



**Universidade de São Paulo**

**Biblioteca Digital da Produção Intelectual - BDPI**

---

Departamento de Física e Ciências Materiais - IFSC/FCM

Artigos e Materiais de Revistas Científicas - IFSC/FCM

---

2009-04

# Dynamics of normal to diffuse and relaxor phase transition in lead metaniobate-based ferroelectric ceramics

---

Applied Physics Letters, Melville, v. 94, n. 17, p. 172901-1-172901-3, Apr. 2009

<http://www.producao.usp.br/handle/BDPI/49295>

*Downloaded from: Biblioteca Digital da Produção Intelectual - BDPI, Universidade de São Paulo*

## Dynamics of normal to diffuse and relaxor phase transition in lead metaniobate-based ferroelectric ceramics

Michel Venet,<sup>1</sup> Jean-Claude M'Peko,<sup>2,a)</sup> Fabio Luis Zabotto,<sup>1</sup> Fidel Guerrero,<sup>3</sup> Ducinei Garcia,<sup>1</sup> and José Antonio Eiras<sup>1</sup>

<sup>1</sup>Departamento de Física, Grupo de Cerâmicas Ferroelétricas, Universidade Federal de São Carlos (UFSCar), CEP: 13565-670 São Carlos/São Paulo, Brazil

<sup>2</sup>Grupo Crescimento de Cristais e Materiais Cerâmicos (GCCMC), Instituto de Física de São Carlos (IFSC), Universidade de São Paulo (USP), C. Postal: 369, CEP: 13560-970 São Carlos/São Paulo, Brazil

<sup>3</sup>Departamento de Física, Facultad de Ciencias Naturales, Universidad de Oriente, C. P. 90500 Santiago de Cuba, Cuba

(Received 7 August 2008; accepted 25 March 2009; published online 27 April 2009)

Tetragonal tungsten bronze-structured materials based on lead metaniobate ( $\text{PbNb}_2\text{O}_6$ ) were studied in terms of thermal dynamics of dielectric properties, showing ferroelectric-to-paraelectric phase transition of diffuse and relaxor type in some specific cases. These features are normally ascribed to defects-induced structural disorder and compositional fluctuations associated with an arbitrary lattice site occupation between dopant and host ions. Nevertheless, for these lead metaniobate-based materials, the drastic change in the phase transition from normal to diffuse and relaxor is shown to take place when dopants are able to significantly shift the transition toward low temperatures, where these compounds are known to exhibit incommensurate superstructures that naturally present diffuse and relaxor dielectric characteristics. © 2009 American Institute of Physics.

[DOI: 10.1063/1.3122149]

Ferroelectric niobates with tetragonal tungsten bronze (TTB)-type structure have been and are widely investigated for applications in electro-optic, nonlinear optic, piezoelectric, and pyroelectric devices.<sup>1-4</sup> The first ferroelectric compound discovered with TTB structure was lead metaniobate,<sup>5</sup>  $\text{PbNb}_2\text{O}_6$  (PN), which transforms from paraelectric (PE) tetragonal (TE)  $4/mmm$  to ferroelectric (FE) orthorhombic (OR)  $m2m$  point group at around 823 K.<sup>5-7</sup> When doped with barium to form stable  $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  (PBN) solid solutions, the FE state crystallizes transiting from the above OR  $m2m$  to TE  $4mm$  symmetry while increasing  $\text{Ba}^{2+}$  content ( $\text{Pb}^{2+}$ - and  $\text{Ba}^{2+}$ -rich PBNs, respectively).<sup>6,7</sup> Toward the lowest temperature region (below 100 K), afterwards, PBN materials were found to exhibit an additional dielectric anomaly (in the thermal spectra of permittivity) that was subsequently identified as involving a phase transition from the TE  $4mm$  to monoclinic (MO)  $m$  symmetry.<sup>8</sup> We recently observed such a dielectric anomaly to also occur in undoped PN (Ref. 9) and  $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  (SBN) (with  $x=0.37$ ) (Ref. 10) below 100 K, suggesting to apparently be a general feature of TTB-structured ferroelectric niobate materials.

Back to the FE-PE phase transformation, undoped PN exhibits a normal-like transition (i.e., with a discrete and frequency-independent temperature of maximum permittivity, known as Curie temperature  $T_C$ ), while a diffuse phase transition (DPT) with relaxor (frequency dependent  $T_C$ ) behavior can be induced through doping. These new characteristics are usually assumed to arise from dopant-induced structural disorder and compositional fluctuations in the system, as crystallographically equivalent sites become markedly occupied by different kinds of atoms, causing a broadening (diffusiveness) of the transition due to the formation of

polar nanoregions with locally different  $T_C$ .<sup>2,11</sup> From the fundamental viewpoint, nevertheless, dynamic nature of DPT and relaxor behaviors in ferroelectrics remains somewhat still a mystery. In the present work, a systematic study on the thermal dynamics of dopant-induced DPT and relaxor effects in particularly PN-based materials was achieved.

Undoped PN and  $\text{Ti}^{4+}$ -doped PN ( $\text{Pb}_{1+x}(\text{Nb}_{1-x}\text{Ti}_x)_2\text{O}_6$  with  $x=0.05$  and  $0.1$ , thereafter denoted as PTN 100x) ceramics were prepared by the conventional method, involving calcination and two thermal treatments, the last one (sintering) at 1270 °C for 4.5 h, as previously reported in Ref. 12. In addition,  $\text{Ba}^{2+}$ -doped PN ( $\text{Pb}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  with  $x=0.30$ ,  $0.34$ ,  $0.37$ ,  $0.40$ , and  $0.44$ , denoted as PBN 100x) and  $\text{La}^{3+}$ -doped PBN44 ( $\text{PBN44}+x$  wt %  $\text{La}_2\text{O}_3$  with  $x=0.5$ ,  $1.0$ ,  $1.5$ ,  $2.0$  and  $4.0$ , denoted as PBLN44/x) ceramics were conventionally prepared and sintered at 1270–1290 °C for 2 h. All the ceramics resulted in high-density materials (above 95% of theoretical density). Real and imaginary parts of permittivity ( $\epsilon'$  and  $\epsilon''$ , respectively) were recorded from 20 Hz to 1 MHz and 15–90 K ranges by using platinum electrodes, an Agilent 4284A precision LCR meter and an ARS (DE-202SI) cryogenic system.

Figure 1 shows the temperature dependence of  $\epsilon'$  and  $\epsilon''$  for PN at different frequencies. The high-temperature dielectric data [Fig. 1(a)] reveal a FE-PE (OR-TE) phase transition at around  $T_C=793$  K, in good agreement with literature.<sup>5,7</sup> In spite of the frequency dispersion of permittivity around  $T_C$ , this characteristic temperature does not show any appreciable variation with frequency, besides coinciding between  $\epsilon'$  and  $\epsilon''$ , as is typical of normal-like ferroelectrics. On the other hand, the low-temperature dielectric data [Fig. 1(b)] evidence the occurrence of two dispersive anomalies, better resolved (and, in fact, indicated for the 1 kHz data) in the thermal spectra of  $\epsilon''$ . As discussed in Ref. 9, these processes are ascribed to the MO-OR phase transition (below 100 K),

<sup>a)</sup>Author to whom correspondence should be addressed. Electronic addresses: peko@ifsc.usp.br and jcpeko@yahoo.com.

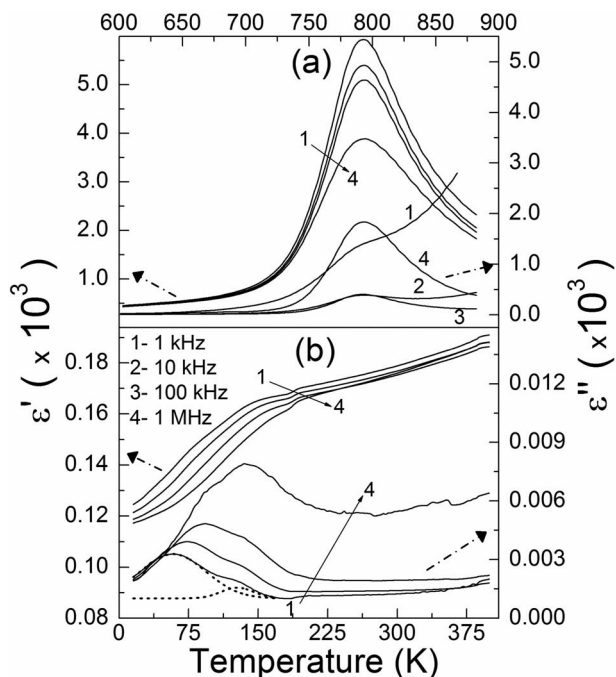


FIG. 1. Behaviors of  $\epsilon'$  and  $\epsilon''$  for  $\text{PbNb}_2\text{O}_6$  (PN) at (a) high and (b) low temperatures, for various measuring frequencies.

as previously reported in PBN materials (for which the MO-TE transition applied),<sup>8</sup> and to incommensurate superstructures (ICS) (extending here up to about 200 K, at least in terms of dielectric dispersion), as found to normally develop in PBN<sup>7,13</sup> and parent TTB-structured SBN materials.<sup>14–17</sup>

Figures 2 and 3 now depict the temperature dependence of  $\epsilon'$  and  $\epsilon''$ , respectively, for  $\text{Ti}^{4+}$ - and  $\text{Ba}^{2+}$ -doped PN samples. In Fig. 2 (PTN10), both high- and low-temperature data do not show any appreciable change with respect to Fig.

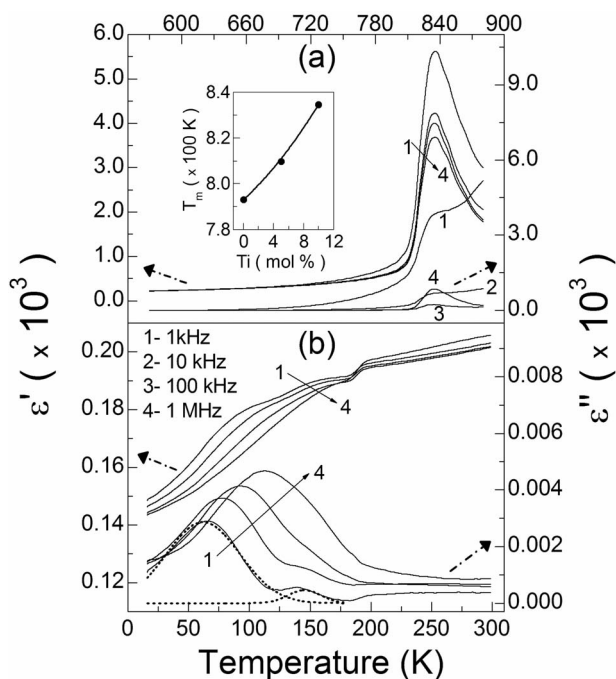


FIG. 2. Behaviors of  $\epsilon'$  and  $\epsilon''$  for  $\text{Ti}^{4+}$ -doped  $\text{PbNb}_2\text{O}_6$  (PTN10) at (a) high and (b) low temperatures, for various measuring frequencies. Dependence of the maximum permittivity temperature ( $T_m \equiv T_C$ ) on dopant content is shown in the (a) inset.

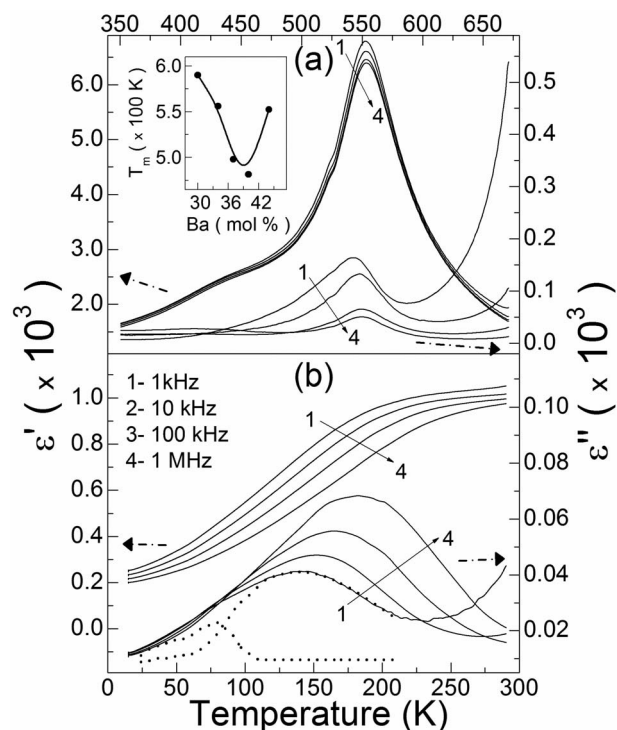


FIG. 3. Behaviors of  $\epsilon'$  and  $\epsilon''$  for  $\text{Ba}^{2+}$ -doped  $\text{PbNb}_2\text{O}_6$  (PBN44) at (a) high and (b) low temperatures, for various measuring frequencies. Dependence of the maximum permittivity temperature ( $T_m \equiv T_C$ ) on dopant content is shown in the (a) inset.

1, except for the increase of  $T_C$  with  $\text{Ti}^{4+}$  [Fig. 2(a) inset], agreeing well with literature.<sup>18</sup> Meanwhile, doping PN with  $\text{Ba}^{2+}$  (Fig. 3, PBN44) reveals an evident increase of the ICS-associated permittivity ( $\epsilon'$  and  $\epsilon''$ ) magnitude, besides extending fairly the ICS temperature region of dielectric manifestation toward higher values approaching 300 K. The dependence of  $T_C$  on  $\text{Ba}^{2+}$  [Fig. 3(a) inset] reproduces also well previous observations.<sup>6,7,13</sup> When  $\text{La}^{3+}$  is additionally incorporated into PBN44 (Fig. 4,  $x=0.5$  wt %  $\text{La}^{3+}$ ), magnitude of the ICS-associated permittivity ( $\epsilon'$  and  $\epsilon''$ ) further increases meaningfully, while  $T_C$  decreases with dopant content [Fig. 4(a) inset], also agreeing with literature.<sup>18</sup>

In all the cases so far presented (Figs. 1–4), normal-like high-temperature FE-PE phase transitions apply, while the two low-temperature processes, with special attention presently paid to the ICS-associated dielectric dispersion, reveal to be of diffuse and relaxor nature, as also observed elsewhere.<sup>8–10,17</sup> In the Fig. 4(a) inset (for which the data were presented only up to  $x=2.0$ ), particularly,  $T_C$  continuously decreases so as approaching the temperature region of ICS dielectric manifestation. Figure 5 summarizes the temperature behavior of  $\epsilon'$  and  $\epsilon''$  of the PBLN44/ $x$  system, for  $x=0.5$ , 2.0, and 4.0, noting that degree of  $T_C$  shift toward lower temperatures has evidently an effective influence on the final DPT and relaxor or not features of the FE-PE phase transition. In effect, according to Fig. 5(c), the PBLN44/4.0 compound turns out to be a ferroelectric material with a properly strong DPT plus relaxor character.

According to literature, development of ICS in TTB-structured materials is presumably associated with displacive structural changes owing to defects-associated ferroelastic oxygen octahedral tilting.<sup>13,14,19</sup> From this viewpoint, undoped PN should then be expected to also originally involve sufficient natural defects to the point of stabilizing low-

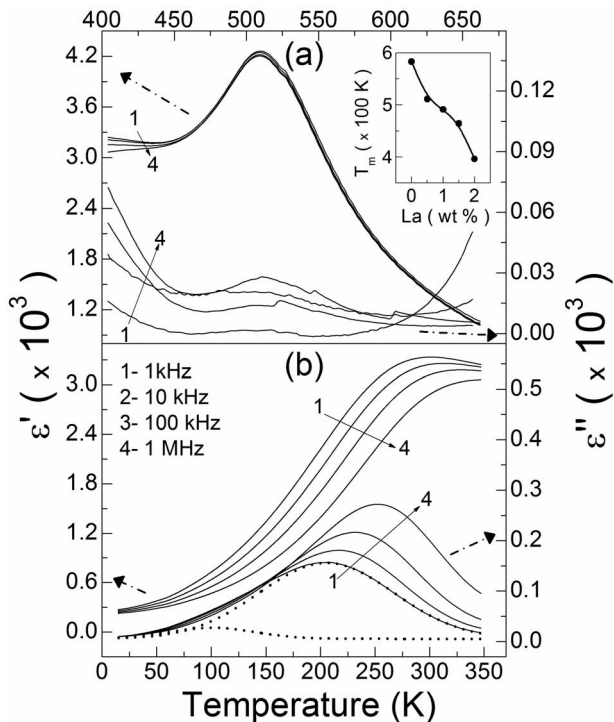


FIG. 4. Behaviors of  $\epsilon'$  and  $\epsilon''$  for  $\text{La}^{3+}$ -doped  $\text{PbNb}_2\text{O}_6$  (PBLN44/0.5) at (a) high and (b) low temperatures, for various measuring frequencies. Dependence of the maximum permittivity temperature ( $T_m \equiv T_C$ ) on dopant content is shown in the (a) inset.

temperature ICS of naturally diffuse and relaxor characteristics [Fig. 1(b)]. Here, thus, the dopant effects of interest are: first, a change in the dipolar dynamics of the superstructure configurations, as may be deduced from the magnification of the ICS-associated dielectric properties for  $\text{Ba}^{2+}$  and  $\text{La}^{3+}$  dopants, accompanied by ICS dielectric manifestation/stabilization over a fairly larger temperature region (compare Figs. 1 and 2 with Figs. 3–5 for both statements); and, second, the shift of  $T_C$  toward lower temperatures to the point of leading both FE-PE phase transition and ICS regions to overlap, as in the case of  $\text{La}^{3+}$  (Fig. 5). The final result, as shown in Fig. 5(c), is the appearance of proper ICS-induced DPT and relaxor behaviors in place of the originally normal-like PN's FE-PE phase transition.

The observation just above reinforces a previous suggestion of an apparent association, at least in terms of contribution, between ICS and FE-PE DPT in SBN materials.<sup>16</sup> Accordingly, in contrast to PBNs, the FE-PE DPT plus relaxor behavior found in some SBN solid solutions should respond to the sufficiently  $\text{Sr}^{2+}$ -induced low  $T_C$  values<sup>10,16,17</sup> so as approaching to overlapping the low-temperature region of the ICS-related diffuse and relaxor dielectric manifestation. Recently, moreover, a work on TTB-structured  $\text{Ba}_2\text{La}_x\text{Nd}_{1-x}\text{Nb}_3\text{Ti}_2\text{O}_{15}$  (BLNNT) showed a relaxorlike behavior developing for  $x=1$ , coincidentally also within the temperature region of ICS manifestation.<sup>20</sup>

In summary, the present study suggests that in PN-based compounds the FE-PE DPT and relaxor behavior appear to be exceptionally induced as dopants force  $T_C$  to shift toward lower temperatures where an ICS-associated dielectric dispersion process, of naturally diffuse and relaxor appearance, manifests in these TTB niobate materials. This observation

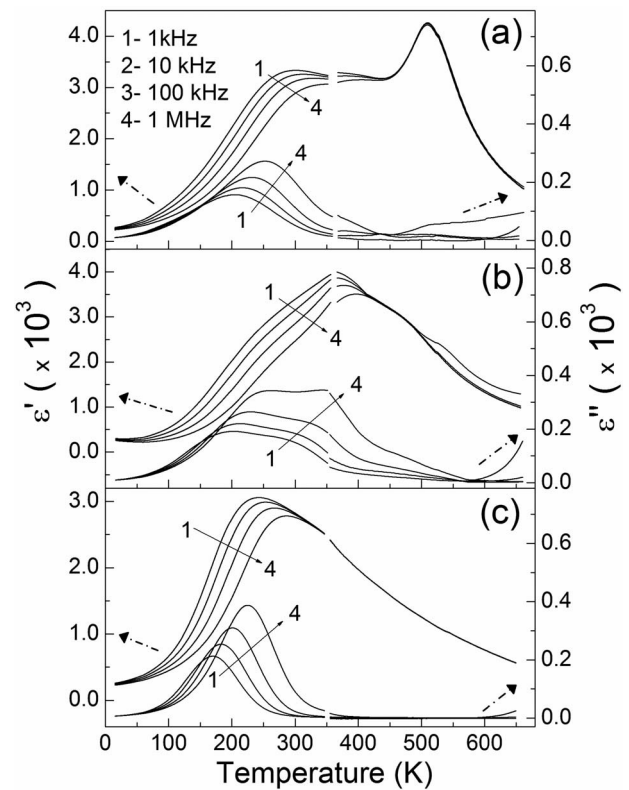


FIG. 5. Temperature dependences of  $\epsilon'$  and  $\epsilon''$  for  $\text{La}^{3+}$ -doped  $\text{PbNb}_2\text{O}_6$ : (a) PBLN44/0.5, (b) PBLN44/2.0, and (c) PBLN44/4.0 at various measuring frequencies.

also applies for other TTB niobate materials, as cited in the text.

The authors gratefully acknowledge technical assistance from Francisco J. Picon, and financial support from FAPESP and CNPq, two Brazilian research-funding agencies.

- <sup>1</sup>K. Uchino, *Ferroelectrics Devices* (Dekker, New York, 2000).
- <sup>2</sup>M. E. Line and A. M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Clarendon, Oxford, 1997).
- <sup>3</sup>M. Venet, I. A. Santos, J. A. Eiras, and D. Garcia, *Solid State Ionics* **177**, 589 (2006).
- <sup>4</sup>M. Venet, A. Vendramini, F. L. Zabotto, F. Guerrero, D. Garcia, and J. A. Eiras, *J. Eur. Ceram. Soc.* **25**, 2443 (2005).
- <sup>5</sup>G. Goodman, *J. Am. Ceram. Soc.* **36**, 368 (1953).
- <sup>6</sup>M. H. Francombe, *Acta Crystallogr.* **13**, 131 (1960).
- <sup>7</sup>R. Guo, A. S. Bhalla, C. A. Randall, Z. P. Chang, and L. E. Cross, *J. Appl. Phys.* **67**, 1453 (1990).
- <sup>8</sup>Y. Xu, Z. Li, W. Li, H. Wang, and H. Chen, *Phys. Rev. B* **40**, 11902 (1989).
- <sup>9</sup>J. De los S. Guerra, M. Venet, D. Garcia, and J. A. Eiras, *Appl. Phys. Lett.* **91**, 062915 (2007).
- <sup>10</sup>M. Venet, J. S. Guerra, I. A. Santos, J. A. Eiras, and D. Garcia, *J. Phys.: Condens. Matter* **19**, 026207 (2007).
- <sup>11</sup>L. E. Cross, *Ferroelectrics* **76**, 241 (1987).
- <sup>12</sup>M. Venet, A. Vendramini, D. Garcia, J. A. Eiras, and F. Guerrero, *J. Am. Ceram. Soc.* **89**, 2399 (2006).
- <sup>13</sup>C. A. Randall, R. Guo, A. S. Bhalla, and L. E. Cross, *J. Mater. Res.* **6**, 1720 (1991).
- <sup>14</sup>L. A. Bursill and P. J. Lin, *Philos. Mag. B* **54**, 157 (1986).
- <sup>15</sup>B. N. Savenko, B. Sangaa, and F. Prokert, *Ferroelectrics* **107**, 207 (1990).
- <sup>16</sup>H.-Y. Lee and R. Freer, *J. Appl. Crystallogr.* **31**, 683 (1998).
- <sup>17</sup>H. Amorin, J. Pérez, A. Fundora, J. Portelles, F. Guerrero, M. R. Soares, E. Martínez, and J. M. Siqueiros, *Appl. Phys. Lett.* **83**, 4390 (2003).
- <sup>18</sup>E. C. Subbarao and G. Shirane, *J. Chem. Phys.* **32**, 1846 (1960).
- <sup>19</sup>P. J. Lin and L. A. Bursill, *Acta Crystallogr. B* **43**, 504 (1987).
- <sup>20</sup>I. Levin, M. C. Stennett, G. C. Miles, D. I. Woodward, A. R. West, and I. M. Reaney, *Appl. Phys. Lett.* **89**, 122908 (2006).