Lattice modulation and structural instability at M-point in PZT single crysatls by X-ray scattering

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In recent years the revival of the interest to the physics of $(PbZrO_3)_{1-x}(PbTiO_3)_x$ (PZT) solid solution is observed. To large extent this revival is related to development in the single crystal growth and to the new experimental possibilities in studying the extremely small single crystals using high-flux synchrotron radiation sources.

Already the structure of pure lead zirconate crystal $PbZrO_3$ (PZO) is extremely complicated. In the Ref.1 it is mentioned that the lattice distortion in PZO is described as a sum of 6 different frozen "modes". The major role is played by the Σ_3 and R_{25} components. Ab-initio calculations of Ph. Gosez et al., demonstrated instability of the Last-type Γ_{15} TO mode and completely flat M-R branch related to the oxygen octahedra tilts. In recent paper [3] it was shown that antiferroelectric transition in PZO can be described by the softening of Γ_{15} mode with Σ_3 order parameter being the result of the flexoelectric TO - TA coulpling and R_{25} order parameter appeared due to the Holakovsky mechanism.

However even in pure PZO intermediate phase (presumably ferroelectric) characterized by the M-type superstructure exists. In PZO this phase is observed only in very narrow temperature region but it becomes stable at 0<x<~6% [4]. The structure of the phase is still under discussion and we will abbreviate it as F.

Until now most of the measurements of this intermediate phase were done using ceramic samples. Single crystal measurements were carried out only using electron diffraction and electron microscopy techniques.

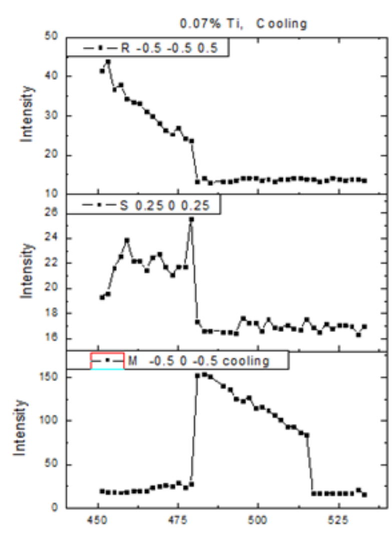


Figure 1 Temperature dependences of the intensity of the superstructure peaks in PZT07

In this report we are going to present the results of the study of PZT single crystals with lead titanate concentrations from 0.7% to 20% (x=0.7%, 1.5%, 3.3%, 6% 20%). To explore the structural changes and critical phenomena in the mentioned single crystals we have used a combination of the X-ray diffraction, diffuse and inelastic X-ray scattering techniques. Diffraction and DS measurements were carried out at Swiss-Norwegian Beam Lines (SNBL) at ESRF using the KUMA (Oxford Diffraction) diffractometer with PILATUS position sensitive detector. Inelastic X-ray measurements were performed at ID28 ESRF beamline.

In the present report we will mostly concentrate on the study of the phase transition from cubic paraelectric to the intermediate phase manifesting itself by M-type (h+½ k+½ l) superstructure peaks.In agreement with earlier published data we have observed a sequence of phase transitions from cubic phase (C) to phase F and then to the orthorhombic AFE phase Figure 1 demonstrates temperature

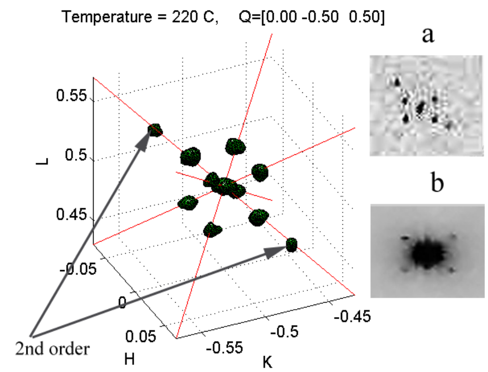


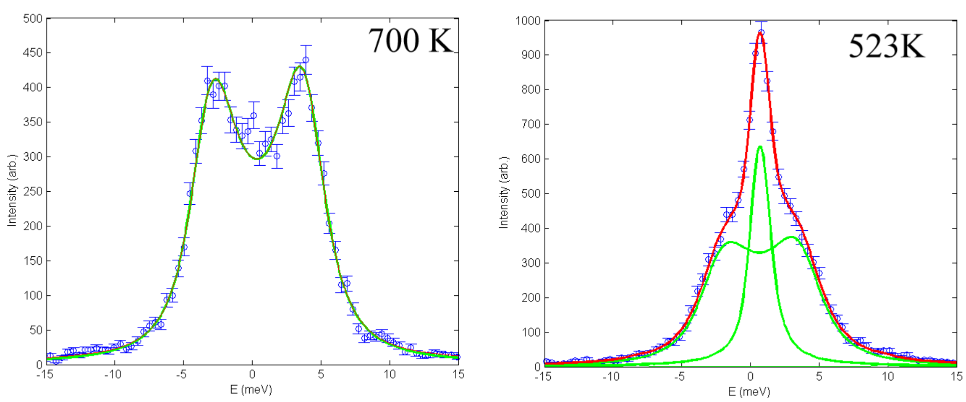
Figure 2 M-superstructure and satellites

evolution of the intensity of the superstructure peaks in PZT07 (x=0.7%). It is clearly seen that C - F and F - AFE transitions are of the first order and F phase is stable in the broad temperature range.

It was shown before (see e.g. [4]) that M-peaks have complicated "fine structure". Electron diffraction experiments demonstrated existence of additional satellites around the M-peaks. Neither X-ray nor neutron scattering experiments confirmed this observation before. In our measurements we have found fine satellite structure for all studied compositions except 20%PT. Superstructure peaks observed in PZT07 are shown in the Figure 2. In the main panel 3-d distribution of the scattering intensity is shown, panel ***a*** demonstrates 2-d map around M position and panel ***b*** 2-d map around "major" Bragg peak. Our observations can be summarized as follows:

- no extinction rules exist. This fact indicates that the M-superstructure is not determined by the oxygen octahedra tilts;
- each M peak is surrounded by 8 1-st order {δδδ} satellites δ≈0.018a*;
- around some of the M peaks second order satellites shifted for 2δ are observed. These satellites usually occur only one of 4 equivalent {111} directions (main panel and panel ***a*** Figure 2);
- In addition to the satellites around M-peaks additional weak spikes were found around major Bragg peaks (panel ***b*** Figure 2);

Both 1-st and 2-nd order satellites around M-peaks can be described in the frames of antiphase domains but we cannot at the moment explain 2-nd order spikes around major Bragg peaks.



To elucidate the microscopic origin of the C - F phase transition we have carried out IXS measurements. Phonon dispersion for in-plane polarized modes was determined and its temperature evolution was traced. Very flat dispersion of the TA branch similar to that in pure PZO was found with weak anomaly around $\boldsymbol{q}_{\Sigma}$=(¼¼0). However no frequency lowering at around M-point was found. Instead on approaching the transition temperature from above strong central peak aroused (Figure 3). At the moment we cannot say if this CP is related to the critical relaxational degree of freedom relevant to the C - F transition or it results from the coupling of the relevant phonon mode to some dynamic disorder (lead rattling ?).

References

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