Pre-transitional evolution of central peaks and transverse acoustic phonon branch in single crystal lead zirconate titanate with Ti concentration 0.7%

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Abstract. Inelastic X-ray scattering measurements have been done to study the lattice dynamics in lead zirconate titanate solid solution with 0.7% of PbTiO₃. The temperature evolution of central peak and low-energy transverse phonon branches has been traced. Temperature dependent in-plane transverse polarized acoustic phonon branch in <1 1 0> direction has been revealed. The central peaks of two types have been found. The central peak at small wave vectors can be attributed to the relaxational-type soft ferroelectric mode, while the latter at \( Q = (1.5 -0.5 0) \) could be linked to the formation of M-superstructure in the intermediate ferroelectric phase.

1. Introduction

Lead zirconate titanate (PZT) is well known and widely used ferroelectric material. PZT attracts a lot of attention because of its exceptionally good piezoelectric properties. Another motivation to study PZT is a variety of properties and structures, demonstrated by PZT with different composition. Pure lead zirconate (PbZr₁₋ₓTiₓO₃ at x=0) is the prototypical antiferroelectric material. According to a set of reports [1–4] between the cubic perovskite paraelectric phase and the antiferroelectric phase, in the narrow temperature range, the intermediate ferroelectric phase exists. Addition of titanium increases the temperature range of stability of the intermediate phase [5]. Cubic-to-intermediate phase transition is accompanied by doubling of the cell parameters of the paraelectric cubic lattice along two directions [6] and results in the appearance of M-superstructure with coordinate \( (H±1 0 K±1 0) \) in the diffraction pattern.

While antiferroelectricity is known for a long time, the understanding of this phenomenon is still incomplete. It has been shown that the antiferroelectricity in lead zirconate originates from the anomalously high impact of flexoelectric coupling on the transverse acoustic spectra [7].
to that the lattice becomes unstable against incommensurate modulations over a large volume in the Brillouin zone along \(<1 1 0>\) directions, but the transition to the incommensurate phase is avoided by lock-in phase transition to the observed antiferroelectric phase due to sufficiently strong Umklapp interaction. This mechanism was confirmed for pure \(\text{PbZrO}_3\) by the analysis of inelastic and diffuse X-ray scattering [7]. However, this description does not account for the appearance of the intermediate ferroelectric phase.

Diffuse scattering could give a hint in the understanding of the lattice dynamics. Our measurements revealed the appearance of strong anisotropic diffuse scattering around integer-value Bragg spots in paraelectric phase of PZT with 0.7 % Ti concentration [8]. The shape of diffuse scattering in the PZT is similar to that observed in pure lead zirconate. Intensity of diffuse scattering demonstrates fast growth on approaching the transition temperature from the high temperature. Such behavior could be explained by the softening of the phonon modes close to the center of the Brillouin zone.

To study the details of the lattice dynamics of lead zirconate-titanate with low Ti concentration we have performed inelastic X-ray scattering at single crystal \(\text{PbZr}_{0.993}\text{Ti}_{0.007}\text{O}_3\).

2. Experimental details
The single crystal of PZT with \(x = 0.007\) has been studied. The synthesis process was described earlier [9]. The crystal preparation included polishing and etching with hydrochloric acid. The resulting crystal was \(100 \times 100 \times 500 \mu\text{m}\). The lattice dynamics in PZT was studied using the backscattering spectrometer ID28 at the European Synchrotron Radiation Facility (France). It was operated at X-ray energy \(E = 21.75 \text{ keV} \) (Si (11 11 11) monochromator) providing the energy resolution of 1.5 meV FWHM.

According to [10] temperature range of the intermediate phase is about 500 - 455 K on heating. Our measurements were performed at 4 temperatures above and at one temperature below the temperature of transition in the intermediate phase.

Previous studies of lead zirconate lattice dynamics [7] have demonstrated that phonons along \(<1 1 0>\) directions have anomalously low and temperature dependent energy. Because of that in this experiment we concentrated on wave vectors \(\mathbf{q}\) along the [-1 -1 0] direction. The measurements were performed in the vicinity of the \((2 0 0)\) reciprocal lattice point. Such choice of the direction and the reciprocal lattice point gives the dominant contribution of the transverse phonon to the experimentally measured spectra. The ID28 spectrometer multianalyzer construction allows us to register 9 reciprocal lattice points simultaneously. As the result the region around \((2 0 0)\) reciprocal lattice point surrounding [-1 -1 0] direction has been studied.

3. Results
Fig.1 shows spectra for a set of reciprocal points and different temperatures. All spectra contain clearly visible symmetric phonon resonances and a central peak (at zero energy transfer). The two low-energy (about 3 meV) Stokes and anti-Stokes peaks are associated with the transverse acoustic (TA) mode with “in-plane” polarization vector. The high-energy (about 8 meV) Stokes and anti-Stokes peaks can be attributed to the transverse optic (TO) phonons. Phonon resonances were fitted using damped harmonic oscillator line shape convoluted with the experimental resolution [11, 12]. The central peak was fitted by Lorentzian function [12]. In Fig.1 the fitting results are shown by lines while experimental data are shown by points.

The obtained dispersion curves for the TA phonons along [-1 -1 0] direction are shown in Fig.2. In the paraelectric phase the TA phonon dispersion branch demonstrates low energy which does not exceed 4 meV. Notable feature of the dispersion curve is the change of its slope at \(q > 0.3\).
The in-plane polarized TA phonons demonstrate a distinct temperature dependence. In the paraelectric phase the temperature decrease results in the lowering of the TA phonon branch energy. In the intermediate phase (at 483K) the energy of the TA in-plane phonon notably increases. No pronounced temperature dependence of the TO in-plane phonon energy has been found. This is in a good agreement with the results obtained for pure lead zirconate.

The anisotropy of TA in-plane phonon was studied. In Fig.3 the TA in-plane phonon energy distribution in reciprocal space is shown for temperature 700K. Along $<110>$ directions minima in phonon energy are clearly observed, a similar anisotropy of the TA phonon was found in pure lead zirconate earlier \[7\].

As in lead zirconate \[7\] in the PZT all spectra contain central peaks. To analyze the central peak features we plotted the contour maps of scattering intensity in the $q$-E coordinates (Fig.4). The energy of the TA and TO phonons, determined from the fits of the experimental spectra, are indicated by points. At small wave vector $q$ the high intensity central peak exists at 523 K, close to the transition temperature. The intensity of this central peak decreases with wave vector increase, at $Q = (1.6 -0.4 0)$ the central peak intensity becomes minimal, as compared to the surrounding $q$-points along the [-1 -1 0] direction. At Brillouin zone boundary ($Q = (1.5 -0.5 0)$) another central peak is clearly observable. Both central peaks demonstrate an increase of intensity on approaching the paraelectric-intermediate phase transition temperature.

Different distributions of central peak intensity in reciprocal space allows to suggest that the central peak at small wavevector $q$ and central peak at the M-point are the results of different
Figure 2. Temperature evolution of TA in-plane phonon dispersion along [-1 -1 0] direction near (2 0 0) reciprocal lattice point ($Q = (2-q -q 0)$). Points are fitting results, lines are guide for eyes.

Figure 3. TA in-plane phonon energy distribution in reciprocal space coordinate around (2 0 0) reciprocal lattice point for temperature 700K.

Figure 4. Contour maps of inelastic X-ray spectra for [-1-10] direction near Bragg reflection (2 0 0) for temperatures 700K and 523K, red points indicates the TA phonon energy, black points – the TO phonon energy.

processes: the central peak at small $q$ could be linked with some critical excitation, related to the dielectric anomaly. The central peak at the M-point could be relevant to the arising of the M-superstructure, which appears below the paraelectric-intermediate phase transition.

4. Conclusions
Using inelastic X-ray scattering the lattice dynamics of the lead zirconate titanate single crystal with Ti concentrations 0.7% has been studied. Anomalously low energy TA in-plane polarized phonon has been found in $< 110 >$ directions. On approaching to the phase transition temperature in the paraelectric phase the energy of the TA phonon decreases. The anisotropy of the phonon surface dispersions is similar to the anisotropy of the diffuse scattering published in [8] for the same material.

The central peaks of two types have been found. The central peak at small $q$ ($q < 0.4$) could be associated with the ferroelectric soft mode, which is responsible for the observed dielectric
anomaly. It has been shown for lead zirconate [13] that soft ferroelectric mode manifests itself as a combination of central peak and optic phonon. As the result while the temperature decreases towards to transition temperature the intensity of this central peak sharply increases and optic phonon energy demonstrates just a little energy change in lead zirconate. This behavior could originate from coupling of the soft optic phonon and some noncritical relaxation process. In this case the critical increase of the central peak intensity in PZT with 0.7% of Ti could be a manifestation of the optic mode softening close to the Brillouin zone center. The central peak at the Brillouin zone boundary could be linked with M-superstructure formation, which appears below the paraelectric-intermediate phase transition.

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References
[1] Tanaka M, Saito R and Tsuzuki K 1982 Electron microscopic studies on domain structure of PbZrO$_3$ *Japanese Journal of Applied Physics* **21** 291
[2] Fujishita H and Hoshino S 1984 A study of structural phase transitions in antiferroelectric PbZrO$_3$ by neutron diffraction *J. Phys. Soc. Jpn.* **53** 226-234
[3] Dec J and Kwapielniski J 1989 Crystallogeometry of phase transitions in PbZrO$_3$, single crystals *J. Phys.: Condens. Matter* **1** 3389-3396
[4] Xu Z, Dai X, Viehland D, Payne D, Li Z and Jiang Y 1995 Ferroelectric domains and incommensuration in the intermediate phase region of lead zirconate *Journal of the American Ceramic Society* **78** 2220-2224
[5] Shirane G, Sawaguchi E and Takagi Y 1951 Dielectric properties of lead zirconate *Phys. Rev.* **84** 476-481
[6] Ricote J, Corker D, Whatmore R, Impey S, Glazer A, Dec J and Roleder K A tem and neutron diffraction study of the local structure in the rhombohedral phase of lead zirconate titanate *Journal of Physics: Condensed Matter* **10** 1767
[7] Tagantsev A et al. 2013 The origin of antiferroelectricity in PbZrO$_3$ *Nature Communications* **4** 2229
[8] Andronikova D et al. 2015 Critical scattering of synchrotron radiation in lead zirconate-titanate with low titanium concentrations *Physics of the Solid State* **57** 2441-2446
[9] Leontiev N, Smotrakov V and Fesenko E 1982 Izv. Akad. Nauk SSSR, Neorg. Mater. **18**
[10] Fesenko O, Smotrakov V and Leontev N 1983 *Physics of the Solid State* **25** 1958-1963
[11] Dorner B 1993 *Coherent Inelastic Neutron Scattering in Lattice Dynamics* Springer Tracts in Modern Physics
[12] Burkovsky R, Andronikova D, Bronwald Y, Krisch M, Roleder K, Majchrowski A, Filimonov A, Rudskoy A and Vakhruhev S 2015 Lattice dynamics in the paraelectric phase of PbHfO$_3$ studied by inelastic x-ray scattering *Journal of Physics: Condensed Matter* **27** 335901
[13] Burkovsky R et al. 2014 Lattice dynamics and antiferroelectricity in PbZrO$_3$ tested by x-ray and brillouin light scattering *Phys. Rev. B* **90** 144301