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Dielectric properties of $PbNb_2O_6$ ferroelectric ceramics at cryogenic temperatures

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Complex dielectric permittivity measurements in $PbNb_2O_6$ ceramics were performed in a frequency and temperature range of 1 kHz–1 MHz and from 15 to 900 K, respectively. The results revealed two dielectric anomalies showing typical characteristics of relaxor ferroelectric materials at cryogenic temperatures. Comparison with other tetragonal tungsten bronze (TTB) structure-type materials suggests the existence of successive phase transitions, which until now were not reported. The observed low temperature dielectric behaviors seem to be due to intrinsic physical characteristics related to the TTB structure. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2769765]

Tetragonal tungsten bronze (TTB) structure-type ferroelectric materials have received special attention for technological applications because of their excellent piezoelectric, pyroelectric, and ferroelectric properties.[1] The prototype of a TTB structure are the lead metaniobate $PbNb_2O_6$ (PN) based ferroelectrics,[2] which have received special attention due to its high potential for high temperature piezoelectric transducer applications.[3] Concerning the densification of PN based ceramics, several attempts were achieved through the addition of doping elements.[4,5] It has been observed that, except for the Ti^{4+} ion, the addition of cations in the PN structure always decreases the paraelectric-ferroelectric phase transition temperature.[4] Nevertheless, less attention has been given to the investigation of fundamental physical properties; in particular, the low temperatures dielectric response. On the other hand, some studied TTB structure sytems, such as strontium barium niobate (SBN),[6] lead barium niobate (PBN),[7] as well as barium sodium niobate (BNN) (Ref. 8) solid solutions have also led to an increasing interest in the electroelectronic industry because of the wide applicability range for electronic devices.[8–10]

All the above-mentioned TTB materials present low temperature dielectric characteristics that are still not clearly understood. In addition to the paraelectric-ferroelectric phase transition (PT), an anomalous behavior observed at lower temperatures, related to additional phase transitions, has been observed in all these previously mentioned systems, specifically in the temperature range of 60–80 K for SBN and PBN (Ref. 11) and around 120 K for BNN.[12] For the SBN system an additional anomaly near 200 K was reported.[13,14] X-ray analysis revealed that the anomalies observed near 80 K were related to an additional tetragonal-monoclinic structural phase transition,[11] where a symmetry change from the point group 4 mm to the point group *m* may be the cause of a tilt in the direction of the polar axis. This result contrasts with the phase transition reported for the BNN near 110 K, where the polar axis was considered to remain in the *c* direction of the crystal cell.[12] Based on dielectric measurements in SBN Povoa *et al.*[14] associated this anomaly to a polarization fluctuation "freezing in," originated from the relaxor nature of the SBN solution, instead of a true structural phase transition. On the other hand, the second dielectric anomaly observed around 200 K (Ref. 14) has been associated to an incommensurate PT,[13] where there exists a strong dependence to the polarization-strain coupling in the *c* axis.

As observed, TTB structure-type systems present from the fundamental point of view the intriguing physical properties at low temperatures, which are reflected in the dielectric response. However, there are conflicting reports concerning to the existence and origin of phase transitions in these systems below T_C. Therefore, a careful investigation of the low temperature dielectric response of the TTB structure prototype PN can be very interesting to contribute to the explanation of the origin of the observed anomalies. Despite their very attractive physical and dielectric properties, no work concerning a systematic study of the low temperatures dielectric properties in the PN system has been reported.

The aim of the present work is to investigate in detail the dielectric properties of $PbNb_2O_6$ ceramics at temperatures down to 15 K in a wide frequency range. The results reveal frequency dependent dielectric anomalies at cryogenic temperatures similar to those observed in modified TTB materials.

PN ceramics were obtained by the conventional ceramic as previously reported in the literature.[15] A single phase compound isostructural with the PN ferroelectric orthorhombic phase was observed by the x-ray analysis.[15] The PN samples were cut, polished, and after that heat-treated at 873 K for 20 min. Platinum electrodes were sputtered on the ceramic samples in the form of disks with 12.4 and 0.80 mm in diameter and thickness, respectively. The real (ε') and imaginary (ε'') components of the dielectric permittivity were measured over a wide temperature and frequency range (15–923 K and 20 Hz–1 MHz, respectively), by using an

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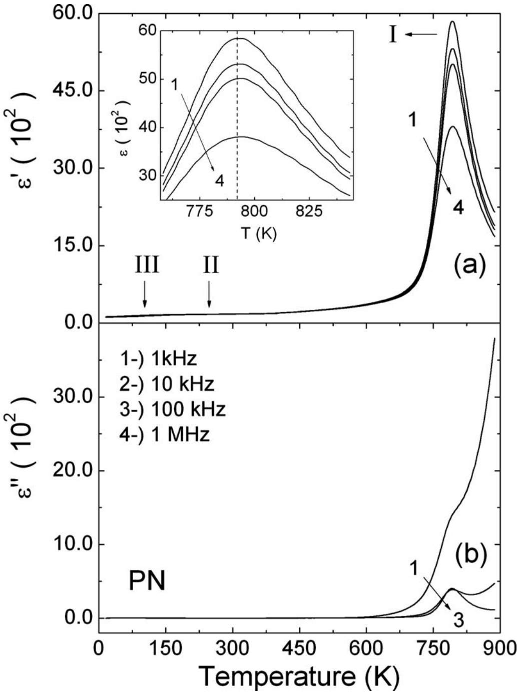

FIG. 1. Temperature dependence of the real and imaginary components of the dielectric permittivity for the PN samples at various frequencies (1 kHz, 10 kHz, 100 kHz, and 1 MHz).

Agilent 4284A precision *LCR* meter and an ARS (DE-202SI) cryogenic system.

Figure 1 shows the temperature dependence of the real (a) and imaginary (b) components of the dielectric permittivity in the temperature range of 15–900 K for four selected frequencies. Three dielectric anomalous regions can be identified in the investigated temperature interval at high, intermediate, and low temperature regions (hereafter labeled as I, II, and III, respectively), as shown in Fig. 1(a). The results obtained at high temperatures (region I) present similar features to those obtained by other authors.[2] The high temperature dielectric anomaly has been correlated to the first-order phase transition from a paraelectric (tetragonal) to a ferroelectric (orthorhombic) phase.[2] The temperature of the maximum dielectric permittivity was observed around 793 K, in agreement with previously reported results.[2,16] As also observed, in Fig. 1(a) (inserted figure), there is no appreciated shift of the temperature of the maximum real dielectric permittivity (T_C) with the increase of the frequency (region I). On the other hand, a normal Curie-Weiss dependence (not shown here) was obtained for temperatures above T_C, with a Curie-Weiss constant about 2.27×10^5 K^{-1}, which reveals typical characteristics of a "normal" displacive paraelectric-ferroelectric PT in the PN.

In order to carefully analyze the anomalies in II and III, the temperature dependence of the real and imaginary components of the dielectric permittivity at different frequencies are shown in Fig. 2, now at temperatures lower than 400 K. As can be seen, a low temperature dielectric anomaly, which extends over a wide temperature interval around 50–150 K (region III), was detected. Different from the high temperature PT peak (region I), this anomaly evidences a notable frequency dependence of T_C, which moves to higher temperature values with the increase of the frequency. This behavior, together with the fact that the maximum imaginary dielectric permittivity is observed at temperatures lower than

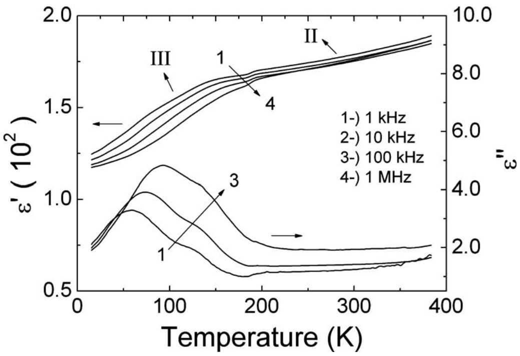

FIG. 2. Temperature dependence of the real and imaginary components of the dielectric permittivity for the PN samples at the low temperature region.

those obtained for the real component, as observed in the same Fig. 2, suggests a diffuse phase transition with relaxor characteristics, as observed in typical relaxor ferroelectric materials.[17] Similar studies carried out by other authors, in the temperature range of 10–1023 K in $PbNb_2O_6$, did not report any anomaly, in addition to the high temperature phase transition, which was observed around 840 K.[18] However, as aforementioned, an additional phase transition was observed in SBN ferroelectric ceramics, which has been detected from the splitting of x-ray diffraction peaks (400) and (140) near 80 K,[11] having similar characteristics to that obtained for the PN system in region III. Also remarkable is the dielectric anomaly in region II, which extends up to around 300 K and down up to those observed in region III. This behavior, which becomes less prominent at higher frequencies, suggests the contribution of more than one polarization mechanism. Thus, the observed anomalies (regions II and III) seem to be related to those previously reported for the SBN and PBN systems for temperatures near 200 and 80 K, respectively. In this way, the anomaly observed in region II should be associated to the existence of incommensurate superlattices (ICSs) in the PN structure, similar to the low symmetry orthorhombic one-dimensional ICS observed for the BNN system.[12] The instability is responsible for the ICS resulting from a collective shearing of the [NbO_6] octahedral, which constitutes the framework of the TTB structure.[19]

Despite similar results found in some TTB structure materials, such as SBN, PBN, and BNN ferroelectric systems,[11,12] there is no plausible explanation for the experimental results obtained for the PN system. Indeed, the obtained results require further investigations of its low temperature structural features, which can be conducted according to the scenario described as follows. One aspect is related to the fact that all the previously reported low temperature anomalies have been observed in TTB systems whose high temperature dielectric properties show relaxor characteristics with a diffuse PT, different for the normal behavior observed in the PN system, at high temperatures. As a second aspect, it is important to point out that all the above described ferroelectric systems have a common factor in its structural characteristics. Indeed, in the $(A_1A_2)BO_6$ TTB structure, all of them possess a great A-site competition between different ions, leading to an increase of the local disorder that may influence the dielectric properties depending upon the $A1/A2$ occupation ratio.

Since there exist some ferroelectric materials whose A sites within the TTB structure can be occupied by a single ion, such as $PbNb_2O_6$ and $PbTa_2O_6$ (PTa), it is improbable that the low temperature dielectric anomalies can be associated to a local disorder due to the *A*1 and *A*2 site occupations, as could be supposed for SBN, PBN, and BNN. Rather, it seems to be a universal behavior characteristic of the TTB structure materials. Further investigations, based on local high resolution techniques, are necessary to clarify the nature of these anomalies.

In summary, the dielectric response of $PbNb_2O_6$ ceramics was investigated by complex dielectric permittivity analysis over a wide temperature and frequency range. A nonpreviously reported behavior, corresponding to two low temperature dielectric anomalies for the PN, was observed for temperatures near 80 K and around 170–300 K, which were similar to those obtained for some other TTB structure-type systems. The results showed a very broad low temperature dielectric anomaly typical of a diffuse phase transition with relaxor characteristics, which extends from 50 to 150 K. The observed dielectric behaviors have been suggested to be due to the influence of intrinsic characteristics related to the TTB structure.

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