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# Brillouin and dielectric studies of the phase transition in the relaxor ferroelectric $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$

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Brillouin scattering has been performed on the relaxor ferroelectric  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN) from 80 to 450 K across its Curie temperature. A diffuse phase transition from the paraelectric to ferroelectric phase, associated with a broad phonon frequency dip and a damping maximum, is observed around 200 K. A relaxation mode in the form of a broad Rayleigh wing, whose frequency is strongly temperature dependent above 190 K, is observed and analyzed based on a modified superparaelectric model. Dielectric studies of PNN have also been carried out at several measurement frequencies. The relation between the measurement frequency and the dielectric maximum temperature was analyzed on a modified Vogel–Fulcher model. © 2002 American Institute of Physics. [DOI: 10.1063/1.1433183]

## I. INTRODUCTION

Their large dielectric constant, piezoelectric coefficient, and electromechanical coupling constant have made relaxor ferroelectric materials of great interest to both fundamental and applied science. Relaxors are distinguished from normal ferroelectrics by the presence of a frequency-dependent dielectric maximum and its corresponding temperature  $T_m$ . Also the maximum in the dielectric constant  $\epsilon$  does not coincide with the maximum in the dielectric loss  $\tan \delta$ .

Brillouin scattering has proven to be a sensitive technique in the study of the phase transition in ferroelectrics. To date, several Brillouin studies have reported on parent relaxor ferroelectrics,<sup>1–3</sup> such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN),  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PZN), and  $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$  (NBT). These materials are characterized by a diffuse ferroelectric transition.

It is believed that the polar microregions (PMRs), embedded in a disordered matrix in the nanometer scale, play an important role in relaxor properties.<sup>4–6</sup> The existence and temperature evolution of PMR in relaxor ferroelectrics have been investigated by several methods, such as transmission electron microscopy,<sup>4</sup> optical microscopy,<sup>7</sup> and Raman scattering.<sup>8,9</sup> Recently, the relaxation of the central peak in the Brillouin spectrum of  $0.64\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.36$

$\text{PbTiO}_3$  was analyzed based on its correlation with the thermal evolution of PMR.<sup>6</sup>

Preliminary dielectric measurements<sup>10–12</sup> on lead–nickel–niobate  $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PNN) suggest that it undergoes a diffuse phase transition within its Curie temperature range centered at  $T_C \approx 153$  K. According to the phase diagram constructed by Kusumoto and Sekiya,<sup>12</sup> PNN is cubic in its paraelectric phase and pseudocubic (rhombohedral) in its ferroelectric phase. We undertook a Brillouin and a dielectric investigation of PNN single crystals to better understand the ferroelectric phase transition in PNN.

## II. EXPERIMENTAL METHOD

Single crystals of PNN were flux grown from the  $\text{PbO}-\text{NiO}-\text{Nb}_2\text{O}$  system in the temperature range from 1473 to 1223 K at a crystallization rate of  $-3$  K/h.<sup>11,13</sup> The crystals of PNN thus obtained are green in color and in the form of polished (001) plates of approximately 2 mm on a side. The single perovskite phase of the synthesized crystals was confirmed by x-ray diffraction. Brillouin spectra were recorded using a JRS Scientific Instruments (3+3)-pass tandem Fabry–Pérot interferometer, with a finesse of 120, equipped with a Perkin–Elmer AQR-16 single photon-counting module. The free spectral range was set at 75 GHz. The 514.5 nm line of an argon ion laser was used with a beam power of 5 mW incident on the sample. The experiment was performed in the  $180^\circ$  backscattering geometry,

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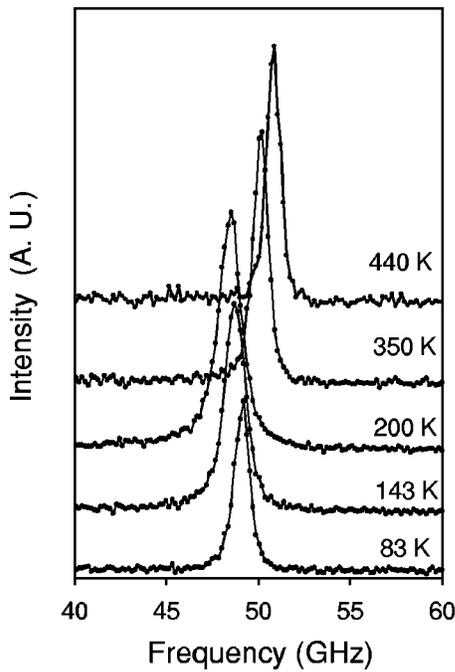


FIG. 1. Brillouin spectra of the LA mode of PNN recorded at various temperatures during the cooling of the crystal.

with the laser beam incident along the (001) crystallographic axis. This means that acoustic phonons propagating in the [001] direction were detected. The temperature was cycled between 80 and 450 K in both heating and cooling sequences using a Linkam THMS600 heating stage for temperatures above 300 K, and an Oxford Instruments Optistat CF-V cryostat for temperatures below 300 K. The dielectric constants were measured between 93 and 273 K at a cooling rate of 1 K/min using a LCR meter. Measurements were performed at frequencies of 10, 100, 200, 1000, and 2000 kHz, for which the corresponding  $T_m$  values, interpolated from the smoothed dielectric curves, are 146, 155, 158, 165, and 169 K, respectively.

### III. RESULTS AND DISCUSSION

Figure 1 shows the temperature evolution of the Brillouin spectrum of the longitudinal acoustic (LA) mode of the PNN crystal recorded during cooling. A weak low-frequency peak ( $\approx 13$  GHz), which was observed at temperatures below  $\approx 150$  K (see Fig. 2), was assigned to a transverse acoustic (TA) mode (see the discussion below). The LA peak was fitted with the Lorentzian function to yield its frequency and full width at half maximum (FWHM). Their temperature dependence data are presented in Fig. 3. Reference to the figure shows that the temperature dependence curves of both the LA frequency and linewidth, obtained on cooling of the crystal, almost coincide with those measured on heating, indicating the absence of a temperature hysteresis.

Figure 3 reveals that both the frequency and FWHM of the LA mode vary smoothly with temperature with a broad frequency dip and damping hump, respectively, at about 200 K. Figure 4 shows the temperature dependence of the dielectric constant  $\epsilon$  and dielectric loss  $\tan \delta$  measured at several

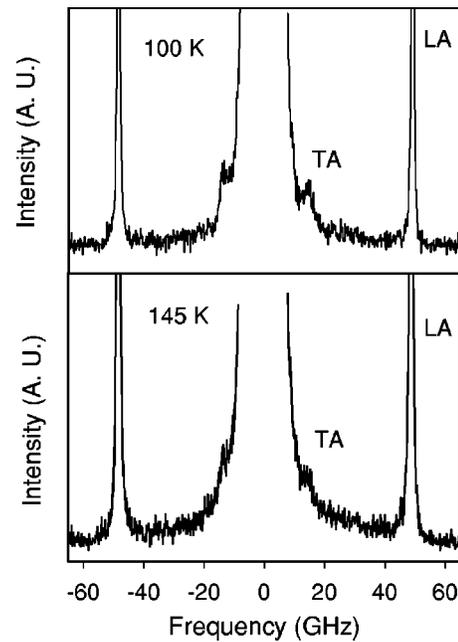


FIG. 2. Brillouin spectra of PNN recorded at two temperatures. In addition to the intense peak due to the LA mode, a weak TA mode was also observed.

frequencies. The dielectric maximum, observed in the transition range around 150 K, is slightly higher than that reported by Sekiya *et al.*<sup>11</sup> The temperature dependence of the dielectric constant shows a strong frequency dispersion for temperatures below  $T_m$ . With increasing frequency, the dielectric maximum shifts to higher temperatures and its magnitude decreases. This is consistent with the results of Sekiya *et al.*<sup>11</sup> The gradual hypersonic frequency softening and damping over a wide temperature range, as well as the broadened dielectric constant maximum, are characteristic of relaxor ferroelectric materials, indicating a so-called diffused

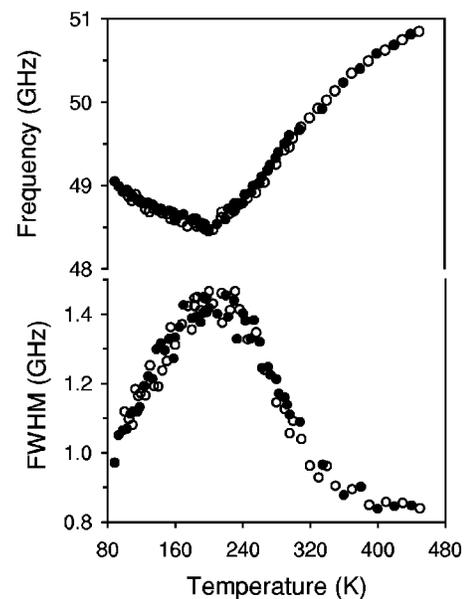


FIG. 3. Temperature dependence of the frequency (top) and FWHM (bottom) of the LA mode of PNN. The open and filled symbols denote data for the cooling and heating processes, respectively.

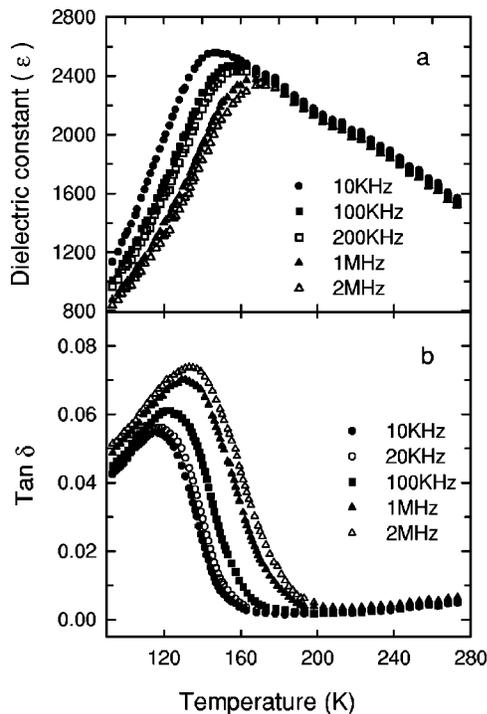


FIG. 4. Dielectric constant (a) and dielectric loss (b) of PNN as a function of temperature at several measurement frequencies for PNN.

phase transition from the paraelectric to the ferroelectric phase. Similar acoustic and dielectric anomalies have also been observed in other parent relaxor ferroelectrics such as PMN, PZN, and NBT.<sup>1-3</sup>

PNN changes its symmetry progressively from the cubic to rhombohedral around 153 K.<sup>12</sup> For the pure 180° back-scattering geometry employed here, scattering from TA modes is not expected for crystals of cubic symmetry.<sup>14</sup> However, the existence of TA modes is detectable by Brillouin scattering for noncubic symmetry. This validates our assignment of the weak low-frequency peak, appearing below 150 K, to a TA mode.

A comparison is now made of the acoustic properties of PNN and those of other parent relaxor ferroelectrics. In their Brillouin study of the hyperpolarized damping of PMN and NBT, Siny *et al.* observed sharp anomalous peaks superimposed on the main damping maxima.<sup>3,15</sup> They pointed out that these anomalous peaks arise from a frustrated ferroelectric phase transition in PMN and the cubic-tetragonal structural phase transition in NBT. No such additional anomaly in damping was observed in the studies of PZN<sup>2</sup> and PNN near the reported Curie temperatures  $T_C \approx 413$  K (PZN) and  $T_C \approx 153$  K (PNN). This suggests that the structural (cubic  $\leftrightarrow$  pseudocubic) and ferroelectric (paraelectric  $\leftrightarrow$  ferroelectric) phase transitions occur simultaneously and thus frustrated ferroelectric transitions are not expected for PZN and PNN. Kuok *et al.*<sup>2</sup> reported that PZN exhibits a large temperature hysteresis between 320 and 400 K. Our results show that PNN, however, revealed no difference in its acoustic behavior between the heating and cooling sequences even though the crystal temperature was varied in steps of 2 K. Thus in a sense, the phase transition in PNN, as monitored

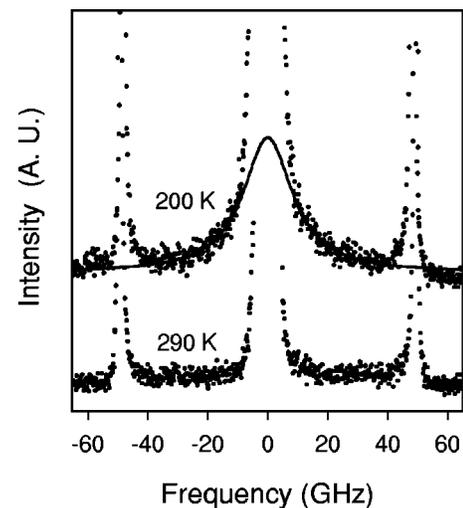


FIG. 5. Brillouin spectra of PNN at 200 K (top) and 290 K (bottom). The solid line is the fit with a Lorentzian function to the central peak.

by the temperature dependence of its LA mode, is more “normal” than that for the PMN, PZN, and NBT relaxor ferroelectrics.

The properties of relaxor ferroelectrics are closely related to their thermally activated polar microregions or microclusters, which evolve when the crystal temperature approaches  $T_m$  from above.<sup>4,16</sup> The thermal evolution of PMR will give rise to a central peak in the Brillouin spectrum due to quasielastic scattering. Such a central peak has been observed by Brillouin scattering in parent relaxor ferroelectrics<sup>1</sup> and solid solutions.<sup>6,17</sup> It is reported that Raman spectra of relaxor ferroelectrics also feature a similar central peak appearing as a Rayleigh wing, whose linewidth varies with temperature.<sup>9,18</sup> The linewidth of the central peak provides information on the relaxation mode of relaxor ferroelectrics, associated with the dynamic precursor microregions.

Figure 5 shows the central peak of PNN recorded at 200 K. It is only observed below about 280 K and still exists at temperatures about 140 K. In order to extract information about the relaxation mode, the central peak was fitted with a Lorentzian profile centered at zero frequency.<sup>19</sup> The fitting yielded the relaxation frequency which corresponds to the half width of the profile and is presented in Fig. 6. It is found that the temperature dependence of the relaxation frequency is more pronounced above  $\approx 190$  K, as shown in Fig. 6.

A superparaelectric model, proposed by Cross<sup>20</sup> to account for the relaxor dielectric properties at high temperatures, has been used in the analysis of the relaxation mode.<sup>6</sup> Based on this model, the polarization flipping frequency  $\nu$  of PMR is related to the activation energy  $H$ , the barrier between two equivalent polarization states, by

$$\nu = \nu_D \exp\{-H/k_B T\} = \nu_D \exp\{-H_0(T_p - T)/T_p k_B T\} \quad (1)$$

where  $H = H_0(T_p - T)/T_p$  for  $T_C \leq T \leq T_p$  as assumed by Jiang and Kojima<sup>6</sup> in their analysis of the relaxation mode of the PMN-PT system, by considering the fact that  $H$  is directly proportional to the volume of the PMR itself, and the size of PMR is temperature dependent.  $H_0$  is the activation

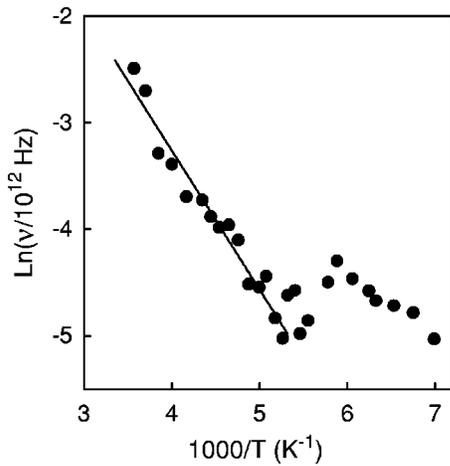


FIG. 6. Relaxation frequency  $\nu$  of the central peak vs temperature, plotted in the form of  $\ln(\nu/10^{12} \text{ Hz})$  vs  $1000/T$ . The solid line is the fit using the modified superparaelectric model.

energy extrapolated to absolute zero, and  $T_p$  is taken to be the characteristic temperature at which the precursor PMR begins to appear.  $\nu_D$  and  $k_B$  are Debye frequency ( $\sim 10^{11} - 10^{13} \text{ Hz}$ ) and the Boltzmann constant, respectively.  $\nu$  is the relaxation frequency corresponding to the half width of the relaxation mode.

Figure 6 shows the temperature dependence of the relaxation mode frequency, plotted as  $\ln(\nu/10^{12})$  versus  $1000/T$ , and the best fit of Eq. (1) to the experimental data above 190 K, the temperature near the phonon damping maximum temperature (see Fig. 3). The fitted parameters are  $T_p \approx 670 \text{ K}$  and  $H_0 \sim 1309 \text{ K} \sim 0.112 \text{ eV}$ . These values are reasonable according to their definitions.<sup>6</sup> Interestingly  $T_p$  is much higher than  $T_m$ , implying that the polar microregions or clusters appear in the paraelectric phase prior to the onset of the diffuse phase transition. The fact that relaxation mode, i.e., the polar clusters, exists at temperatures higher than  $T_m$  is phenomenally in agreement with other findings on various relaxors using different methods.<sup>4,7,17</sup>

The local polarization in relaxor ferroelectrics is very similar to that in polar-glassy systems, which have thermally activated polarization fluctuations above a static freezing temperature. Based on this macroscopic similarity, the Vogel–Fulcher (VF) model has been introduced to characterize the relation between frequency  $f$  and the dielectric maximum temperature  $T_m$  of relaxor ferroelectrics.<sup>21</sup> Our analysis based on the VF model yielded an attempt frequency of  $1.12 \times 10^{16} \text{ Hz}$  and an equivalent temperature of activation energy  $T_0$  of  $\approx 2748 \text{ K}$ . These values are obviously too high to be physically acceptable.<sup>22</sup> As the VF model approximates relaxors as a Debye medium (i.e., a classic dielectric) and ignores the dielectric relaxation strength, it has been modified by Cheng *et al.*<sup>22</sup> in the characterization of the dielectric behavior of PMN–PT relaxors. In the modified model

$$f = f_0 \exp\left\{-\left(T_0/T_m\right)^p\right\}, \quad (2)$$

where  $f_0$  is the attempt frequency and is considered to be a constant,  $T_0$  is the equivalent temperature of activation energy, and  $p$  is an empirical parameter that can be used to characterize the dielectric relaxation strength (i.e., degree of

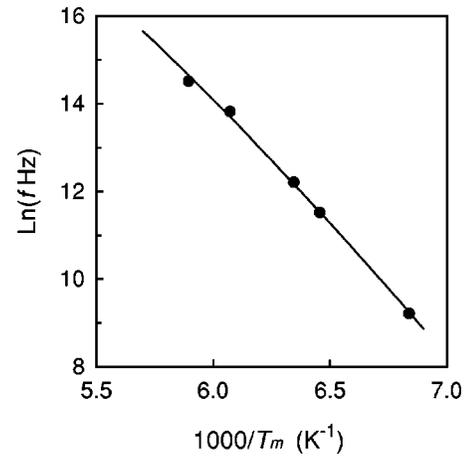


FIG. 7. Experimental data and fitted curve of frequency vs  $T_m$  for PNN. The solid line denotes the fit with the modified VF relationship.

diffusiveness) of the relaxor ferroelectrics.  $p$  is larger than 1 and increases with decreasing dielectric relaxation strength. The experimental data and the fitted curve are shown in Fig. 7. The fitting yielded  $f_0 = 1.07 \times 10^{13} \text{ Hz}$ ,  $T_0 \approx 660 \text{ K}$ , and  $p = 2.04$ . The value of  $T_0$  is about half that of  $H_0 \sim 1309 \text{ K}$  obtained from Eq. (1). This is reasonable as  $H_0$  is the activation energy at a temperature of absolute zero, while  $T_0$  is the equivalent temperature of average activation energy of the PMRs.

For comparison, the fitting was also performed on the relaxor solid solution 0.8PNN–0.2PT, whose dielectric constants have been measured by Sekiya *et al.*<sup>11</sup> The resulting value of  $p = 7.8$ . The value of  $p = 2.04$  for PNN is consistent with the definition of this parameter and indicates that, compared to  $p = 7.8$  for 0.8PNN–0.2PT and  $p = 8.8$  for 0.9PMN–0.1PT,<sup>22</sup> the parent relaxor PNN has larger dielectric relaxation strength and thus a higher degree of diffuseness. This is not surprising since the content of PT, the normal ferroelectric, will sharpen the ferroelectric phase transition of a solid solution, and decrease the dielectric relaxation strength near  $T_m$ .

#### IV. CONCLUSIONS

The acoustic and dielectric properties of relaxor PNN have been studied over a wide temperature range across its phase transition. It undergoes a typical diffuse phase transition as evidenced by both the broad phonon softening and damping and the strong frequency dispersion of dielectric constant as a function of temperature. A relaxation mode was observed by Brillouin scattering and analyzed with a modified superparaelectric model. The analysis of the relation between the dielectric maximum temperature and measurement frequency with a modified VF relationship revealed a much larger degree of diffuseness of PNN compared to the solid solution PNN–PT and PMN–PT. Unlike other parent relaxors like PMN, PZN, and NBT, PNN does not exhibit any anomaly such as a frustrated phase transition and a temperature hysteresis in its phase transition.

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