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Comparison of Acoustic Anomalies Between Tetragonal and Rhombohedral Ferroelectric (1-*x*)$Pb(Zn_{1/3}Nb_{2/3})O_3$-*x*$PbTiO_3$

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1. Introduction

Relaxor ferroelectric (RFE) materials with a disordered ABO_3 perovskite structure have become one of the frontline topics among the ferroelectrics research community, because of their very promising physical properties and potential industrial applications [1]. These materials are used for hydrophones, actuators, receivers, projectors, sonar transducers and in micro-positioning devices. Phenomenologically, the so-called polar micro or nano regions (PNRs) (that appear below Burns temperature (T_B) [2]) are at the heart of almost all the physical models proposed so for to understand the relaxor physics. $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) are the two prototypical RFEs that form solid solutions with pure ferroelectric compound $PbTiO_3$ (PT) resulting in giant piezoelectric properties specially near the morphotropic phase boundary (MPB) (e.g. for PZN-PT, d_{33}~2500 pC/N and strain as large as ~1.7%). It has also been argued [3] that enhanced piezoelectric response might be related to the existance of a tripple point as indicated in phase diagram of PZN-*x*%PT (Fig. 1).

PZN-x%PT is subject of present investigations due to its interesting dynamical features across the phase diagram. Lattice symmetry of PZN-x%PT is tetragonal (*P*4*mm*) above the MPB and rhombohedral (*R*3*m*) below MPB. Whereas, MPB itself is composed of various monoclinic and orthorhombic symmetries. What about the paraelectric cubic phase of PZN-x%PT relaxor relative to a pure FE system such as $BaTiO_3$ in the presence of dynamical PNRs? In order to address this question we have measured elastic properties of PZN-x%PT single crystals by using micro-Brillouin scattering spectroscopy (MBSS) [4] and analyzed the acoustic anomalies with phenomenological approach based on the meanfield approximation [3, 5]. MBSS is a powerful technique to investigate the gigahertz dynamics in a microscopic area in many materials materials such as glasses, proteins, and normal and relaxor ferroelectrics etc. [4].

2. Experimental

A 3+3 pass tandem Fabry-Perot interferometer was used to measure the high-resolution micro-Brillouin spectra by employing the backward scattering geometry. PZN-*x*%PT (*x*=4.5%, 15%) [001]-oriented single crystals grown by the Bridgeman technique, were polished to optical quality, for precise measurement of the acoustic phonon modes along [001] pseudocubic direction., excited by a diode pumped solid state laser at a wavelength of 532 nm. For temperature variations, the crystal was put inside a cryostat cell (THMS 600) placed on the stage of an optical microscope and experiments were performed in the ambient conditions upto ~600 °C.

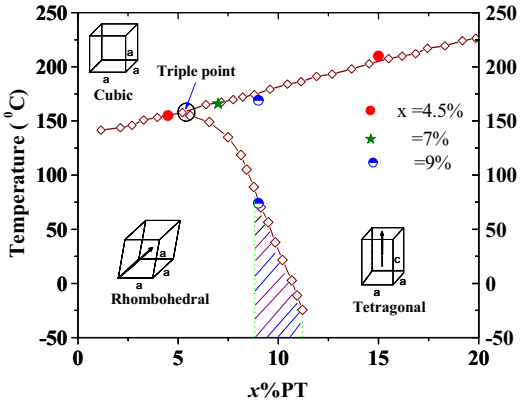

Fig.1. Standard composition-temperature phase diagram of PZN-*x*%PT single crystal showing data points measured by high-resolution micro-Brillouin scattering.

3. Results and discussion

In order to extract the Brillouin frequency shift (Δν) of the longitudinal acoustic (LA) phonon mode from the measured spectra, the Stoke and anti-Stoke components of the LA mode were described by the spectral response function of damped harmonic oscillator of amplitude *A*:

$$I(\nu) = \sum_i \frac{A_{oi}\Gamma_i \nu_{0i}^2 \nu}{(\nu^2 - \nu_{0i}^2)^2 + \Gamma_i^2 \nu^2} \qquad (1)$$

where Γ_i and ν_{oi} are the damping factor mode frequency, respectively.

The calculated values of Δν for the two crystals are plotted in Fig. 2 in which the existence of different acoustic anomalies can be clearly differentiated. The observed paraelectric to

ferroelectric phase transition temperatures fit very

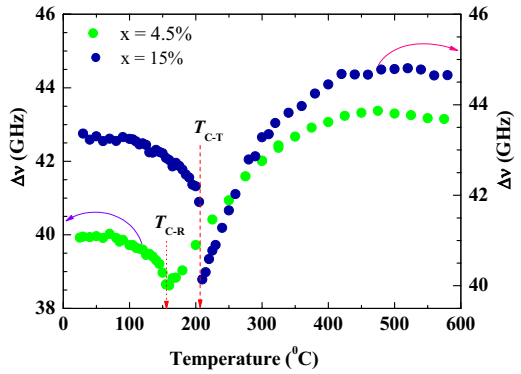

Fig. 2. Temperature dependence of frequency shift of the longitudinal acoustic phonon mode of PZN-*x*%PT single crystals.

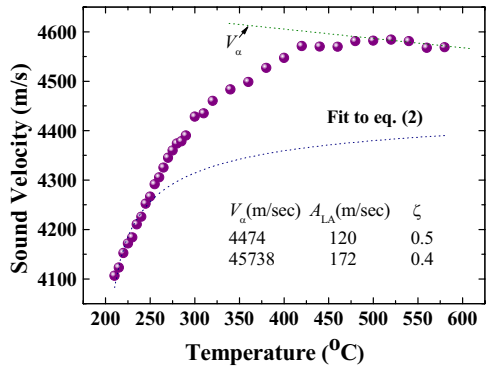

Fig. 3. Best fit of Eq. (2) to the measured sound velocity of PZN-15%PT crystal for $T>T_{C\text{-}T}$.

well in the well established phase diagram of PZN-*x*%PT (Fig. 1).

In the light of mean field approximation, anomalous part of ultrasonic velocity of $BaTiO_3$ in the paraelectric phase can be approximated [6] to the following equation in the vicinity ($T_C\langle T\langle T_C$+40 ^{o}C) of the phase transition temperature (T_C).

$$V_{LA} = V_\alpha - A_{LA}\left(\frac{T-T_C}{T_C}\right)^{-\zeta} \qquad (2)$$

where V_α and A_{LA} are fitting parameters while the exponent ζ was either fixed to 0.5 (theoretical value) or considered as a free variable.

The experimental data for both crystals could not be fitted to a reasonable approximation, however, it is important to mention that for PZN-15%PT the best possible values of fitting parameters were relatively better as compared to PZN-4.5%PT. Interestingly the values of fitting parameters (shown inside Fig. 3) are comparable to those observed for $BaTiO_3$ [6] but the reason for this similarity is needed to be investigated further.

In order to further understand the behavior of acoustic parameters in the paraelectric phase, a logarithmic temperature scale [7] approach under the mean field approximation was applied to the measured data. According to this approach the elastic constant c_{11} (=c_{22}=c_{33}) in the paraelectric phase may be described as:

$$c_{11}(T) = c_\infty - ALog\left(\frac{T-T_o}{T_o}\right) \qquad (3)$$

where c_∞ is the unrelaxed elastic constant in the absence of order parameter, and A and T_o are fitting parameters.

A fairly good agreement between the experimental and fitted values of c_{11} could be obtained up to $T_{C\text{-}T}$+75 ^{o}C for PZN-15%PT crystal. On the other hand, for PZN-4.5%PT, fitting process gave non-physical values of fitting parameters even by further narrowing the upper temperature limit. The exact reason for this discrepancy is not known but it can be argued at least on qualitative basis that Eq. 3 is applicable to compositions with enhanced ferroelectric character *i.e.* higher PT contents in PZN-*x*%PT phase diagram. It is anticipated that PNRs have substantial effect on the elastic properties of RFEs in the paraelectric regime above the FE structural phase transition temperature.

References

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