

## Dielectric relaxation and electrical properties of $0.94\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.06\text{PbTiO}_3$ single crystals

Jie Wang,<sup>a)</sup> X. G. Tang, H. L. W. Chan, and C. L. Choy  
*Department of Applied Physics, The Hong Kong Polytechnic University, Hung Hom, Hong Kong, People's Republic of China.*

Haosu Luo  
*The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 215 Chengbei Road, Jiading, Shanghai 201800, People's Republic of China*

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Dielectric response and electrical conduction properties of  $0.94\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3-0.06\text{PbTiO}_3$  single crystals grown by the Bridgman method were studied. It was found that the single crystals did not show any sign of the presence of Curie temperature between room temperature and  $300^\circ\text{C}$ . However, they exhibited very high dielectric constant at a frequency lower than  $100\text{ kHz}$ , in the order of  $10^5$ . Relaxation occurred at higher frequencies with a large decrease in dielectric constant, to about 1500. The thermal activation energy for relaxation was found to be  $\sim 0.17\text{ eV}$ , which is quite close to that for ac conductivity. It followed that the relaxation was attributed to the carriers hopping conduction, which is related to the possible jump motion of additional  $3d$  electron between the equivalent positions of Fe ions. © 2005 American Institute of Physics.  
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Lead iron niobate  $\text{Pb}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$  (PEN) is a lead based complex perovskite which is of great interest for multilayer capacitors owing to its high dielectric constant.<sup>1</sup> Recently, excellent dielectric and piezoelectric properties were found in the lead based relaxor ferroelectrics  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})-\text{PbTiO}_3$  (PMN-PT),<sup>2</sup> and  $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})-\text{PbTiO}_3$  (PZN-PT).<sup>3</sup> PFN, like PMN and PZN, having a rhombohedral structure, and a Curie temperature of  $114^\circ\text{C}$ , therefore becomes a possible candidate for making new relaxor ferroelectrics exhibiting attractive piezoelectric properties. It was previously reported that PFN-PT single crystals can be grown by the Bridgman method and their dielectric properties were reported.<sup>4</sup> It was found that the dielectric constant was very high, about 30 000 at room temperature, but the loss tangent was about 0.4. No detail analysis was made concerning the mechanisms of that very high dielectric constant and loss tangent. In this report, we describe a detailed characterization on dielectric and electrical conduction properties of  $0.94\text{PFN}-0.06\text{PT}$  single crystals grown by Bridgman method.

The detail of the single crystal growth was described elsewhere.<sup>4</sup> For electrical measurement, 001-oriented crystals were cut into  $5 \times 5 \times 1\text{ mm}$  in size and silver paste was applied on the two large faces and fired at  $600^\circ\text{C}$  for 15 min. The dielectric constant and loss tangent of the PFN-PT single crystal were measured with an impedance analyzer HP4192A under various temperatures. The samples were placed in a computer controlled oven and the measurement was carried out during the slow heating of the oven ( $0.5^\circ\text{C}/\text{min}$ ). Figure 1 shows the temperature dependencies of dielectric constant  $\epsilon_r$  and loss  $\tan\delta$  for the as-grown  $0.94\text{PFN}-0.06\text{PT}$  single crystal measured at frequencies of 100 Hz, 1 kHz, and 10 kHz, respectively. The temperature range was between room temperature and  $350^\circ\text{C}$ . We see that the di-

electric constant increases monotonously with the increasing of temperature. There is no evidence of Curie transition temperature within the measurement range. The dielectric constant was found to be very high, in the order of  $10^5$ . On the other hand, the loss factors were high as well. The lowest value was found at a frequency of  $10\text{ kHz}$ , where the loss tangent varied between 0.1 and 0.5. Comparing with the previous report<sup>4</sup> on the dielectric properties of  $0.52\text{PFN}-0.48\text{PT}$ , the dielectric constant of  $0.94\text{PFN}-0.06\text{PT}$  single crystals are higher. In both cases, they showed high dielectric loss factors. An earlier investigation on dielectric behaviors of  $\text{PFN}-\text{Pb}(\text{Co}_{1/3}\text{Nb}_{2/3})\text{O}_3$  also revealed the feature of high dielectric loss.<sup>5</sup>

We also carried out measurement on the frequency dependence of the real and imaginary part of dielectric constant,  $\epsilon'$  and  $\epsilon''$ , in the temperature range of  $10-110^\circ\text{C}$ . The results are shown in Fig. 2. From the real part and imaginary part of the dielectric constant, we observed two relaxations, one is located below  $100\text{ Hz}$ , the other in the range of

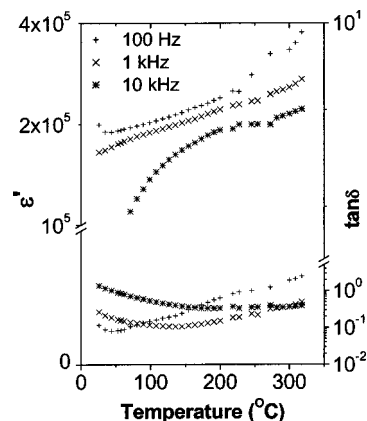


FIG. 1. Dielectric constant and loss tangent measurement of the PFN-PT single crystal.

<sup>a)</sup>Electronic mail: apapwang@polyu.edu.hk

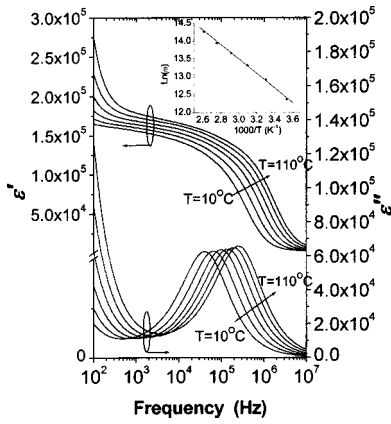


FIG. 2. Frequency dependence of real and imaginary part of dielectric constant of PFN-PT single crystal measured at various temperatures. The inset shows the linear relationship between  $\text{Ln}\omega$  and  $1/T$ .

$10^4$ – $10^6$  Hz. For the second relaxation the  $\epsilon''$  curves show peaks of maximum  $\epsilon''$  at relaxation frequency  $\omega_p$ , indicating a Debye-like relaxation. It is well known that in dielectric materials several polarization mechanisms may be responsible for the relaxation phenomena, namely: space charge, interfacial, and dipolar polarizations. Generally speaking the dielectric relaxation due to space charge or interfacial polarization occurs at low frequency. While dipolar relaxation appears usually in the radio frequency or microwave frequency ranges. Waser *et al.*<sup>6</sup> showed that the doubly charged oxygen vacancy and related defects play an important role in the low frequency relaxation in oxide ferroelectric materials. We believe that the relaxation observed in the lower frequency spectrum in Fig. 2 should belong to this kind of process. Presumably the space charges conduction may be due to the oxygen vacancy. For the relaxation we observed in Fig. 2 at around several hundred kHz, it is seen that the relaxation frequency  $\omega_p$  increases with increasing temperature. A thermally activated process relating relaxation frequency  $\omega_p$  to the temperature can be described as:

$$\omega_p = \omega_0 \exp(-E_{\text{relax}}/kT), \quad (1)$$

where  $\omega_0$  is a characteristic frequency and  $k$  the Boltzmann's constant and  $E_{\text{relax}}$  is the activation energy for the relaxation. Using Eq. (1),  $E_{\text{relax}}$  was calculated to be 0.17 eV. This value is far less than the value of previously reported activation energy for the migration of oxygen vacancy in perovskite oxide materials (0.91 eV)<sup>7</sup> and that obtained through conductivity measurement (1 eV),<sup>6</sup> so the relaxation we observed in Fig. 2 at around several hundred kHz should not be attributed to this kind of space charge conduction.

Figure 3 shows the temperature dependence of ac conductivity for the PFN-PT single crystal measured at frequencies of 100 Hz–10 MHz. The complex conductivity  $\sigma^*$  of a dielectric material can be presented in term of complex dielectric constant  $\epsilon^*$  by the relation<sup>8</sup>  $\sigma^* = i\omega\epsilon_0\epsilon^* = i\omega\epsilon_0\epsilon' + \omega\epsilon_0\epsilon''$ , where  $\epsilon'$ ,  $\epsilon''$  and  $\omega$  are the real and imaginary part of the dielectric constant and angular frequency, respectively. The ac conductivity was calculated by the formula  $\sigma' = \omega\epsilon_0\epsilon''$ . It was found that the ac conductivity was temperature dependent for 100 Hz, 1 MHz, and 10 MHz. While for 1, 10, and 100 kHz, the ac conductivity was almost independent of the temperature. The linearity between  $\log \sigma$  and  $1/T$  was obtained for 100 Hz, 1 MHz, and 10 MHz at the mea-

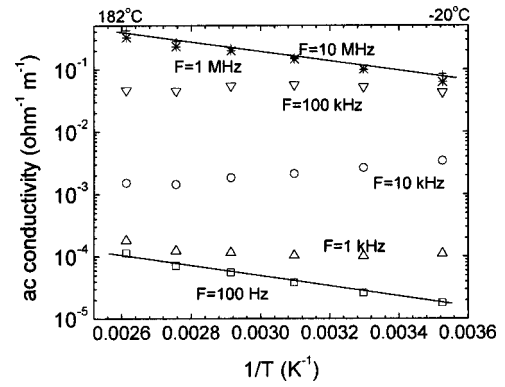


FIG. 3. Logarithmic plot of ac conductivity against inverse of the temperature in Kelvin scale for the PFN-PT single crystal.

surement temperature range. For these frequencies, the conduction can be described by a thermally activated process with the relation:

$$\sigma' = \sigma_0 \exp\left(-\frac{E_{\text{cond}}}{k_B T}\right), \quad (2)$$

where  $\sigma_0$  is a constant,  $k_B$  the Boltzmann's constant, and  $E_{\text{cond}}$  is the activation energy for conduction. The fitting results according to Eq. (2) gives  $E_{\text{cond}}$  values of 0.17 eV for 100 Hz and 0.155 eV for 1 and 10 MHz. These activation energy values are quite close to  $E_{\text{relax}}$  obtained from the relaxation measurement. It is well known that in this case the relaxation is controlled by the ac conduction due to hopping (jump motion) of carriers. Jump motion controlled relaxation was previously reported in ferrites.<sup>9</sup>

As for the origin of hopping, it is well known that the coexistence of  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions on the equivalent crystallographic sites can frequently give rise to conduction due to the jump of addition  $3d$  electron between adjacent  $\text{Fe}^{+2}$  and  $\text{Fe}^{+3}$  ions.<sup>10</sup> The existence of  $\text{Fe}^{+2}$  ions may be due to oxygen deficiency taking into account that the crystal growth was made at high temperature and in a sealed Pt crucible.

Previous work on  $\text{CuPc}$ <sup>8</sup> showed that when the conductivity is due to hopping, the ac conductivity varies as  $\sigma' \sim \omega^3$  in specific temperature and frequency range. Figure 4 shows the frequency dependence of  $\sigma'_{\text{ac}}$  at several temperatures. It is seen that in the middle of the frequency range, a linear relation is observed between  $\log \sigma'_{\text{ac}}$  and  $\log f$ . This indicates clearly that the conduction is due to carrier hopping.

It is also worth discussing the origin of giant dielectric constant observed in the PFN-PT single crystals. It was recently reported that giant dielectric constant in  $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

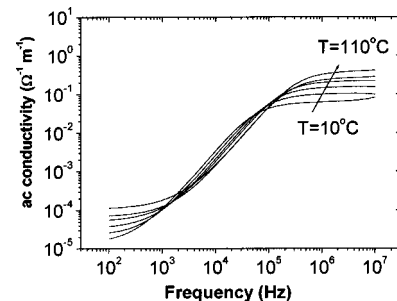


FIG. 4. Logarithmic plot of ac conductivity vs frequency for PFN-PT single crystal measured at various temperatures.

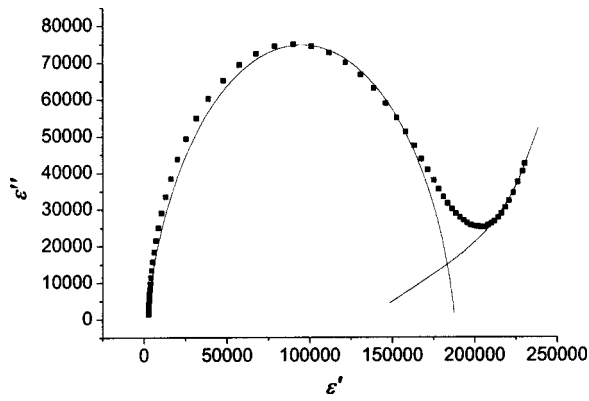


FIG. 5. Room temperature Cole–Cole plots of measured complex dielectric constant (closed square) and fitted data (line).

(CCTO) ceramics and single crystals.<sup>11,12</sup> The similarity between PFN-PT and CCTO is that they all exhibited a relaxation frequency which increases with increasing temperature. The relaxation was attributed to a dynamical slow down of relaxor-like nanosized polar regions. It is proposed that the giant dielectric constant in PFN-PT has the same origin in that, below the relaxation frequency, the additional  $3d$  electrons of  $F_e^{+2}$  ions are localized and may induce local polarization of the lattice, or polarons, which, owing to its dynamics, contributes to the dielectric response.

Although it was assumed that the giant dielectric constant is due to its nanostructure, we may also speculate that the high dielectric constant is enhanced by its microstructure. Figure 5 shows the complex plane plot of room temperature complex dielectric constants (Cole–Cole plot).

For a Debye-like relaxation the Cole–Cole plot can be described as:<sup>9</sup>

$$\epsilon^* = \epsilon_\infty + \frac{\epsilon_s - \epsilon_\infty}{1 + (i\omega\tau)^\alpha} - i \frac{\sigma}{\epsilon_0\omega}, \quad (3)$$

where  $\epsilon_s$  and  $\epsilon_\infty$  are the static and high-frequency  $\epsilon'$ ,  $\tau$  is the relaxation time,  $\alpha$  a constant, and  $\sigma$  is the dc conductivity.

A tail at the low frequency range of the semicircle characterizes the Cole–Cole plot in Fig. 5. This is a typical two parallel capacitor configuration.<sup>9</sup> Using Eq. (3), the experi-

mental data (dots) were fitted, as shown by the solid lines. The fitting yields the following results:  $\epsilon_{s1}=188\,000$ ,  $\epsilon_{\infty1}=1500$ ,  $\alpha_1=0.86$ ,  $\tau_1=0.02$  ms, and  $\epsilon_{s2}=1\,500\,000$ ,  $\epsilon_{\infty2}=134\,000$ ,  $\alpha_2=0.19$ ,  $\tau_2=2000$  s,  $\sigma=4e-5$  S, so we get a dielectric constant of 1500 after the relaxation. This value is in the same order for a ferroelectric oxide. It can also be seen that the single crystal seems to be composed of two kinds of microstructures in parallel, one is capacitive having short relaxation time; another is a leaky capacitor with long relaxation time. Such a microstructure can give rises to high dielectric constant due to barrier layer mechanism.<sup>13</sup> Indeed our recent investigation<sup>14</sup> on the microstructure of 0.96 PFN-0.04 Pt single crystals by TEM has shown that, in PFN-PT single crystals various domains patterns exists which would give rise to different electrical properties in each domain.

In summary, giant dielectric constant was observed in PFN-PT single crystal. The relaxation behavior and ac conductivity were analyzed. It was concluded that the relaxation was primarily due to carrier hopping controlled ac conduction.

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