Effect of lithium carbonate modification on the ferroelectric phase transition diffusion in lead ferroniobate ceramics

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The paper discusses the features of the effect of modification with lithium carbonate on the dielectric dispersion of lead ferroniobate ceramics. The modifier has been previously shown to change the ways of the recrystallization sintering and therefore reduce the sintering temperature of the ceramics, increase their average grain size, and improve their dielectric and piezoelectric properties. In this study, the emphasis is placed on the analysis of the diffusion effects of the ferroelectric phase transition upon such modification considered from the standpoint of the chemical specifics of the modifier and its location in the structure of the parent compound.

Keywords: Multiferroics; ferroelectric relaxors; ceramics; dielectric dispersion.

1. Introduction

Lead ferroniobate ($PbFe_{1/2}Nb_{1/2}O_3$; PFN) is one of the most famous representatives of the class of multiferroics, in which the interaction of electrical and magnetic subsystems is observed. Despite the fact that in PFN the ferroelectric (FE) and magnetic properties combine only below 140–170 K,[1] it remains a very interesting object at the same time both from the application point of view (used in microwave and sensor technologies) and from the position of opportunities to study magnetoelectric interaction,[2–4] often found in the literature as a component of promising multiferroic systems of solid solutions[5–9] and composites.[10] Despite a rather extensive bibliography,[11–17] many details of phase transformations in PFN, as well as some features of dielectric responses associated with this, are not fully understood. The purpose of this study was to perform a detailed study of the dielectric properties of PFN in wide temperature (300–520 K) and frequency (25 Hz–2 MHz) ranges, as well as to determine the effect of its modification with lithium carbonate (LCO) on the degree of diffusion of the FE phase transition (PT).

2. Experimental Details

The objects of the experimental study were ceramics of PFN: pure and modified with 1, 2, and 3 wt.% LCO above stoichiometry (PFNL1, PFNL2, and PFNL3, respectively). Samples were prepared by solid-state reactions: mixtures of high-purity PbO, Fe_2O_3, Nb_2O_5, and Li_2CO_3 (analytical or reagent grade) were fired in two steps, with intermediate grinding. Details of the ceramics preparation and X-ray diffraction characterization are given in Ref. 11. The experimental samples were disks with a diameter of 10 mm and a thickness of 1 mm with silver-containing electrodes deposited (by double firing) on the flat end surfaces.

The dependences of the real (ε') and imaginary (ε'') parts of the complex relative permittivity ($\varepsilon^*/\varepsilon_0 = \varepsilon'/\varepsilon_0 - i \cdot \varepsilon''/\varepsilon_0$) on the temperature were studied at different frequencies of the alternating electric field in the 25-Hz–2-MHz range using a high-temperature furnace with an RTD temperature sensor (PT100 platinum resistance), a PTC10 programmable temperature controller (Stanford Research Systems, USA), an E4980A LCR meter (Keysight, USA), and a personal

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computer. Measurement, recording of data, and calculation of parameters were carried out automatically using specially developed software. The measurements were carried out in the 300–620-K temperature range in the regimes of monotonous heating and cooling at a rate of 0.3 K/min.

To describe the degree of diffusion of an FE PT, we used algorithms based on generally accepted expressions. It should be noted that for the first time the method of qualitative and quantitative description of the diffusion of the PT was presented in Refs. 18–20,

$$\frac{\varepsilon_m}{\varepsilon} = 1 + \frac{(T - T_m)^2}{2\delta^2}, \tag{1}$$

where T_m and ε_m are the temperature and magnitude of the $\varepsilon'/\varepsilon_0(T)$ curve, and δ is the measure of the degree of diffuseness of the peak.

Later, in the work of Bokov and Ye,[21] a new empirical relation (2) was proposed, which most accurately described the temperature dependence of the dielectric constant at $T > T_m$ in FE relaxors,

$$\frac{\varepsilon_A}{\varepsilon} = 1 + \frac{(T - T_A)^2}{2\delta_A^2}. \tag{2}$$

This expression uses as coefficients some virtual values of the maximum dielectric constant (ε_A) and the corresponding temperature (T_A). It is assumed that these parameters, as

well as the diffusion parameter (δ_A) calculated in this way, should not depend on the frequency of the measuring signal, which makes them a convenient measure for assessing the degree of diffusion of the dielectric constant peaks in various materials. The calculation of these parameters was carried out using nonlinear approximation of $\varepsilon'/\varepsilon_0(T)$ curves with the help of plug-in library of algorithms ALGLIB.[22] The temperature range for approximation was chosen automatically in two stages: at the first stage, the range was limited based on the maximum of the correlation coefficient; at the second, the homoscedasticity of the approximation residues in the selected range was taken into account.

3. Results and Discussion

Figure 1 shows the $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ dependences of the pure and modified ceramics on the temperature and frequency of the measuring signal (f).

To analyze dielectric data, we used a special approach, which consisted in smoothing and subsequent interpolation of the experimental curves.[17] The quality of the interpolation was ensured by a large number of experimental points recorded due to the low rate of temperature change.

This approach made it possible to check the $\varepsilon'/\varepsilon_0(T)$ maxima shifts in the case of both PFN and PFNL, which are illustrated by Fig. 2, where the dependences of the logarithm of the frequency $\omega = 2\pi f$ as a function of the maxima
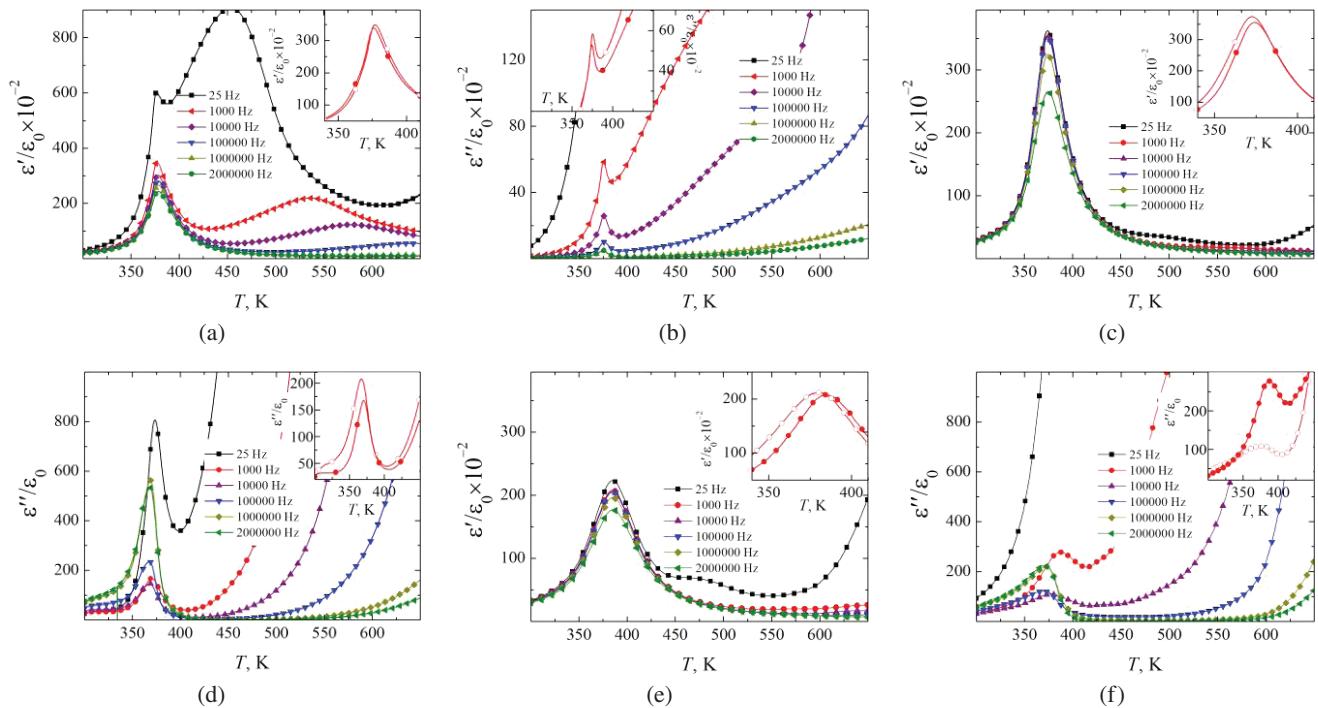

Fig. 1. Dependences of $\varepsilon'/\varepsilon_0$ and $\varepsilon''/\varepsilon_0$ on temperature for (a), (b) PFN, (c), (d) PFNL1, (e), (f) PFNL2, and (g), (h) PFNL3 ceramics on cooling, respectively. The insets show the corresponding dependences measured at $f = 1$ kHz both on the heating (filled markers) and cooling (open markers).
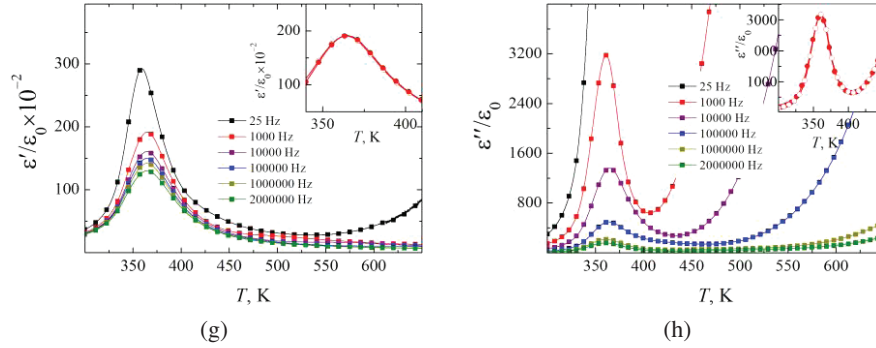
(g)   (h)

Fig. 1.   (*Continued*)

(a)   (b)
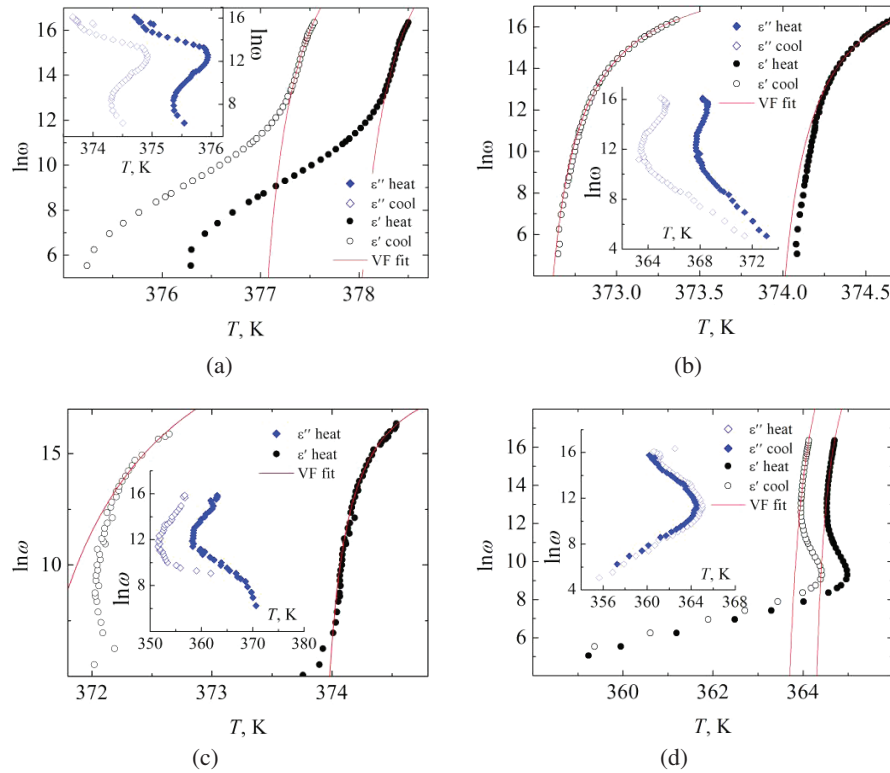
(c)   (d)

Fig. 2.   Dependences of the logarithm of the frequency $\omega = 2\pi f$ on the $\varepsilon'/\varepsilon_0(T, \omega)$ maxima temperatures for (a) PFN, (b) PFNL1, (c) PFNL2, and (d) PFNL3 ceramics, respectively. The solid lines illustrate the implementation of the Vogel–Fulcher law. The insets show similar dependences for the maxima of $\varepsilon''/\varepsilon_0(T, \omega)$. Open markers correspond to data obtained in cooling mode, and filled ones correspond to heating mode.

temperature (T_m) for $\varepsilon'/\varepsilon_0(T, \omega)$ and $\varepsilon''/\varepsilon_0(T, \omega)$ are shown. All the dependences obtained have the regions of higher-temperature relaxation, which is consistent with the Vogel–Fulcher (VF) law (solid lines in Fig. 2),

$$\omega = \omega_0 \exp\left(\frac{E_a}{k(T - T_{VF})}\right),$$

where E_a is the average height of the potential barrier, T is the absolute temperature, k is the Boltzmann constant, ω_0 is the pre-exponential factor, and T_{VF} is the freezing temperature of

the relaxation process. The calculated values of these coefficients for each investigated object are presented in Table 1. The relaxation width in the frequency range of 190 kHz– 2 MHz is no more than half a degree — as noted in Ref. 23, such weak relaxation can be observed in FE relaxors, where the characteristic temperature associated with the destruction of the classical domain structure is quite high and close to the T_m area.

To quantitatively describe the diffusion of the FE PT in the PFN and PFNL samples, we used expression (2), an example of its application for a PFN sample is shown in Fig. 3.

Table 1. The coefficients of Vogel–Fulcher law approximation of the $\varepsilon'/\varepsilon_0(T, \omega)$ relaxation processes observed on heating for the PFN and PFNL ceramics.

	T_{VF} (K)	E_a (eV)	ω_0 (rad/s)
PFN	377.69	5.71×10^{-4}	5.33×10^{10}
PFNL1	373.84	2.42×10^{-4}	3.84×10^{8}
PFNL2	373.81	2.25×10^{-4}	4.45×10^{8}
PFNL3	364.02	5.07×10^{-4}	7.45×10^{10}

Fig. 3. Temperature dependence of $\varepsilon'/\varepsilon_0$ at 100 kHz and the fitting curve to the empirical law [Eq. (2)] for PFN. The range of the best fit is highlighted in color, the residuals for which are shown in the inset.

Figure 4 shows the parameters T_A, ε_A, and δ_A calculated in this way as a function of frequency, as well as the dependence of the latter, calculated at 100 kHz, on the LCO concentration. It is clearly seen that in the case of PFNL1 and PFNL2, these parameters are practically independent of frequency. We associate the nonlinearity observed above 1 MHz with an increase in the measurement error, while the low-frequency behavior is associated with the contribution of the through conduction. However, the latter has a much greater effect on the parameters in the case of PFN and PFNL3, which confirms the formation of an unfavorable defect structure here. Moreover, if in the case of PFN the main type of defects are oxygen vacancies, then in the case of PFNL3, lithium atoms occupying irregular positions in the crystal lattice of the material are apparently responsible for defect formation.
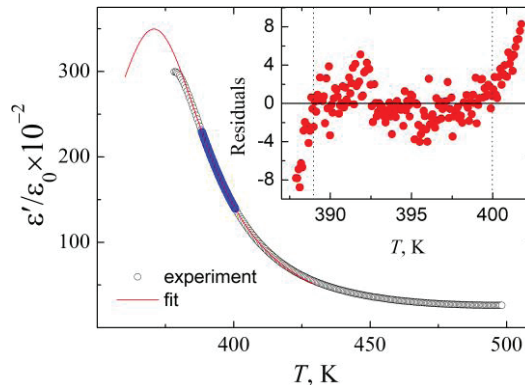
Since the observed is not accompanied by an unambiguous enhancement of the relaxor properties (in particular, an increase in the width of the temperature range of the shift of the maxima of the dielectric constant corresponding to different frequencies of the measuring signal), it can be assumed that it is this mechanism that is responsible for the monotonic increase in the smearing parameter with an increase in the LCO concentration.
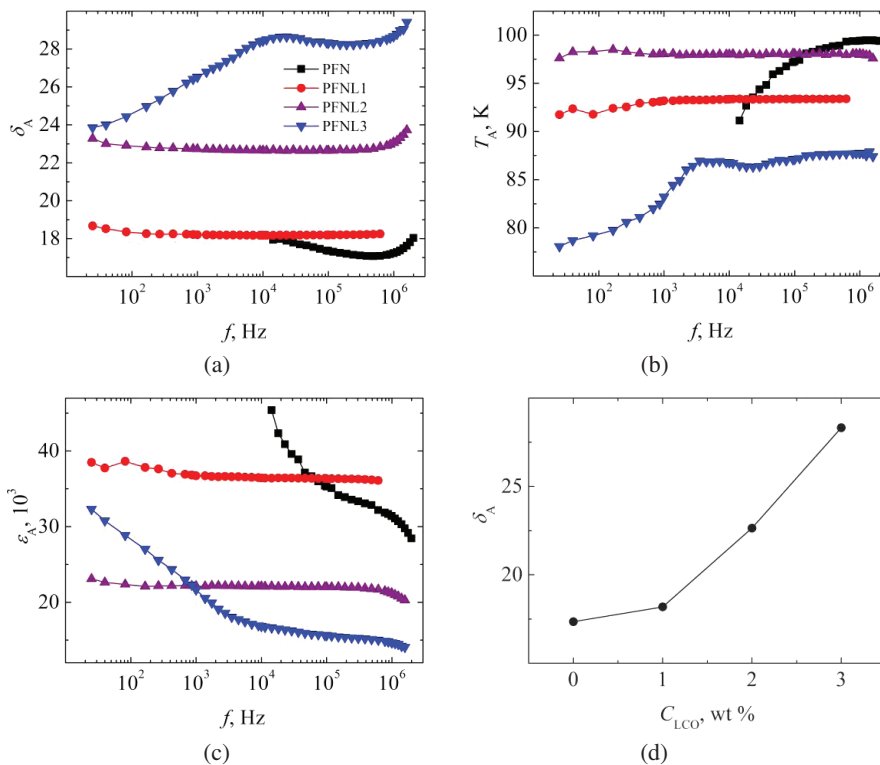

Fig. 4. (a)–(c) Dependences of the parameters of the empirical law [Eq. (2)] for PFN and PFNL ceramics on the frequency of the measuring signal; and (d) dependence of the degree of diffuseness (δ_A) on LCO concentration.

4. Conclusions

In this paper, we carried out the dielectric dispersion of lead ferroniobate ceramics, pure and LCO-modified, at the stage of synthesis. All the studied objects were found to possess the relaxation of the dielectric constant maxima temperatures in the region of FE–PE state transition described by the Vogel–Fulcher law, characteristic of ferroelectric relaxors. Dependences of the degree of diffuseness for PFN and PFNL ceramics on the frequency of the measuring signal and LCO concentration were obtained. Analysis of the results obtained showed that as the concentration of Li atoms in the system increases, there is a significant decrease in the value of the dielectric constant at the PT point along with a significant increase in its diffusion, which has little effect on the relaxation parameters of the maxima of the dielectric constant. This allowed us to conclude that with an increase in the concentration of the modifier, Li atoms prefer to occupy irregular positions in the crystal lattice, increasing the "impurity" disorder, without the formation of locally ordered regions (nanodomains), which leads to the smearing of the phase transition in objects.

Acknowledgments

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