

Central-Peak Behaviors of Uniaxial Tungsten-Bronze Relaxor Ferroelectrics

Jae-Hyeon KO*

Department of Physics, Hallym University, Chuncheon 200-702

Do Han KIM[†] and Seiji KOJIMA

Institute of Materials Science, University of Tsukuba, Tsukuba, Ibaraki 305-8573, Japan

A Brillouin light-scattering study has been carried out on tungsten-bronze ($\text{Sr}_{0.61}\text{Ba}_{0.39}$)₅Nb₁₀O₃₀ (SBN-61), $\text{K}_{5.80}\text{Li}_{3.82}\text{Nb}_{10.12}\text{O}_{30}$ (KLN-1) and $\text{K}_{5.20}\text{Li}_{2.34}\text{Nb}_{10.88}\text{O}_{30}$ (KLN-2) single crystals. Polarized central peaks (CPs) were observed in SBN-61 and KLN-1, which exhibited diffused ferroelectric phase transitions. However, no CP was observed from KLN-2 that did not show any signature of structural phase transformation as well as relaxor behaviors. The CP in KLN-1 persisted even at temperatures above T_c , where dielectric dispersion was observed. In this respect, CP behaviors in uniaxial relaxor ferroelectrics were interpreted to reflect the anisotropic polarization fluctuations correlated with the fast dynamics of precursor polar nano regions (PNRs).

PACS numbers: 77.80.-e, 78.35.+c, 62.20.Dc

Keywords: Uniaxial relaxor, Tungsten-bronze, Brillouin scattering, Central peak, Polar nano region

I. INTRODUCTION

Tungsten-bronze (TB) crystals have attracted increasing attention for many applications, due to their superior pyroelectric, piezoelectric, photorefractive, and non-linear optical properties. TB crystals show various interesting phase sequences depending on the cations and their site occupancies, and disorder in the cation distribution usually provides the phase transition with diffuseness to some degree [1]. For example, the unfilled TB ($\text{Sr}_{0.61}\text{Ba}_{0.39}$)₅Nb₁₀O₃₀ (SBN-61) shows diffuse ferroelectric phase transitions from paraelectric $4/mmm$ to polar $4mm$ symmetry upon cooling, exhibiting relaxor behaviors, which were interpreted in the framework of the random-field Ising model [2]. An ideally stoichiometric potassium lithium niobate, $\text{K}_6\text{Li}_4\text{Nb}_{10}\text{O}_{30}$ (KLN), is known to be a completely filled TB system. However, this ideal KLN is not stable within the TB structure and can be stabilized only in the presence of excess Nb [3]. The phase transition behavior of KLN is known to be very sensitive to the composition and the structural disorder [4].

A polar nano region (PNR) has been suggested as a key concept for the understanding of the peculiar characteristics of ferroelectric relaxors. Relaxors are commonly characterized by lattice disorder such as lattice defects and chemical substitution. A PNR is a nano-sized region where local symmetry breaking occurs and thus fluctu-

ating dipolar polarization appears. In the case of TB relaxor crystals, substitutional charge disorder gives rise to quenched random fields (RFs), whose spatial fluctuations are responsible for the correlation of the dipolar fluctuations resulting in PNRs. The formation and temperature evolution of PNRs have been accompanied by many unusual properties, such as the deviation of the dielectric constant from the high-temperature Curie-Weiss law as well as significant dielectric dispersion upon cooling, appearance and growth of diffuse elastic scattering, deviations of the index of refraction and the volume of the cubic cell from high-temperature linearities, *etc.* [5, 6]. Although macroscopic dipolar polarization is zero at high temperatures, due to the randomness of the polarization directions of PNRs, the square of the local polarization is not zero, from which electrostrictive coupling between the polarization and other degrees of freedom is expected. Upon cooling, the correlation length of PNRs increases and the sample may either undergo cooperative ferroelectric phase transition or keep the relaxor state without long-range order, depending on whether PNRs percolate the sample or not.

A quasielastic central peak (CP) centered near zero frequency shift, observed in either the light-scattering or the neutron-scattering spectrum, has been studied from the viewpoint of critical dynamics of structural phase transitions [7]. Many origins have been suggested for the appearance of CPs, such as entropy fluctuations, molecular reorientations, dielectric relaxation, phonon density fluctuations, over-damped soft modes, *etc.* CPs are also observed in relaxor ferroelectrics and considered to be another signature representing the dynamics of PNRs,

*E-mail: hwangko@hallym.ac.kr; Fax: +82-33-256-3421

[†]Present address: PDP Research Lab., PDP Division, LG Electronics Inc., Gumi 730-702

because thermally fluctuating dipole moments in PNRs are usually induced by off-center ions. It is well known that the reorientation of off-center ions in multi-well potentials is responsible for the formation of dynamic CPs. The width of CP is inversely proportional to the relaxation time of the PNRs. Systematic investigations of the acoustic properties and the CP behaviors of lead-based relaxors have been carried out by Brillouin scattering [8–10]. The temperature dependence of CP behaviors of uniaxial SBN-61 has also been reported previously [11, 12], and the integrated intensity of CP showed a maximum near the diffuse phase transition temperature, ~ 325 K. In the case of KLN crystals, absolute values of elastic stiffness coefficients of two kinds of KLN have been investigated in our previous study [13]. However, qualitative and quantitative analyses of the CP behaviors of these TB crystals are still lacking, and the correlation between the CP and the dynamics of PNRs requires a more systematic approach from both the experimental and the theoretical point of view.

In this paper, detailed characteristics of broadband Brillouin spectra of SBN-61 and two kinds of KLN crystals are reported. We suggest that the appearance of CP in uniaxial TB relaxor crystals is clearly related to the diffuse phase transition, and hence to the formation and growth of PNRs. In addition, it is found that the quasielastic CP of SBN-61 consists of two different components by using a broadband spectroscopic approach.

II. EXPERIMENT

Congruently melting strontium barium niobate SBN-61 was grown by the Czochralski technique. Two kinds of KLN single crystals were grown from non-stoichiometric melts with mole ratios of $\text{K}_2\text{CO}_3 : \text{Li}_2\text{CO}_3 : \text{Nb}_2\text{O}_5 = 3 : 2.5 : 5$ and $3 : 2 : 5$ by the Czochralski method [14]. Exact compositions were confirmed to be $\text{K}_{5.80}\text{Li}_{3.82}\text{Nb}_{10.12}\text{O}_{30}$ (KLN-1) and $\text{K}_{5.20}\text{Li}_{2.34}\text{Nb}_{10.88}\text{O}_{30}$ (KLN-2) by using an inductively coupled plasma emission spectrophotometer (Shimadzu ICP-1000). A 3+3 pass Sandercock-type tandem Fabry-Perot interferometer was used to measure the Brillouin spectra at a special right-angle scattering geometry for CP [15] and a backward scattering geometry for obtaining the elastic stiffness coefficient, c_{33} . A diode-pumped solid-state laser (DPSS-532) was used to excite the samples with a wavelength of 532 nm and a power of about 100 mW. The Brillouin spectrum was recorded by using a conventional photon-counting system. In the case of right-angle scattering geometry, the polarization of the incident laser was along the c -axis, and both the polarized (VV) and depolarized (VH) spectra were obtained at the $\bar{a}(cc)\bar{b}$ and $\bar{a}(c\bar{a})\bar{b}$ scattering geometries, respectively, where \bar{a} and \bar{b} denote the directions of the incident and scattered light in the plane perpendicular to the c -axis. \bar{a} and \bar{b} are inclined at 45° with respect to the tetragonal

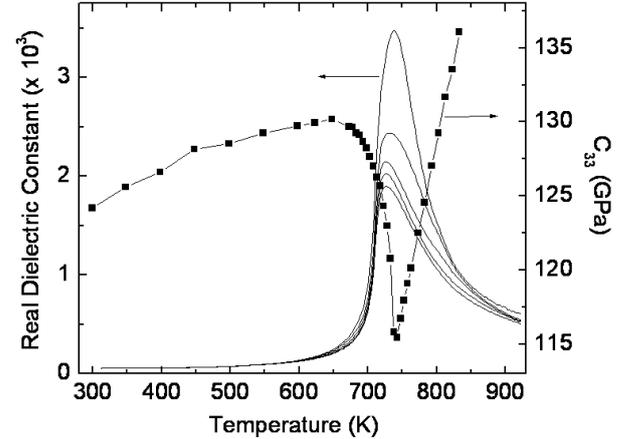


Fig. 1. Temperature dependence of the real part of the dielectric constant and the elastic stiffness coefficient, c_{33} , of KLN-1 single crystals. The measurement frequencies are 1, 3, 10, 30 and 100 kHz. The largest dielectric constant is for the lowest frequency, and the smallest for the highest frequency; the curves in between are in order of increasing frequency.

a and b axes. In order to cover a wide frequency range for probing CP of SBN-61, several free spectral ranges (FSRs) were used to obtain Brillouin spectra in a wide frequency range.

III. RESULTS AND DISCUSSION

Figure 1 shows the temperature dependences of the real part of the complex dielectric constant of KLN-1 obtained from the c -plate sample and the elastic stiffness coefficient, c_{33} , measured at a $c(aa)c$ scattering geometry, where a and c denote the tetragonal axes. The real dielectric constant exhibits a sharp drop at the phase transition temperature, (T_c) ~ 725 K, with decreasing temperature as well as a significant frequency dispersion. c_{33} shows a substantial softening upon approaching from both high- and low-temperature regions toward T_c , resulting in a minimum at T_c . Since the direction of the order parameter of the tetragonal ferroelectric TB crystals is along the polar c axis, strong coupling is expected between the polarization and the acoustic phonon propagating along the same direction. Frequency dispersion in the dielectric constant above T_c might be a signature of relaxor behaviors and hence the existence of PNRs in the paraelectric phase of KLN-1. In this case, electrostrictive coupling between the square of polarization of the PNRs and the strain may partly be responsible for the elastic instability in c_{33} in the temperature range above T_c . Other elastic stiffness coefficients did not show any anomaly near T_c . On the other hand, it was found that KLN-2 showed a very broad real-part dielectric maximum over a wide temperature range without any anomaly in dielectric loss [16]. Differential thermal

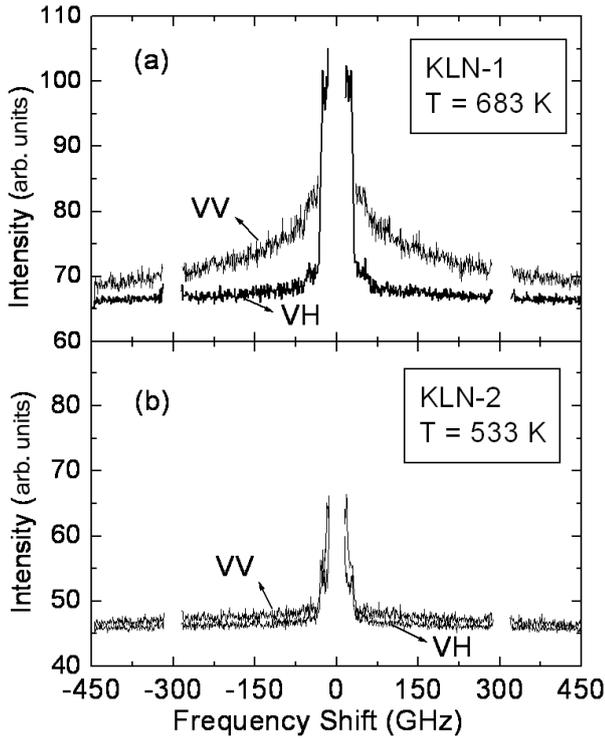


Fig. 2. Polarized and depolarized Brillouin spectra of (a) KLN-1 and (b) KLN-2.

analysis also did not reveal any anomaly in the same temperature range [14]. All these results suggest that KLN-2 experiences neither a structural phase transition nor a diffuse relaxor-like transformation, whereas KLN-1 exhibits a ferroelectric, but diffused, phase transition at ~ 725 K.

In order to investigate the distinct phase transition behaviors of KLN-1 and KLN-2 in more detail, the broadband inelastic light-scattering spectrum was measured for both single crystals. Figures 2(a) and (b) show the polarized and depolarized Brillouin spectra of KLN-1 and KLN-2, respectively. The measuring temperature of each sample was lower than the temperature at which its real dielectric constant becomes a maximum by approximately 40 K. KLN-1 shows a strong CP in the polarized spectrum, while KLN-2 does not. In the case of the depolarized component of the spectrum, both KLNs do not exhibit any CP. Sharp rises in intensity near ± 30 GHz are due to the acoustic phonons. CP of KLN-1 is substantially polarized and strongest at the scattering geometries of $\bar{a}(cc)\bar{b}$. This is consistent with the polarization dependence of CP of SBN-61 [11]. CP of KLN-1 persists up to high temperatures, even at 873 K, far above T_c , but begins to grow substantially at about 773 K upon cooling. The growth of CP in the temperature range of 773 \sim 673 K is accompanied by significant dielectric dispersion. These results, combined with the fact that the non-ferroelectric KLN-2 does not show any CP, clearly suggest that the CP observed in KLN is cor-

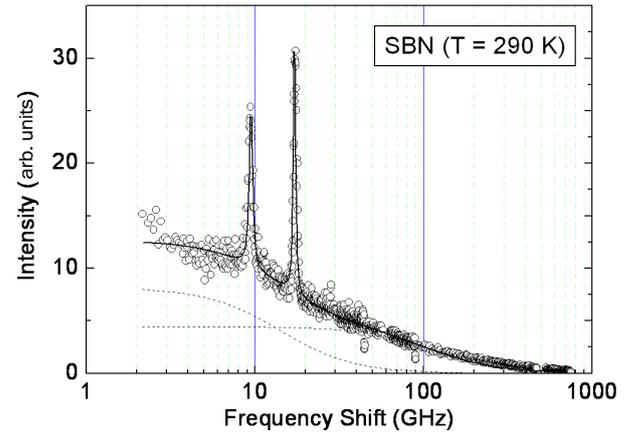


Fig. 3. Polarized Brillouin spectrum of SBN-61, measured at 290 K, shown in semi-log plot. The solid line is the fitted line for the whole spectrum, while the two dashed lines are two Lorentzian functions for CPs.

related with the polarization fluctuations of the PNRs oriented mainly along the polar c axis. The relaxation time of the PNRs of KLN-1 can be obtained by using the full width at half maximum (FWHM) of CP and is estimated to be approximately 1.5 ps.

Figure 3 shows the polarized Brillouin spectrum of SBN-61 measured at the $\bar{a}(cc)\bar{b}$ geometry at 290 K; this is shown in semi-log plot. Three FSRs were used to cover the spectral range from 2 to 750 GHz. Two sharp peaks appearing near 10 GHz correspond to transverse and longitudinal acoustic phonons. A CP can be seen over the whole spectral range. The spectral shape of the CP could not be explained by assuming one Lorentzian function centered at zero frequency shift, and thus two Lorentzian functions were used to fit the CP, as applied to $0.71\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-}0.29\text{PbTiO}_3$ relaxor [17]. The curve fitting using two Lorentzian functions was enough to explain the whole spectrum in Figure 3, except for the high-frequency range above 200 GHz, where a slight deviation between the fitting line and data points is seen. This might be due to an additional contribution to the spectrum from nearby Raman lines. Two dashed lines in Figure 3 represent the two Lorentzian functions convoluted by the Gaussian instrumental function obtained from the curvefitting. The FWHMs of the two CPs are 232 ± 12 and 28 ± 2 GHz, and the corresponding relaxation times are approximately 1.4 ps and 11 ps, respectively. This result indicates that the quasielastic light-scattering spectrum observed from SBN-61 shows two-component CPs and seems to be related to at least two relaxation processes. The detailed temperature dependence of these two-component CPs has recently been reported elsewhere [18].

IV. CONCLUSION

From the broadband Brillouin studies carried out on two kinds of KLN and SBN-61 single crystals, we can clarify the following results regarding the origin of the quasielastic CP: (1) KLN-1 and SBN-61 show both diffuse ferroelectric phase transitions accompanied by substantial dielectric dispersion and polarized CP in the light-scattering spectrum, while the non-ferroelectric KLN-2 does not. This result provides clear evidence that CP observed in uniaxial TB relaxors reflects the relaxor behaviors, and, in particular, the polarization fluctuations of the PNRs oriented mainly along the polar c axis, which are expected to form at a high temperature far above T_c . (2) Since the CPs of KLN-1 and SBN-61 appear in the polarized scattering geometry, the CP originates from fluctuation of the diagonal component of the polarizability tensor related to the polarization fluctuations in PNRs. This indicates that the electric polarization in PNRs mainly fluctuates along the polar c -axis, owing to the uniaxial nature of the TB structure. (3) The CP of SBN-61 observed at room temperature extends from 2 to 750 GHz, which can be explained by assuming at least two relaxation processes. The relaxation times estimated from the linewidth of CP are approximately 1.4 ps and 11 ps for the faster and the slower processes, respectively.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Tae-Hoon Kim and Professor. Ji Hyun Ro for supplying us with KLN single crystals of high optical quality. This work was supported by Korea Research Foundation Grant funded by the Korean Government (MOEHRD, Basic Research Promotion Fund) (KRF-2006-331-C00088). This work was presented at the Ferroelectric Joint Symposium, which was held at Muju in Korea in February, 2007.

REFERENCES

- [1] M. E. Lines and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon Press, Oxford, 1977).
- [2] W. Kleemann, J. Dec, V. V. Shvartsman, Z. Kutnjak and T. Braun, *Phys. Rev. Lett.* **97**, 065702 (2006) and references therein.
- [3] B. A. Scott, E. A. Giess, B. L. Olson, G. Burns, A. W. Smith and D. F. O'Kane, *Mater. Res. Bull.* **5**, 47 (1970).
- [4] J. S. Kim and H.-S. Lee, *J. Crystal Growth* **223**, 376 (2001).
- [5] L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- [6] G. Burns and F. H. Dacol, *Ferroelectrics* **104**, 25 (1990).
- [7] H. Z. Cummins and A. P. Levanyuk, *Light Scattering Near Phase Transitions* (North-Holland Publishing Company, Amsterdam, 1983).
- [8] J.-H. Ko, D. H. Kim and S. Kojima, *J. Korean Phys. Soc.* **49**, S536 (2006).
- [9] D. H. Kim, S. Kojima and J.-H. Ko, *J. Korean Phys. Soc.* **46**, 131 (2005).
- [10] G. Shabbir and S. Kojima, *J. Korean Phys. Soc.* **46**, 128 (2005).
- [11] F. M. Jiang, J.-H. Ko and S. Kojima, *Phys. Rev. B* **66**, 184301 (2002).
- [12] J.-H. Ko and S. Kojima, *J. Korean Phys. Soc.* **41**, 241 (2002).
- [13] D. H. Kim, J.-H. Ko, S. Kojima, T.-H. Kim and J.-H. Ro, *J. Korean Phys. Soc.* **42**, S1080 (2003).
- [14] T. H. Kim, Y. B. Kim, J. N. Kim and J. H. Ro, *Cryst. Res. Technol.* **35**, 927 (2000).
- [15] J.-H. Ko, D. H. Kim and S. Kojima, *J. Electroceram.* **17**, 515 (2006).
- [16] J.-H. Ko, S. Kojima, S. G. Lushnikov, R. S. Katiyar, T.-H. Kim and J.-H. Ro, *J. Appl. Phys.* **92**, 1536 (2002).
- [17] S. Tsukada, Y. Ike, J. Kano, T. Sekiya, Y. Shimojo, R. Wang and S. Kojima, *Appl. Phys. Lett.* **89**, 212903 (2006).
- [18] J. -H. Ko and S. Kojima, *Appl. Phys. Lett.* **91**, 082903 (2007).