Dynamic Polar Nanoregions and Broken Local Symmetry in Relaxor Ferroelectrics Probed by Inelastic Light Scattering

Seiji Kojima*, Ryu Ohta, Takuma Ariizumi, and Junta Zushi
Graduate School of Pure and Applied Sciences, University of Tsukuba, Tsukuba, Ibaraki
305-8573, Japan
*kojima@bk.tsukuba.ac.jp

Abstract

The precursor dynamics of relaxor ferroelectrics are studied by Brillouin and Raman scattering. Above $T_C$, Raman scattering spectra reflect the existence of polar nanoregions (PNRs) by broken local symmetry in a cubic matrix. The polarization fluctuations in dynamic PNRs induce elastic anomaly and an intense broad central peak below Burns temperature $T_B$. The average size of dynamic PNRs was estimated as a function of temperature assuming the local piezoelectricity in PNRs owing to the lack of the center of symmetry. The marked growth of the size towards $T_C$ was found in a cubic paraelectric phase. In normal ferroelectric KTN, BaTiO$_3$ also show the precursor dynamics related to dynamic PNRs.

KEYWORDS: relaxor, ferroelectric, polar nanoregion, broken symmetry, elastic anomaly, central peak, Brillouin scattering

1. Introduction

Ferroelectric oxides with perovskite structure have been mostly studied by the structural simplicity and rich of application as functional materials. The origin of ferroelectricity in BaTiO$_3$ has been discussed extensively by the displacive model in which the condensation of anharmonic soft optic mode causes spontaneous polarization. However, the order-disorder nature was also discussed on the basis of the pseudo Jahn-Teller effect (PJTE) and the diffraction study. Recently it was reported that the coexistence of displacive and order-disorder processes still remain even in the lowest temperature rhombohedral phase. Such a coexistence in perovskite ferroelectrics was also discussed by the polarizability model and it was predicted that both dynamics appear in different time scales. The recent Brillouin scattering study of BaTiO$_3$ clarified the order-disorder behavior in a gigahertz range, and SHG signals were observed above $T_C$ owing to the broken local symmetry.

In contrast to normal ferroelectric BaTiO$_3$, relaxor ferroelectrics (RFs) such as Pb(Mg$_{1/3}$Nb$_{2/3}$)$_3$O$_5$ (PMN), Pb(Sc$_{1/2}$Nb$_{1/2}$)$_3$O$_5$ (PSN) with B-site disorder undergoes diffusive phase transitions and remarkable dielectric dispersion near Curie temperature $T_C$. Another
interest on RFs is the colossal piezoelectric response observed in PMN-PbTiO$_3$ solid solutions. The origin of RF behaviors has been attributed to the nanoscale heterogeneity, namely, chemical ordered regions (CORs) and the polar nanoregions (PNRs), which are related to random fields. However, the recent study shows that CORs only contribute diffuseness partly and PNRs plays the dominant role in RFs. The current interests of PNRs are the temperature evolution and the roles of static/dynamic PNRs. The schematic temperature evolution of PNRs is shown in Fig. 1. At Burns temperature $T_B$ which is typically a few hundreds degrees above $T_C$, the nucleation of PNRs starts and their size/volume gradually increase on cooling. $T_B$ was defined by the change of refractive index owing to the second order electro-optic (Kerr) effect induced by polarization islands in a nanometer scale. It was suggested that $T_B$ can be associated with the formation of short lived correlations between the off-centered ions without local strain fields. For further cooling from $T_B$, the existence of the intermediate temperature $T^*$ was detected by acoustic emissions (AEs) in several kinds of relaxor ferroelectrics. It is speculated that at $T^*$ PNRs start to correlate to each other, transforming from dynamic to static. The precursor dynamics related to the evolution of PNRs is not yet understood well and it becomes one of the most important topics in condensed matter physics.

![Fig. 1](image)

Fig. 1 Evolution of dynamic and static polar nanoregions in relaxor ferroelectrics, where $T_B$, $T^*$, $T_m$, and $T_C$ denote Burns temperature, intermediate temperature, dielectric maximum temperature, and Curie temperature, respectively.

In the high-symmetry paraelectric phase, local symmetry breaking occurs in PNRs. Both static and dynamic PNRs induce the Raman scattering of forbidden modes in a high-symmetry paraelectric matrix in the terahertz range. Brillouin scattering in the gigahertz range shows elastic anomaly through the local piezoelectric coupling in dynamic PNRs and broad central peak owing to the local polarization fluctuations in dynamic PNRs. This paper reports the
recent progress to understand dynamic PNRs in RFs. The precursor dynamics and the
temperature evolution of dynamic PNRs are investigated using the broadband inelastic light
scattering spectroscopy. The precursor dynamics of normal ferroelectric phase transitions is
also discussed.

2. Broken local symmetry in a paraelectric cubic phase of relaxor ferroelectrics

In the most of perovskite oxide ferroelectrics, the high-temperature prototypic paraelectric
phase is cubic system with the space group of \( Pm\bar{3}m \) (\( Z=1 \)). In the first-order Raman selection
rule, optical modes have Raman inactive \( T_{1u} \) and \( T_{2u} \) symmetry. It is known that Raman
scattering is very sensitive to the local symmetry breaking by the observation of the forbidden
optical bands arising from local symmetry breaking. As a typical case, the appearance of the
first order Raman scattering in a cubic paraelectric phase is shown in Fig. 2. It shows Raman
scattering spectra of relaxor ferroelectric \( 0.85\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.15\text{PbTiO}_3 \) (PZN-15PT) above
and below \( T_C = 481 \) K observed at the backward scattering geometry \( a(cc)a \).\(^{15} \) Main Raman
peaks are the Pb-localized mode near 55 cm\(^{-1} \), the B-cation localized mode near 255 cm\(^{-1} \), and
the polar oxygen octahedral mode near 815 cm\(^{-1} \). The intense first order Raman scattering still
remain above \( T_C \), it indicates the existence of local lattice distortion which destroys the center
of symmetry in cubic matrix. As the origin of the broken cubic symmetry, the fluctuating local
polarization along [111] direction predicted by PJTE\(^2 \) may appears in a dynamic PNR below \( T_B \).
Such local polarizations break the center of symmetry through the local rhombohedral
distortions induced by the local piezoelectric coupling in PNRs.

Figure 2 shows the another important feature of relaxor ferroelectrics. In displacive-type
ferroelectrics, a soft optic mode is usually observed below 100 cm\(^{-1} \). However, the Pb-localized
mode near 55 cm\(^{-1} \) does not show such a softening. In general, Pb-based perovskite relaxor
ferroelectrics do not show any soft mode, while show a temperature dependent broad central
peak related to polarization fluctuations of dynamic PNRs as discussed in 3.2.
3. Precursor dynamics of relaxor ferroelectrics

In this section, dynamics related to the temperature evolution of PNRs in a paraelectric phase are discussed in relation with elastic anomaly, central peak, and size of dynamic PNRs.

3.1 Elastic anomaly

When the LA mode propagates in RFs, it interacts with local polarization fluctuations of dynamic PNRs through electrostrictive coupling in cubic matrix and local piezoelectric coupling in PNRs. The dominant change of phase velocity of LA mode, $V_L$, occurs according to the following equation as similar to the Kerr effect which is proportional to $\langle P_iP_j \rangle$,

$$V_L = V_L^0 + V_L^1 \langle P_iP_j \rangle$$ \hspace{1cm} (1)

where $V_L^0$ and $V_L^1$ are constants, $\langle \rangle$ means ensemble average.

In a paraelectric phase above $T_C$, there is no first order term of polarization according to Neumann’s principle of symmetry. At very high temperatures, it holds that

$$\langle P_iP_j \rangle = 0 \quad \text{for} \quad T > T_B .$$ \hspace{1cm} (2)

However, below $T_B$ dynamic PNRs with local polarization appears. Then,

$$\langle P_iP_j \rangle \neq 0 \quad \text{for} \quad T < T_B .$$ \hspace{1cm} (3)

Since the $V_L^0$ shows the linear temperature dependence, $V_L$ shows the deviation below $T_B$ as shown in Fig. 3 for the case of B-site disordered PSN. Below $T_B$, the second term of

![Raman scattering spectra of PZN-15PT above and below $T_C$.](image)
$V_L^2 \langle P_i P_j \rangle$ increases gradually owing to the growth of PNRs toward $T_C$. Such an anomaly is generally observed in relaxor ferroelectrics. The growth process of PNRs is important and the temperature variation of the size of dynamic PNRs is discussed in 3.1.

![Brillouin scattering spectrum](image)

**Fig. 3** Broadband Brillouin scattering spectrum of PZN-30PT above and below $T_C = 500$ K observed at the backward scattering geometry $ax/cc/a$. The sharp peaks at 32 and 50 GHz are TA and LA peaks, respectively. The broad central peak of quasi-elastic scattering from relaxation mode of local polarization fluctuations becomes very week above $T^* \sim 560$ K.

### 3.2 Central peak

The quasi-elastic scattering due to relaxation process appears as broad Rayleigh wings in an inelastic light scattering spectrum. It is called a central peak (CP), which has been observed not only in ferroelectrics but also in supercooled liquids. The width of CP is approximately proportional the reciprocal of relaxation time. The critical slowing down of relaxation time is observed in the order-disorder type phase transition. As a general aspect in Brillouin scattering spectra of relaxor ferroelectrics an intense broad CP appears below $T_B$ and its intensity increases toward $T_C$, and becomes weak below $T_C$ as shown in Fig. 4 for the case of 0.70PSN-0.30PT (PSN-30PT). Simultaneously the CP width shows remarkable narrowing from $T_B$ down to $T_C$. Under the assumption of a single Debye relaxation process, the relaxation time $\tau_{CP}$ is determined by the relation $\pi \times (\text{CP width}) \times \tau_{CP} = 1$. The temperature dependence of the reciprocal of $\tau_{CP}$ is plotted in Fig. 5. It shows the critical slowing down of dynamic PNRs toward $T_C = 500$ K. Such a critical slowing down has been generally observed in relaxor ferroelectrics not only perovskite but also tungsten bronze structures.
Fig. 4 Temperature dependence of LA mode frequency of PZN-30PT related to elastic anomaly above and below $T_C = 500\, \text{K}$. The deviation from the linear part appears below $T_B$.

Fig. 5 Plots of reciprocal relaxation time which shows critical slowing down in PZN-30PT which obeys Curie-Weiss law.

3.3 Size of dynamic polar nanoregions

The growing process of PNRs is one of the most important topics in ferroelectrics. It is possible to observe the images of static PNRs by TEM or piezoforce microscopy.\textsuperscript{20} However, it is difficult to observe fluctuating dynamic PNRs by such conventional experimental methods. Therefore, the average size of dynamic PNRs was estimated by Brillouin scattering measurement.\textsuperscript{12,21}
The thermally fluctuating of the local spontaneous polarization in a particular PNR induces flipping of local strain by the local piezoelectric coupling due to the lack of the center of symmetry in PNRs. By the bilinear coupling between polarization and strain, the speed of the propagation of local polarizations in a PNR can be equal to the speed of the propagation of local strain flipping motion in a PNR. Therefore, the size of a flipping PNR can be approximately equal to the propagation length of the LA mode during the flipping period. The length, \( l_{PNR} = V_{LA} \times \tau_{CP} \), may give the rough estimation of the average size of dynamic PNRs. The temperature dependence of the average size of PNRs of PSN-30PT is shown in Fig. 6.12 Below the intermediate temperature \( T^* \), at which the rapid growth of PNRs starts, the remarkable increase of the size occurs towards \( T_C \). The CP is very sensitive for the fluctuations of dynamic PNRs, while is not sensitive to static local polarizations in static PNRs. Therefore, it is expected that the size of static PNRs become much larger than that of dynamic one just above \( T_C \).

![Figure 6](image_url)

**Fig. 6** Temperature dependences of size of dynamic polar nanoregions of PSN-30PT with \( T_C = 500 \) K.

4. **Precursor dynamics of normal ferroelectrics**

Nowadays the existence of PNRs and the role in relaxor nature have been widely accepted. In this section, precursor dynamics of normal ferroelectric are discussed. The dielectric anomaly of normal ferroelectrics obeys Curie-Weiss law, in contrast with diffuse and dispersive dielectric anomalies in RFs.

In BaTiO\(_3\), Burns reported the deviation of refractive index from the linear temperature dependence about 120 K above \( T_C \) as similar to that of RFs.22 The existence of the intense first order Raman scattering was also observed above \( T_C \). These results suggested broken local symmetry in a cubic paraelectric phase with space group \( Pm\bar{3}m \) (Z=1). To clarify the precursor...
dynamics intensively, the temperature dependence of SHG was measured accurately. In a BaTiO$_3$ crystal, the SHG intensity appears clearly above $T_C$. The power law of the SHG integrated intensity showed the crossover, near $T_B$~580 K, from the exponent $\gamma=1$, reflecting the scattering by polarization fluctuations, into the larger exponent $\gamma=2$, reflecting the scattering by PNRs having strongly correlated polar displacements. According to PJTE, the displacement of a Ti ion along a [111] direction from the center of an oxygen octahedron was predicted in agreement with the x-ray diffraction study. The local polarizations coupled to the local rhombohedral distortions may enhance the first order Raman scattering in a cubic paraelectric phase. Recently the critical slowing down of order-disorder nature has been observed in the vicinity of $T_C$ by Brillouin scattering study.

KTa$_{1-x}$Nb$_x$O$_3$ (KTN) undergoes a ferroelectric phase transition similar to BaTiO$_3$. The intense first order Raman scattering appears also in a paraelectric phase with space group $Pm\bar{3}m$. KTN32 ($x=0.32$) crystals with $T_{C-T}=258$ K were studied by broadband Brillouin scattering. The elastic anomaly and the broad central peak owing to local polarization fluctuations of PNRs were observed above $T_C$. The acoustic emission count rate was also studied as a function of temperature, and $T_B=620$ K and $T^*=310$ K were found. The average size of a dynamic PNR was estimated as a function of temperature, and the marked growth of the size starts at $T^*$ predicted by the recent AE study as shown in Fig. 7. The size increases gradually in relaxor PSN-30PT, while the size of KTN32 shows the rapid increase just above $T_C$. Such a difference has the correlation with the very sharp dielectric anomaly of KTN32 in the vicinity of $T_C$.

According to these experimental results it is concluded that, at least for perovskite oxide ferroelectrics, the precursor dynamics of PNRs can be common nature in a cubic paraelectric phase not only RF but also normal ferroelectrics. The difference of dynamics between normal and RFs can be ascribed to static PNRs and CORs related to the random fields of RFs, which suppress the growth of dynamic PNRs and enhance the dynamic to static transition of PNRs below $T^*$. Brillouin scattering is also a powerful tool to study diffusive nature caused by static PNRs and CORs through the observations of the diffuse elastic anomaly and the extended slowing down of the relaxation time.
**Fig. 7** Temperature dependences of size of dynamic polar nanoregions of KTN32 with $T_C=258$ K.

5. **Conclusion**

The dynamical precursor dynamics of relaxor ferroelectrics are studied by Brillouin and Raman scattering. Above $T_C$, Raman scattering spectra reflect the existence of dynamic PNRs by broken local symmetry in a cubic matrix. The polarization fluctuations in dynamic PNRs induces elastic anomaly related to the second order effect of polarization and the intense broad central peak by the relaxation process, which shows the critical slowing down of relaxation time $\tau_{cp}$ above $T_C$. The average size of a dynamic PNR was estimated as a function of temperature, and the marked growth of the size toward $T_C$ was found in a cubic paraelectric phase. In normal ferroelectric KTN, BaTiO$_3$ also show the precursor dynamics related to dynamic PNRs. The difference between relaxor and normal ferroelectrics is attributed to the static PNRs and CORs related to random fields of relaxor ferroelectrics.

**Acknowledgements**

The authors are thankful for the collaboration to Prof. Z.-G. Ye, Prof. K.-H. Ko, Prof. S. Tsukada, Dr. M. Ahart, Dr. G. Shabbir, and Dr. V. Sibasbramanian. The author (S. K.) is grateful for the discussion with Prof. A. Bussmann-Holder, Prof. I. B. Bersuker, Prof. M. Kaplan, and Prof. H. Koizumi during the 21st International Symposium of the Jahn-Teller Effect, 26-31 August, 2012, Tsukuba.

**References**

1. W. Cochran: Adv. Phys. 9 (1960) 387.
2. I. B. Bersuker: Phys. Lett. 20 (1966) 589, Phys. Rev. Lett. 108 (2012) 137202.
3. R. Comes, M. Lambert, and A. Ginner, Solid State Commun. 6, 715 (1968).
4. G. Völkel and K. A. Müller, Phys. Rev. B 76 (2007) 094105.
5. Annette Bussmann-Holder, J. Phys.: Condens. Matter 24 (2012) 273202.
6. J.-H. Ko, T.H. Kim, K. Roleder, D. Rytz, and S. Kojima: Phys. Rev. B 84 (2011) 094123.
7. A. M. Pugachev, V. I. KOvalevskii, N. V. Surovtsev, S. Kojima, S. A. Prosandeev, I. P. Raevski, and S. I. Raevskaya, Phys. Rev. Lett. 108, 247601 (2012).
8. G.A. Smolenskii, J. Phys. Soc. Jpn. 28 (1970) 26.
9. X. Zhao, W. Qu, X. Tan, A.A. Bokov, and Z.-G. Ye, Phys. Rev. B 79 (2009) 144101.
10. S. Kojima, M. Ahart, V. Sibasbrumanian, A.A. Bokov, and Z.-G. Ye, J. Adv. Diele. 2 (2012) 1241004.
11. Y. P. Shi and A. K. Soh: Appl. Phys. Lett. 99 (2012) 092908.
12. S. Kojima, S. Tsukada, A.A. Bokov, and Z.-G. Ye, J. Appl. Phys. 109, 084114 (2011).
13. G. Burns and F. H. Dacol, Phys. Rev. B 28, 2527 (1983).
14. M. Roth, E. Mojaev, E. Dul’kin, P. Gemeiner, and B. Dkhil, Phys. Rev. Lett. 98, 265701 (2007).
15. Md. S. Islam, S. Tsukada, W. Chen⁴, Z.-G. Ye, and S. Kojima, (to be submitted).
16. M. Ahart, A. Hushur, Y. Bing, Z. Ye, R. J. Hemley, and S. Kojima: Appl. Phys. Lett. 94 (2009) 142906.
17. S. Kojima and J.-H. Ko: Curr. Appl. Phys. 11 (2011) S22.
18. V. Sivasburamanian and S. Kojima, Phys. Rev. B 85 (2012) 054104.
19. J.-H. Ko and S. Kojima: Appl. Phys. Lett. 91 (2007) 082903.
20. V. V. Shvartman and A. L. Kholkin: J. Adv. Diele. 2 (2012) 1241003.
21. S. Kojima and S. Tsukada, Ferroelectrics 405 (2010) 32.
22. G. Burns and F. H. Dacol, Ferroelectrics 104, 25 (1990).
23. R. Ohta, J. Zushi, T. Ariizumi, and S. Kojima, Appl. Phys. Lett. 98, 092909 (2011).
24. E. Dul’kin, S. Kojima, and M. Roth, Euro. Phys. Lett., 97, 57004 (2012).
25. S. Tsukada and S. Kojima: Phys. Rev. B 78 (2008) 144106.