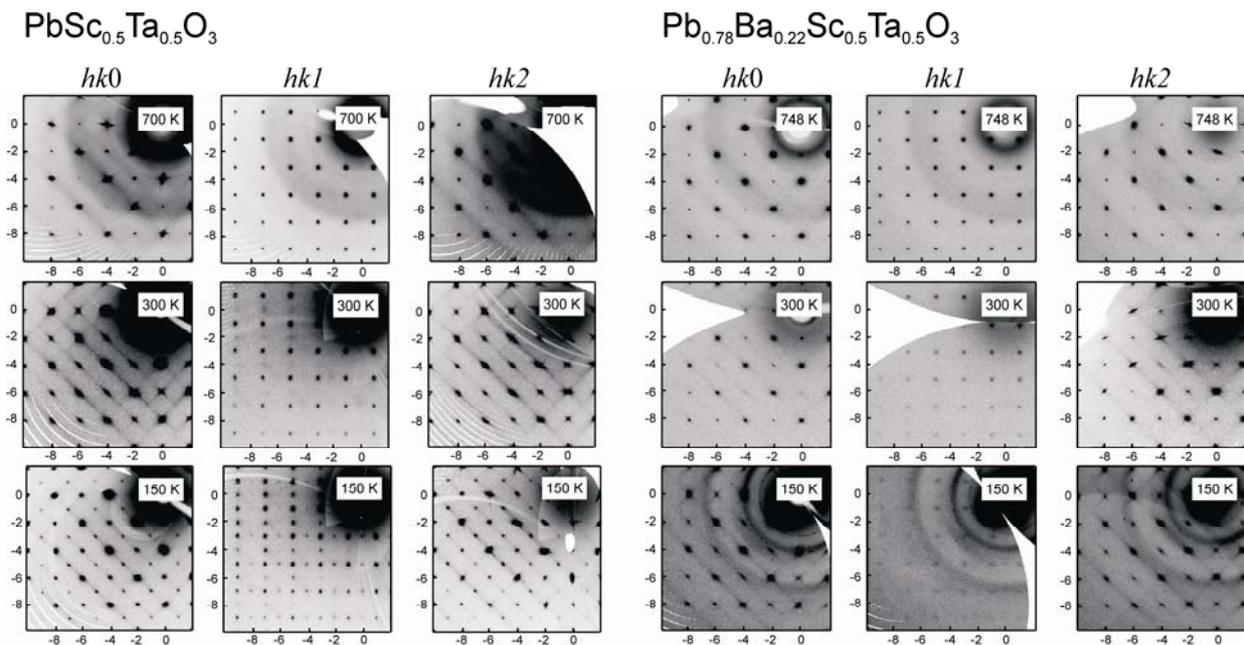


Figure 1: $(hk0)$, $(hk1)$ and $(hk2)$ layers of the reciprocal space for $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ and $\text{Pb}_{0.78}\text{Ba}_{0.22}\text{Sc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ at three different temperatures; Miller indices are given in a cubic double-perovskite ($Fm\bar{3}m$) unit cell. The round features are artificial contribution from the quartz capillary.

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References

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