Enhanced polarization fluctuation in KF-substituted $BaTiO_3$ single crystals

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(Received 19 April 2009; revised manuscript received 21 June 2009; published 24 July 2009)

The longitudinal acoustic (LA) phonon of a $Ba_{088}K_{0.12}TiO_{2.88}F_{0.12}$ perovskite crystal was investigated through micro-Brillouin scattering measurements to clarify the effect of KF substitution in $BaTiO_3$ on the dynamical properties related to the ferroelectric phase transition. It was found that the LA phonon correlates with the relaxation of dipoles via the piezoelectric coupling inside the polar nanoclusters and that the relaxation has a time scale of 10^{-13} s; this relaxation is attributed to the hopping of Ti ions in the off-centered sites, even in the high-symmetry cubic phase. Upon KF substitution, the anomalies in the LA phonon become large, indicating that the fluctuation of the order parameter originating from the competition between dipolar forces and thermal agitation is enhanced. We consider that the fluctuation is enhanced by the random electric field induced by the KF substitution.

DOI: 10.1103/PhysRevB.80.012102 PACS number(s): 77.80.Bh, 78.35.+c, 77.84.Dy

Ferroelectric ordering in $BaTiO_3$ (BT) with an ABO_3 perovskite structure is now known to occur as a result of the freezing of one relaxation, although it had been believed to be a typical displacive-type ferroelectric material in which the soft optical mode is recognized as the Slater mode.[1] This order-disorder-type interaction in BT has been suggested as a result of various measurements such as diffuse scattering,[2] NMR,[3] and x-ray absorption fine structure.[4] It has also been suggested that the fluctuating order parameter (spontaneous polarization) originates from the electric dipole induced by a hopping Ti ion around its equilibrium cubic site at temperatures far above its Curie temperature $T_C \sim 403.5$ K. Recently, as expected from the concept of the order-disorder nature, critical slowing down has been found at approximately T_C in both the paraelectric cubic and ferroelectric tetragonal phases by measuring a central peak that is separated by Slater, Last, and Axe modes in the time scale of 10^{-13} s.[5–7]

The situation in which the order parameter fluctuates largely in the wide temperature range above T_C resembles that of relaxor ferroelectric materials.[8] However, as exhibited by the dielectric constant, there are many differences.[1,8] At the present stage, it is important to clarify the similarities and differences from the viewpoint of the behavior of the order parameter fluctuation. Relaxor ferroelectrics are widely used in the field of piezoelectric application; therefore, the comparison may indicate potential to next generation lead-free piezoelectric materials.

One candidate lead-free piezoelectric material is KF-substituted BT ($Ba_{1-x}K_xTiO_{3-x}F_x$:KF-BT/x) where K and F ions are replaced by Ba and O ions, respectively. As one of the authors (Y.A.) reported, the fluctuation of the order parameter becomes larger with the substitution of KF; simultaneously, the piezoelectric constant is enhanced to $d_{33} \sim 300$ pC/N at room temperature ~ 290 K.[9,10]

In the present Brief Report, we show the enhanced anomaly in the longitudinal acoustic (LA) phonon of a KF-BT/0.12 single crystal by measuring the micro-Brillouin scattering (inelastic light scattered by acoustic phonons). KF-BT/0.12 has a cubic-to-tetragonal phase transition at $T_C \sim 285$ K and our study shows a larger anomaly in the LA phonon than that of BT owing to the enhanced fluctuation of the order parameter. By comparing our results with those for BT, the effect of KF on the ferroelectric phase transition is discussed. Moreover, the difference between KF-BT/0.12 and relaxor ferroelectrics is explained on the basis of the behavior of the fluctuating order parameter.

A single crystal of KF-BT/0.12 with a slight yellow color was grown by the flux technique described in Refs. 9 and 10. $T_C \sim 285$ K was verified using a polarized-light microscope. Each surface is perpendicular to $[100]_C$ of the pseudocubic orientation. Micro-Brillouin scattering was measured with a high-contrast 3+3-pass tandem Fabry-Perot interferometer (JRS Scientific Instruments) combined with an optical microscope (Olympus). A diode-pumped solid-state laser (Coherent) with a single-frequency operation at 532 nm with 100 mW was used. A 180°-scattering geometry without a polarizer (vertical to open, VO) was adopted for observing the LA phonon. In the scattering geometry, the observed acoustic phonon propagates along $[100]_C$ in the cubic phase (above T_C). Before starting the measurement, the sample was annealed for 1 h at 673 K to remove any memory effect of previous treatments. The measurement was performed upon cooling.

Figure 1 gives the Brillouin scattering spectra of KF-BT/0.12 measured at several temperatures. Brillouin scattering from the LA phonon is observed in the 180°-scattering geometry without a polarizer, while that from the transverse acoustic (TA) phonon is not observed because of the symmetry restriction in a cubic phase. By considering the elasto-optical coefficient and Christoffel equation of a cubic crystal, it is apparent that the LA phonon is related to the complex elastic stiffness constant $c_{11}^{*}=c_{11}'+ic_{11}''$. In addition to Brillouin scattering, a central peak is observed with a broad frequency range, which will be discussed in our following paper. To extract the frequency shift and width of each peak in the light-scattering spectra, we used Voigt functions, where the width of the Gaussian component in the Voigt function was fixed as an instrumental function. Brillouin shift ν and

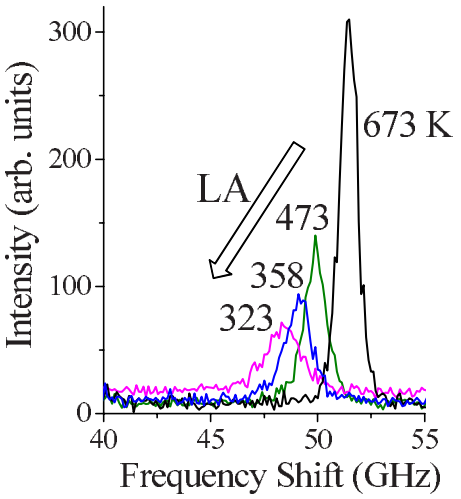

FIG. 1. (Color online) Inelastic light-scattering spectra of KF-BT/0.12 in the cubic phase at four temperatures. Peaks around 50 GHz denote the Brillouin scattering. Note that 1 [meV] =242 [GHz].

full width at half maximum (FWHM) Γ are shown in Fig. 2 with solid circles (●). ν and Γ of BT are also shown in Fig. 2 with open squares (□). The differences between KF-BT/0.12 and BT are clear. One difference is that T_C is decreased by KF substitution. We consider this occurs for two reasons: (i) the random electric field induced by the KF substitution and (ii) the high electronegativity of F. The random electric field tends to keep pinning the high-symmetry phase owing to its static randomness; i.e., (i) suppresses T_C.[11,12] Meanwhile, the high electronegativity leads to more ionic bonding. It is known that the bond between the Ti ion and the O ion in BT has high covalency.[13,14] If the O ion is substituted by the F ion, the covalency becomes weaker, leading to a decrease in the Born effective charge of the Ti ion.[14] It is

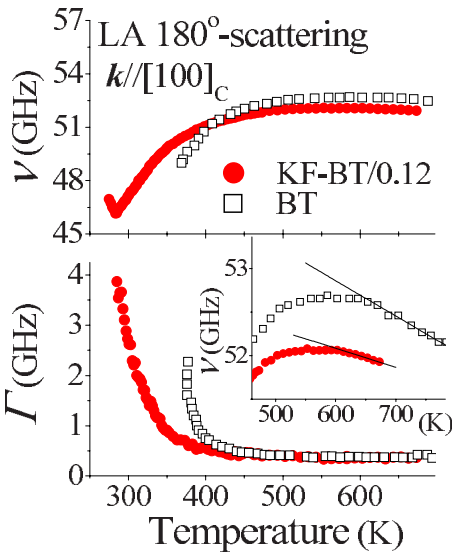

FIG. 2. (Color online) Temperature dependences of the Brillouin shift ν and width Γ of KF-BT/0.12 (●) and BT (□)[5] upon cooling in the 180°-scattering geometry. Solid lines in the inset are fitted curves by ν_∞=A-BT, with A and B are constant.

known that the smaller covalency leads to a smaller T_C.[14] Note that interpretation (ii) applies to lower-covalency systems such as titanates; on the other hand, the situation is different in a higher-covalency system such as niobates: T_C increases upon weakening the covalent bond, because the ion at the B site can move and polarize more easily.[15] The chemical pressure can also be used to tune T_C. When BT is substituted with KF, negative chemical pressure is applied. The negative chemical pressure generally causes an increase in T_C, which is opposite to the present result. Therefore, we consider that the chemical pressure has only a minor effect on this ferroelectric phase transition. As a result, T_C is suppressed by both (i) and (ii).

The anomalous behavior of the LA phonon is observed in a wide temperature range from ~620 K to T_C; ν deviates from the usual linear temperature dependence below 620 K, as shown in the inset of Fig. 2. At the same time, Γ increases upon cooling. By the substitution of KF, the anomalies in both ν and Γ become large, in other words, the first-order ferroelectric phase transition of BT approaches the second-order one after the KF substitution. The difference between KF-BT/0.12 and BT is more apparent in Fig. 3, where the horizontal axis is renormalized by T_C. ν and Γ of both samples behave similarly, indicating that anomalies are induced by the same origin, the hopping of Ti ions. The magnitude of the anomalies of KF-BT/0.12, on the other hand, becomes larger than those of BT. We attribute this to the random electric field generated by the KF substitution (i), and not to the high electronegativity of F (ii). This is because the smaller effective charge leads to a smaller polarization fluctuation. We consider that the strength of the electric field induced by K and F ions with $x \sim 0.12$ approaches the end point in the E-T phase diagram; therefore, the anomalies in the LA phonon become large, and also the first-order ferroelectric phase transition of BT approaches the second-order one.[8]

Both ν and Γ of KF-BT/0.12 and BT resemble those of relaxor ferroelectric materials in which the mesoscopic structure "polar nanoregion" plays an important role in the ferroelectric phase transition.[5,16,17] The similarity is in the anomalies in the LA phonon occurring in a wide temperature range, whereas most normal ferroelectrics show anomalous behavior in a narrow temperature range of about 10 K.[18–21] The temperature below which ν deviates from a linear temperature dependence is called the Burns temperature T_B in relaxor ferroelectrics,[22] and the polar nanoregion appears below T_B.[18,19] A similar scenario can be applied to KF-BT/0.12 and BT. The off-centered Ti ion of KF-BT/0.12 and BT correlates with other Ti ions, and the correlated region behaves as a polar nanocluster. In other words, KF-BT/0.12 can be in the paraelectric phase with no dynamic fluctuation of the order parameter detectable with light above 620 K, where ν shows a linear temperature dependence owing to the lattice anharmonicity induced by a change in temperature.[23] The Brillouin shift at the high-frequency limit ν_∞ is shown in the inset of Fig. 2.

The large deviation of ν from ν_∞ above T_C indicates a large fluctuation, which suggests that the Ti ion condenses into the restricted condition (leans to one side, i.e., hopping in four sites) toward T_C.[2] The increase in Γ ($\Gamma \propto c''_{11}$) gener-

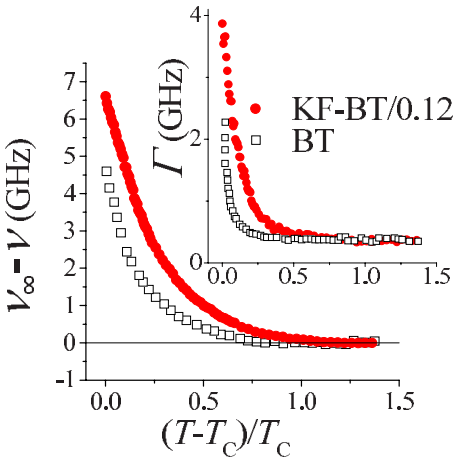

FIG. 3. (Color online) Magnitude of the change in ν, $\nu_\infty - \nu$ and width Γ of KF-BT/0.12 (●) and BT (□)[5] as a function of renormalized temperature. ν_∞ were determined by fitting ν at high temperature using $\nu_\infty = A - BT$ (inset of Fig. 2).

ally results from energy dissipation, and the energy transfers to the fluctuation, i.e., the hopping Ti ions (relaxation of polarization). Although defect dipoles are generated by KF in KF-BT, we excluded the effect of the relaxation of the defect dipoles because the defect dipole K'_{Ba}-$F^{\cdot}_{O}$ is reported to be static.[24] The anomalous behavior in the dynamic susceptibility is usually understood using the fluctuation-dissipation theorem (FDT):[21,25,26]

$$c''_{mn}(\omega_s) = \frac{\omega_s V}{2k_B T}\int_{-\infty}^{\infty} \exp(i\omega_s t)\langle \delta\sigma_m(t)\,\delta\sigma_n^*(0)\rangle dt, \qquad (1)$$

which connects the imaginary part of the susceptibility with the Fourier transform of the time-correlation function of internal stress fluctuation $\delta\sigma_m$ in volume V. ω_S is the angular frequency of the acoustic phonon. By a Kramers-Kronig transformation, the anomaly in c'_{mn} is also described. $\delta\sigma_m$ comprises a random force, originating from the order parameter fluctuation δP_i. We consider a linear coupling, which connects $\delta\sigma_m$ with δP_i as $\delta\sigma_m = \Sigma_i \beta_{im}\delta P_i$, because a polar nanocluster of BT has polar symmetry and the collective motion of its flipping (relaxation) is considered to be a soft mode. In other words, the polarization fluctuation inside the polar nanocluster is proportional to the stress fluctuation. Then Eq. (1) is written as

$$c''_{mn}(\omega_s) = \sum_{i,j} \beta_{im}\beta_{jn}\,\mathrm{Im}\,\chi_{ij}(\omega_s), \qquad (2)$$

using the FDT with the dielectric susceptibility $\chi_{ij} = \chi'_{ij} + i\chi''_{ij}$;

$$\chi''_{ij}(\omega_s) = \frac{\omega_s V}{2k_B T}\int_{-\infty}^{\infty} \exp(i\omega_s t)\langle \delta P_i(t)\,\delta P_j^*(0)\rangle dt. \qquad (3)$$

By taking into account only one Debye-type dielectric relaxation, Eq. (2) reduces to the Landau-Khalatnikov mechanism, and we can determine the relaxation time τ from[18–20]

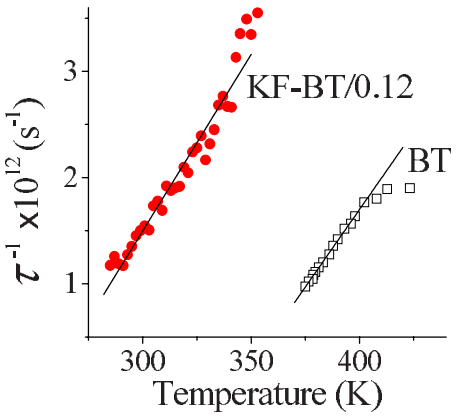

FIG. 4. (Color online) Relaxation times of KF-BT/0.12 and BT[5] as a function of temperature. Note that τ of KF-BT/0.12 was determined by the LA phonon, while τ of BT was determined by the central peak.[5]

$$\tau = \frac{\Gamma_T}{2\pi(\nu_\infty^2 - \nu^2)}, \qquad (4)$$

where Γ_T denotes the FWHM related to the phase transition. The determined temperature dependence of τ^{-1} is liner, as shown in Fig. 4. This behavior is typical in the order-disorder-type dipole alignment, and is called a "critical slowing down." The critical slowing down in the paraelectric phase is usually expressed, by using τ^{-1}, as

$$\tau^{-1} = \tau_0^{-1}(T - T_0), \qquad (5)$$

where τ_0^{-1} and T_0 denote the characteristic rate and the extrapolated temperature at $\tau^{-1}=0$, respectively.[27] τ^{-1} of BT is also shown in Fig. 4, which was determined by the width of the central peak.[5] The solid lines in Fig. 4 which were calculated using Eq. (5) with the parameters $\tau_0^{-1} = 3.3 \times 10^{10}$ K^{-1} s^{-1} and $T_0 = 255$ K for KF-BT/0.12, whereas $\tau_0^{-1} = 2.9 \times 1010$ K^{-1} s^{-1} and $T_0 = 341$ K for BT give excel-

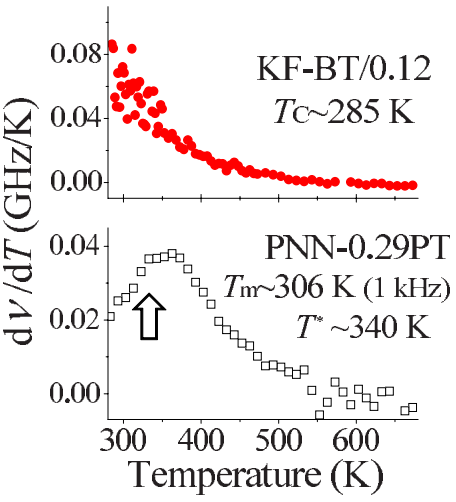

FIG. 5. (Color online) First derivatives $d\nu/dT$ of KF-BT/0.12 (●) and PNN-0.29PT (□)[19] as a function of temperature. A white arrow denotes T^* which locates between T_m and T_B.

lent agreement with the experimental values. The origins of relaxation must be identical for both samples; the hopping of Ti ions, and the differences in τ_0^{-1} and T_0 between two samples should be due to both (i) the random electric field and (ii) the high electronegativity of F, as we discussed above. Geneste calculated the local free energy related to Ti ion hopping by a molecular dynamics (MD) simulation.[28] He calculated the relaxation time above T_C to have a time scale of $10^{-11}-10^{-13}$ s, which is comparable to the result in Fig. 4. On the basis of his result, it is confirmed that the relaxation observed in this study originated from the hopping of Ti ions on (100) planes, not on (110) or (111) planes.

The LA phonon of KF-BT/0.12 shows similar behavior to that of the relaxor ferroelectrics. In contrast, the dielectric constants (susceptibility corresponds to the order parameter) of KF-BT/0.12 and BT differ from those of the relaxor ferroelectrics.[8] We consider this to be attributed to the behavior of the polar nanocluster. In our previous report on the relaxor ferroelectric $0.71Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.29PbTiO_3$ (PNN-0.29PT),[18] we demonstrated the maximum $d\nu/dT$ to be that shown in Fig. 5. The same behavior is also observed in $0.93Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.07PbTiO_3$ at T^*, where the intensity of acoustic emission was detected.[19,29] On the other hand, no maximum is found in the $d\nu/dT$ of KF-BT/0.12, as shown in Fig. 5; $d\nu/dT$ monotonically increases with cooling to T_C. This difference might be reflected by how the mesoscopic order relates to the ferroelectric phase transition.

In conclusion, we observed the LA phonon of KF-BT/0.12 by measuring the micro-Brillouin scattering, and discussed the fluctuating order parameter of the ferroelectric phase transition. The characteristic time of the fluctuation was determined to be on the time scale of 10^{-13} s, and it clearly exhibits critical slowing down. The fluctuation of the order parameter is enhanced by the KF substitution, which we attributed to the random electric field. Furthermore, we pointed out the similarities and differences between KF-BT/0.12 and BT and the relaxor ferroelectrics.

The authors would like to express their cordial gratitude to J.-H. Ko, M. Iwata, Y. Kuroiwa, S.-I. Ikeda, J. Kano, F. Shikanai, and H. Shigematsu for fruitful discussions. The present study was partially supported by the JSPS Research Foundation for Young Scientists (Grant No. 19-1404) and the Grant-in-Aid for Scientific Research (Grant No. 19360299) from JSPS.

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