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Dielectric behavior of the $PbNb_2O_6$ ferroelectric ceramic in the frequency range of 20 Hz to 2 GHz

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Abstract

Ferroelectric materials with high Curie temperature are highly desirable to construct transducers for high temperature piezoelectric applications. Among them, the lead niobate system is one that displays such characteristic. In this work, the dielectric behavior of lead niobate ferroelectric ceramics was analyzed in the frequency range of 20 Hz to 2 GHz. Ceramic samples with nominal formula $PbNb_2O_6$ (PN) were prepared by the solid-state reaction method. The diffuse phase transition was investigated with the Santos–Eiras' phenomenological model. The values of ξ are close to 1, indicating a conventional ferroelectric phase transition. A low frequency dispersion process, which may be associated to a conduction mechanism, was observed up to 50 kHz. The PN materials show a typical high frequency dispersion process, which may be associated to the domain wall dynamic, as observed in ferroelectric materials in the microwave frequency region, rather than the nano-clusters relaxation process or low frequency dispersion.

Keywords: Phase transition; Dielectric properties

1. Introduction

Lead meta-niobate $PbNb_2O_6$ (PN) ferroelectric materials, possessing tetragonal-tungsten–bronze structure,[1] have a high potential to be used as high temperature piezoelectric transducers.[2] They exhibit very good piezoelectric properties with a high Curie temperature next to 570 °C, low dielectric permittivity at room temperature and low quality factor (Q).[1] These dielectric characteristics are important for applications in the fabrication of ultrasonic transducers in high temperature applications, such as flow detectors, where the $Pb(Zr,Ti)O_3$ and other piezoelectric materials can not be used.

The applications of the PN materials have widely been investigated in the form of ceramic samples.[3] However, it has been found that one of the most common problem lies in the processing and synthesis of the PN system; indeed, it is very difficult to obtain high density ceramics, which difficult the use of these materials for practical applications.[1,3]

On the other hand, it is known that all the above mentioned properties are basically influenced by the temperature and the frequency in perovskites and tetragonal-tungsten–bonze (TTB) structure-types materials. Therefore, it is necessary the detailed investigation concerning the type of the phase transition in this kind of materials. Specifically, the temperature dependence of the dielectric permittivity (ε) above its maximum value (ε_m), has been widely studied and reported as an important feature in order to determine the character of the phase transition in ferroelectric materials.[4] To the best of our knowledge, no works focusing the study of the dielectric properties in the PN system in a very wide frequency interval, including the microwave frequencies, have been reported in the literature. The objective of the present work is to investigate the dielectric properties of the $PbNb_2O_6$ ferroelectric ceramics in a wide temperature and frequency range, including the high frequency region (radio and microwave frequencies). Two dielectric relaxation processes, low- and high frequency dispersions, were found in the whole studied frequency interval. The obtained results were discussed concerning the contribution of the dynamics properties of the polar regions in ferroelectrics materials. Specifically, the ferroelectric domain wall motion was used as the main cause for the observed dielectric anomalies in the high frequency region.

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2. Experimental procedure

Ceramic powders of $PbNb_2O_6$ were prepared by the solid-state reaction method.[3] Analytical graded precursors with a 2 wt.% PbO were mixed in a ball mill containing isopropyl alcohol and stabilized ZrO_2 cylinders, during 20 h. The mixture was dried and calcined at 1050 °C for 3.5 h, and milled again for 22 h. The powder of PN was heat treated at 1300 °C for 1 h in order to obtain the room temperature (RT) orthorhombic ferroelectric phase. After that, 3 wt.% PbO was added in order to compensate the lead losses during the sintering process, which was carried out at 1270 °C for 4.5 h. The RT lattice parameters and the phase qualitative analysis were determined by the X-ray diffraction measurements. Computer assisted dielectric characterization was performed as a function of the temperature from the RT up to 650 °C, using an HP-4194A Impedance Gain Phase Analyzer, which cover a frequency range of 20 Hz to 10 MHz. High frequency dielectric measurements were carried out in the temperature range of 25–180 °C using a Network Analyzer HP-8719 C in the frequency range of 50 MHz to 2 GHz. The complex dielectric permittivity was determined from the measured complex reflection coefficient by the reflectometric technique.[5]

3. Results and discussion

Fig. 1 shows the temperature dependence of the complex dielectric permittivity (real, ε' and imaginary, ε'' components) at different frequencies for the PN ceramics. As can be seen, in the whole studied frequency interval, there is not an appreciated shift of the temperature of the maximum dielectric permittivity (T_m) with the increase of the frequency. On the other hand, a normal Curie–Weiss dependence (linear dependence of the converse dielectric permittivity with the temperature) was observed for temperatures above the T_m, which is a fundamental characteristic in ferroelectrics with "normal" paraelectric–ferroelectric phase transition. However, a slight dispersion of the maximum dielectric permittivity with the frequency was observed around T_m, in agreement with the results obtained for some other studied ferroelectric ceramics.[6] This behavior has been associated to the domain walls motion of the ferroelectric material, where the micro-domain that marks a normal-type transition prevails.

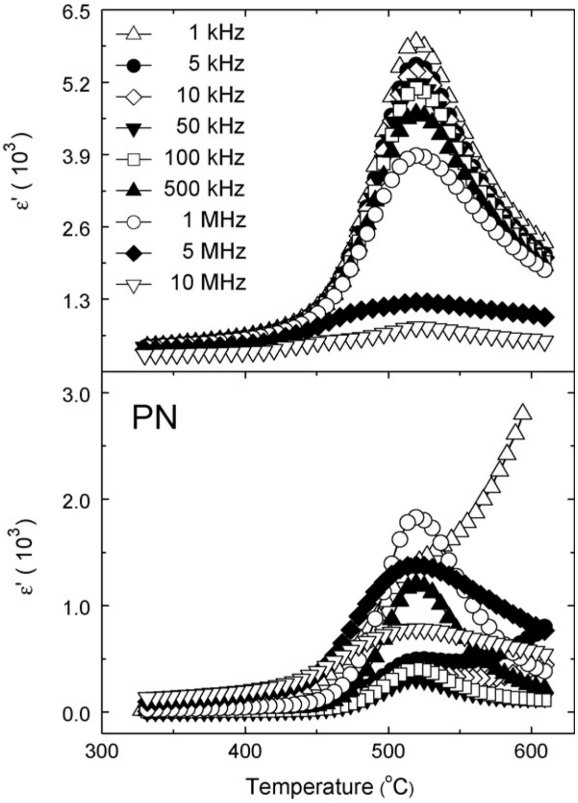

Fig. 1. Temperature dependence of the complex dielectric permittivity (real, ε' and imaginary, ε'' components, a and b, respectively) as a function of the frequency, for the PN ceramics.

In order to analyze the main characteristics of the ferroelectric phase transition in the PN ceramics, the dielectric permittivity versus temperature curves were fitted with the Santos–Eiras' equation[4] (Eq. (1)) at different frequencies:

$$\varepsilon' = \frac{\varepsilon'_m}{1 + (T - T_m/\Delta)^{\xi}} \tag{1}$$

where, ε'_m is the maximum dielectric permittivity, T_m is the temperature of the maximum dielectric permittivity, Δ is a parameter that defines the degree of the diffuseness of the ferroelectric phase transition and ξ indicates the character of the phase transition.

The parameters ε'_m, T_m, Δ, and ξ were obtained from the fitting process. The fitted parameters are listed in the Table 1. The values of ε'_m decrease with the increase of the frequency, as has been reported for relaxor ferroelectrics,[7] however T_m remains almost constant. The values of ξ are close to 1 in all the cases, indicating a conventional ("normal") ferroelectric phase transition. The parameter Δ is small when compared with that observed in ferroelectrics with a diffuse phase transition type. This result is in agreement with the normal Curie–Weiss behavior aforementioned and could be interpreted as follows: when a typical ferroelectric is cooled from the paraelectric to the ferroelectric phase, the ferroelectric clusters rise up at a temperature above but very close to the T_C (the Curie temperature). This clustering dynamics is accompanied by strong interactions between the ferroelectric clusters.[8]

On the other hand, the Fig. 2 shows the frequency dependence of ε' and ε''. As can be seen, an anomalous behavior, character-

Table 1
Dielectric parameters obtained by the Santos–Eiras' relation

Frequency	ε'_m	T_m (°C)	Δ (°C)	ξ
1 kHz	6106.75	531.17	51.10	1.053
5 kHz	5716.88	529.16	42.69	1.004
10 kHz	5619.08	528.32	40.73	1.084
50 kHz	5491.67	527.26	40.54	1.151
100 kHz	5419.46	527.53	40.64	1.151
500 kHz	5346.76	527.67	40.80	1.156
1 MHz	5298.19	527.94	40.93	1.155
5 MHz	4851.52	530.07	43.22	1.147
10 MHz	4072.72	533.23	48.35	1.150

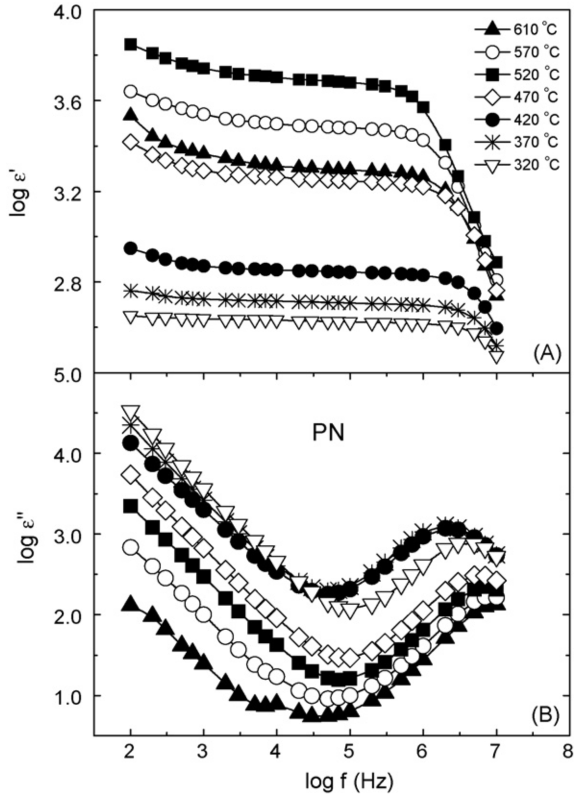

Fig. 2. Frequency dependence (low frequency region) of the real, ε' (A) and imaginary, ε'' (B) component of the dielectric permittivity as a function of the temperature.

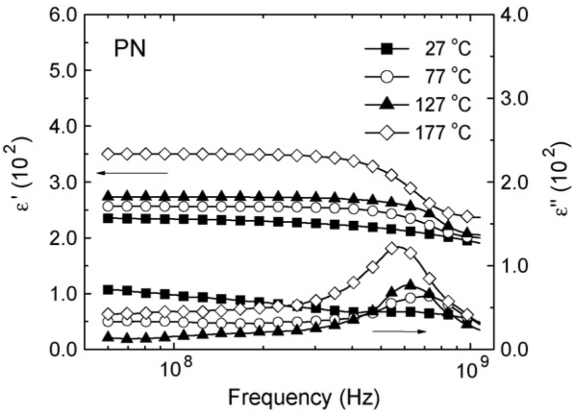

Fig. 3. Frequency dependence (high frequency region) of the real (ε') and imaginary (ε'') component of the dielectric permittivity in the temperature range of 25–180 °C.

istic of a low frequency dielectric dispersion, was observed in the whole analyzed low frequency region. The maximal variation of the dielectric permittivity (between 6500 and 600, for the difference between the low and high frequency dielectric permittivity values, respectively) was obtained at a temperature of 520 °C. For temperatures higher than 520 °C this anomalous behavior becomes less intensified, that is to say, the low frequency dielectric dispersion increases with the increase of the temperature, traversing a maximum and then diminishes. It is noticeable an additional dispersion process that appears in the lowest frequency region up to 50 kHz. A lineal increment of the permittivity with the decrease of the frequency can be observed, which may be associated to a conductive process, related with the accumulation of charges carrier in the grains boundary and in the interface between the electrode and the sample surface, originating an interfacial polarization. It is important to appoint out that, for frequencies above 50 KHz, the maximum value of the imaginary dielectric permittivity increases with the increase of the frequency, traversing a maximum around 2 MHz, for all the analyzed temperatures. This behavior may be related to the overlapping between both, the normal dipolar process (characteristic of the dipolar materials) and the strong low frequency conductive process.

The Fig. 3 illustrates the frequency dependence of ε' and ε'' measured in the temperature and frequency range of 25–180 °C and 50 MHz to 2 GHz, respectively. Similar to that observed in the Fig. 2, the obtained behavior in the high frequency region shows characteristics of a relaxation process,[9] which is evidenced in all ferroelectric materials in this frequency range. This microwave dielectric dispersion, observed in the PN ceramics, has been associated to the vibration of the boundaries of the polar regions,[9] which is the common mechanism responsible for the microwave dielectric dispersion process in ferroelectric materials.

On the other hand, the temperature dependence of the characteristic parameters of the dielectric dispersion (the characteristic frequency, f_R and dielectric strength, $\Delta\varepsilon$), is shown in the Fig. 4. As appointed out in recent works,[9] the temperature dependence of the characteristic parameters, becomes a fundamental key in order to identify the ferroelectric-type phase transition. Thus, the determination of a relationship between the ferroelectric polar structures and their respective dynamical response, which is one of the fundamental point involving the investigation of dielectric properties of ferroelectrics, may be well investigated by considering the thermal variation of these parameters not only for temperature above the T_m, but also for temperatures below T_m.

As observed, the results in the Fig. 4 present a decrease of the f_R and an increase of the $\Delta\varepsilon$, with increasing the temperature, in the whole presented temperature interval. Since the characteristic parameters variations in the microwave region have been

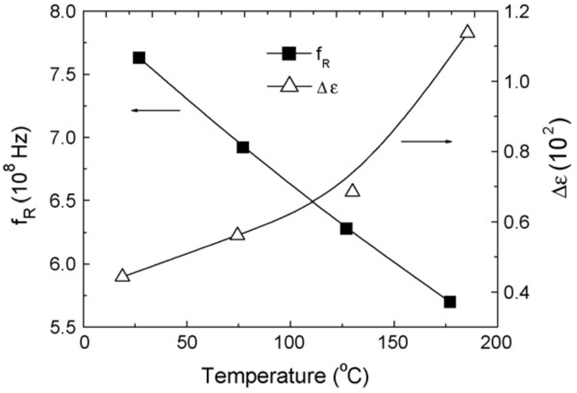

Fig. 4. Temperature dependence of the characteristic frequency, f_R and the dielectric strength, $\Delta\varepsilon$ for the PN ceramics.

attributed to the existence of polar regions (ferroelectric domains and/or polar clusters for normal and relaxor ferroelectrics, respectively) it would be expected that the obtained behavior could be associated to the size/interaction of the polar regions. Investigations to better understand the responsible mechanism for the observed dielectric dispersion are in progress.

4. Conclusion

In summary, the dielectric properties of the PN ceramics were, for the first time, investigated in the frequency range of 20 Hz to 2 GHz and a wide temperature interval. The results showed a "normal" ferroelectric–paraelectric phase transition around the temperature of the maximum dielectric permittivity. Above this temperature, a linear behavior of the Curie–Weis law was observed for all the analyzed frequencies. The parameters characterizing the ferroelectric–paraelectric phase transition were determined by using the Santos–Eiras' expression. The obtained values for ζ and Δ, were found to be close to 1 and in the range of 40–51, respectively, far away from those reported for materials with diffuse phase transition. Two dielectric relaxation processes were obtained in the whole frequency range. The low and high frequency relaxations were related to the low frequency dispersion associated to a conductive process and the dynamics of the domain walls motion, characteristic in ferroelectric materials in the microwave frequency region, respectively.

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