ESRF	**Experiment title:** Short range ordering of cations in PMN and PMT ferroelectric single crystals	**Experiment number**: HS 3723
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Report:

The aim of this experiment was to determine the short-range arrangement of atoms in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN) and $PbMg_{1/3}Ta_{2/3}O_3$ (PMT) relaxor ferroelectrics by means of the x-ray diffuse scattering holography. Our plan was to measure the x-ray holograms using the anomalous diffuse scattering from lead atoms in the vicinity of their K absorption edge (88.005 keV) and niobium atoms in the vicinity of their K absorption edge (18.986 keV) in order to get holograms and thus the positions and mean electron densities of the atoms in the vicinity of the Pb and Nb atoms, respectively [1]. A similar experiment was planned with a PMT single crystal using anomalous signal of tantalum in the vicinity of its K absorption edge (67.416 keV). The use of high energies is very advantageous for consequent data processing because of negligible absorption in the sample, negligible scattering in the air, and low fluorescence signal. In the case of PMT, in contrast to a PMN single crystal, the high-energy absorption edge of the element in the site *B* in perovskite structure can be exploited. The real-space reconstruction of these holograms should results in the local neighbourhood of the anomalous scatterers and the local neighbourhood of atoms in *B* sites in perovskite structure in the ratio of 1:2.provides more information on the short-range order arrangement of atoms. Finally, with respect to the impossibility to reach the energies lower than 23 keV at the ID11 beamline because of the problems with a beamline mirror, we were not able to carry out the measurements in the vicinity of niobium absorption edge. Inspite of this problem, interesting results were obtained.

The PMT sample was a single crystals in the form of a thin plate with the thickness of about 50 μm with its surface parallel to the (001) crystallographic planes.. The sample was illuminated by a monochromatic beam of the cross-section of 200×200 μm^2. Two-dimensional intensity patterns were recorded in the transmission mode using a large CCD detector FreLoN16 (array of 2048×2048 pixels of the size of 46×46 μm^2) positioned at the distance of 123 mm behind the sample. The reciprocal space was scanned by rotating the sample around the axis perpendicular to the incident beam in the range from -185° to 185°. We measured such a large region of the reciprocal space because we want to reconstruct the local atomic structure without using the "long-range" symmetry deduced on the basis of Bragg reflections. The sample was moving during each exposure in 0.5° steps. The acquisition time for each frame was 4 s - the aim was to get diffuse scattering patterns with good statistics but without an oversaturation of detector pixels when passing through the Bragg reflections. The data sets were collected at photon energies $E_1 = 67.41$ keV (at the absorption edge), $E_2 = 67.61$ keV (above the edge), and $E_3 = 67.01$ keV (below the edge). Several data sets were collected for each energy in order to improve the data precision. A similar experimental procedure wa applied to a PMN sample.

The most critical and time-consuming part of holography experiment consists in the data processing and required to develope a package of computer programs written in IDL. First, the background and the scattering from the air was subtracted using scattering patterns collected with no sample present. The data were corrected carefully also for the fluorescence, the inelastic scattering, the beam polarization, the absorption in the sample, and the detector efficiency. It was also necessary to remove numerically the intense Bragg reflections using a median filter. Then sets of the corrected experimental data points were transformed to a regular grid in the reciprocal space which resulted in a three-dimensional map of the reciprocal space. The cuts through the reciprocal space are shown in Fig. 1. It is evident, that strong structured diffuse scattering occur not only in the vicinity of Bragg peaks (left) but also between nodes of the reciprocal lattice. The most prominent are peaks in positions (h/2,k/2,l/2) (right) that proves the short-range ordering of Mg and Ta atoms in the crystal lattice. As it can be seen from Fig. 2, three-dimensional intensity pattern of PMN exhibits similar features and short-range ordering of Mg and Nb atoms.

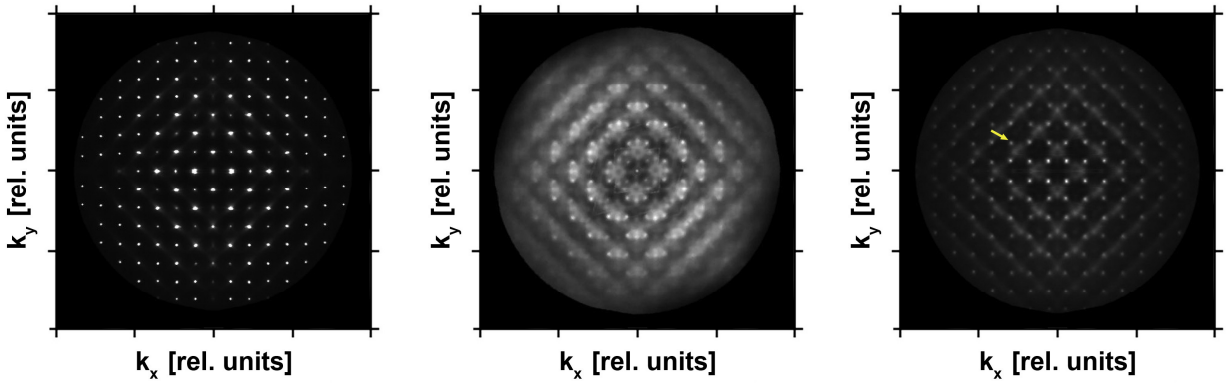

Figure 1: Cuts through the reciprocal space of a PMT single crystal in planes $k_z = 4a^*$ (left), $k_z = 4½a^*$ (middle), and $k_z = 4¾a^*$ (right). The arrow points to the short-range order peaks.

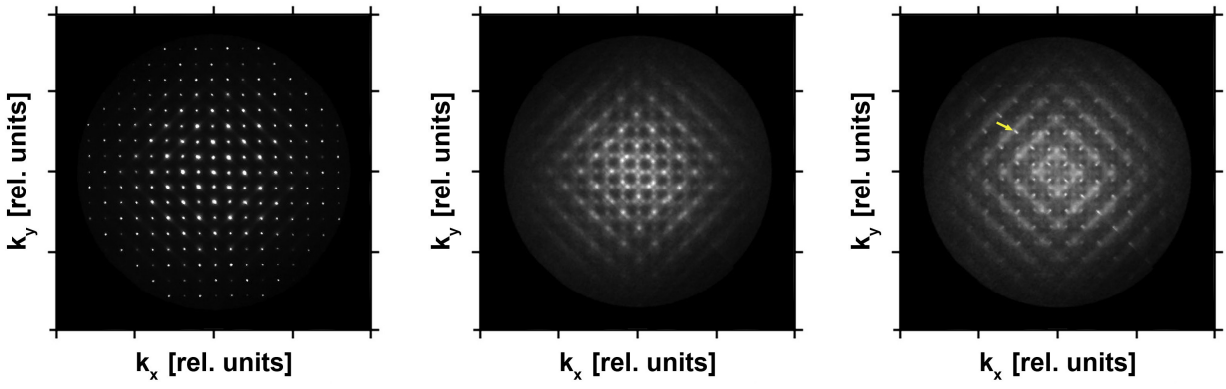

Figure 1: Cuts through the reciprocal space of a PMN single crystal in planes k_z = 3a* (left), k_z = 3½a* (middle), and k_z = 3¾a* (right).

The real-space reconstruction of the measured 3D scattering pattern provided a clear pair distribution function. However, the aim was to reconstruct the difference of the intensity patterns collected at two energies with different contributions of the anomalous scattering in order to obtain holograms and thenthe reconstructed local neighbourhood of tantalum atoms. But first, we have to solve problems with systematic errors that implement some distortion to the 3D image and does not allow a precise subtraction of 3D pattern collected at different energies. We plan to use positions of sharp Bragg peaks and to develope a software package, that will correct these geometrical distortions automatically. In any case, we were able to measure anomalous portion of diffuse scattering which is a crucial step of success.