Micro-Brilouin scattering study of field cooling effects on ferroelectric relaxor PZN-9%PT single crystals

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I. What is relaxor ferroelectrics?

- Diffused, rounded and frequency-dependent dielectric constant (high dielectric constant near room temperature)
- Existence of nanopolar clusters at high temperatures
- No macroscopic change of the symmetry in many compounds
- Dipolar glass model / random field model

\[ \text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3 \]
Examples of Ferroelectric Relaxors

- **Complex Perovskites**
  
  **B-site complex**
  
  Lead magnesium/zinc niobate $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$, $\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3$
  
  Lead scandium/magnesium tantalate $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$, $\text{PbMg}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (cf: $\text{BaMg}_{1/2}\text{Ta}_{1/2}\text{O}_3$)

  **A-site complex**
  
  Lead lanthanum zirconate titanate
  
  $(\text{Pb}_{1-x}\text{La}_x)(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ (PLZT100(x/y/1-y))

- **Tungsten bronze structure compositions**
  
  Strontium barium niobate $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$
Complex Perovskite Relaxors

- Relaxor-based complex perovskite ferroelectrics:
  - Pb[(Zn_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3 (PZN-x%PT)
  - Pb[(Mg_{1/3}Nb_{2/3})_{1-x}Ti_x]O_3 (PMN-x%PT)
- outstanding piezoelectric properties when the electric field is along non-polar direction like [001]
  - strain level ~ 1.7 %
  - electromechanical coupling constant > 90%
- promising materials for electromechanical applications like actuators, transducers…
- superior to PZT due to the single crystal form
• What changes can we expect from field cooling studies on PZN-9%PT rather than 8% composition?
• Comparison between PZN-8%PT and PZN-9%PT is necessary for our better understanding of the morphotropic phase boundary (MPB).
II. Experimental Details:

Tandem multi-pass Fabry-Perot interferometer

1. The conventional scanning-type tandem multipass Fabry-Perot Interferometer is characterized by high contrast and resolution.
2. The combination of tandem FPI and a microscope made it possible to examine elastic properties of very small samples whose sizes are only a few microns.
3. The phonon propagating direction was along [001] of PZN-9%PT at a backward scattering geometry, which was the same direction of the applied DC bias field. Incident polarization was [010], and no analyzer was used for the scattered light.
III. Results (1) – temperature dependence of Brillouin spectra of PZN-9%PT under ZFC

- Typical Brillouin spectra consisted of one longitudinal acoustic (LA) mode, one weak transverse acoustic (TA) mode and a central peak (CP), where the TA mode is noticeable only in the low-temperature rhombohedral phase below 73 °C.

- From a symmetrical point of view since the TA mode is not allowed at the present scattering geometry in both cubic and tetragonal phases.
III. Results (2) – Comparison of Brillouin data between PZN-4.5% and 9%PT

- Clear hysteresis can be seen from the Brillouin shift measured during heating and cooling in both components.
- It may indicate complex dynamics related to the formation of microdomains and glassy dynamics at low temperatures in case of PZN-4.5%PT and first-order character of the successive phase transitions in case of PZN-9%PT.
III. Results (3) – Brillouin frequency shift and hypersonic damping of 9%PT

- Two abrupt step-like changes in frequency shift and FWHM are very significant at two phase transition temperatures from cubic-to-tetragonal and tetragonal-to-rhombohedral phases ($T_{C-T}$ and $T_{T-R}$).
- The differences of frequency shift and FWHM in both phases below $T_{C-T}$, observed at the same measured point of PZN-9%PT during heating and cooling processes, may reflect the microheterogeneity which is inherent in ferroelectric relaxors near MPB.
III. Results (4) – Field cooling effects on the Brillouin spectra of PZN-9%PT

1. The temperature range of the tetragonal phase is significantly extended into both high- and low-temperature sides under the electric field along the [001] direction.

2. The discontinuity at $T_{C-T}$ under ZFC process is smeared out during the FC process as the amplitude of the biasing electric field increases.

3. The phonon damping has been greatly suppressed by the application of the poling field probably due to the marked decrease of scattering at domain walls.
III. Results (5) – Bias-field dependence of the Brillouin data at constant temperatures

- At temperatures far above $T_{C-T} \sim 162$ °C, LA induced by the biasing field gradually approaches the value of the tetragonal phase. However, as the temperature approaches closer to $T_{C-T}$, the change of the frequency shift becomes more drastic.
- At temperatures of 180 and 170 °C above $T_{C-T}$, the smallest applied fields of 1.1 kV/cm was enough for making the frequency shift equal to the value of a tetragonal phase.
- On the other hand, a tetragonal phase is induced from a rhombohedral a phase at 50 °C by applying an electric field of 6.7 kV/cm. Only at 30 °C a low-temperature rhombohedral phase can be stable under the biasing field up to 6.7 kV/cm.
III. Results (6) — Tentative E-T phase diagram of PZN-9%PT

A E-T phase diagram of PZN-9%PT can be constructed from the present study by observing the changes of the frequency shift as a function of the temperature under the constant biasing field or of the biasing field at a constant temperature.

- The change of the Curie temperature (Tc) under the applied field gives the values of $dTc/dE \approx 7.8 \times 10^{-3}$ K cm/V and $-5.8 \times 10^{-3}$ K cm/V for $Tc-T$ and $T_{T-R}$ phase boundaries, respectively.
Conclusions

• Variation of phase transition have been examined in PZN-9%PT under the electric field along the [001] direction by the high-resolution micro-Brillouin scattering. Very sharp step-like changes in both LA mode frequency and damping factor have been observed in ZFH and ZFC processes. The significant thermal hysteresis was observed in cubic-to-tetragonal and tetragonal-to-rhombohedral phase transitions. The absolute values of frequency shift and damping factor depend on the thermal history, which may reflect the microheterogeneity of relaxor ferroelectrics.

• The first-order nature of the cubic-to-tetragonal phase transition seems to disappear at the poling field of 6.7 kV/cm along the [001] direction, while the sharp step-like transition from tetragonal to low-temperature phase still remained. The temperature range of a tetragonal phase of PZN-9%PT has been significantly widened under the electric field along [001] into both low-temperature and high-temperature sides, which is in contrast to the situation of PZN-8%PT. A new electric field-temperature phase diagram of PZN-9%PT has been determined based on the changes of the phase transition temperatures.
References