

06,11

Relaxation processes in the region of structural phase transitions on the example of ceramics based on sodium niobate

© O.V. Malyshkina¹, M. Ali^{1,2}, N.E. Malysheva³, K.V. Patsuev¹

¹ Tver State University,
Tver, Russia

² Tver State Medical University,
Tver, Russia

³ Military Academy of Air and Space Defence named after Marshal of the Soviet Union G.K. Zhukov,
Tver, Russia

E-mail: Olga.Malyshkina@mail.ru

Received July 15, 2022

Revised July 15, 2022

Accepted July 19, 2022

Comparative studies of the temperature dependences and dispersion of the complex permittivity of sodium niobate and sodium-lithium niobate ceramics have been carried out. It is shown that the structural transition to the *R*-phase (370°C) of sodium niobate ceramics is a ferroelectric phase transition. For sodium niobate ceramics, the existence of three fundamentally different mechanisms of relaxation processes has been established: classical (Debye type), linear, and relaxation, the existence of which is determined by the structural phase. The addition of 10% lithium niobate to the sodium niobate ceramics not only increases the temperature of the structural phase transition, but also eliminates the mechanisms for the occurrence of relaxation polarization.

Keywords: piezoelectric ceramics, lead-free materials, permittivity, relaxation processes.

DOI: 10.21883/PSS.2022.12.54388.461

1. Introduction

Scientific interest in the ceramics of terracotta sodium niobate NaNbO_3 (NN) is due to the fact that synthetic NN has seven different structural phases [1–6], and, consequently, a large number of heterogeneous phase transitions in the temperature range of 360–640°C. According to [2], coexistence of ferroelectric phase *Q* and antiferroelectric phase *P* is possible in the temperature range of 25 to 360°C, depending on NN synthesis conditions. The authors of [1], who also note the existence of the *Q*-phase above 25°C, do not specify its upper boundary. Nominally, a ferroelectric phase transition is a phase transition at 640°C, since this is a transition from the tetragonal T_2 ($P4/mbm$)-phase to the cubic phase *U* ($Pm\bar{3}m$). The symmetry of all lower-temperature phases (*R*, *S*, T_1) allows for existence of a spontaneous dipole moment at the unit cell level. The authors made the corresponding conclusions based on the detailed X-ray diffraction studies. At the same time, there is no data about study of macroscopic dielectric and, in particular, ferroelectric properties of NN ceramics in the temperature ranges which correspond to the high-temperature phases (beginning with *R*).

We have previously shown, based on studies of the domain structure and macroscopic polarization [7,8], that the samples of NN ceramics obtained by single synthesis of the material have ferroelectric properties at room temperature and, therefore, are in the *Q*-phase.

Stabilization of the *Q*-phase, according to [1,9], is caused by substitution of sodium ions by lithium ions in a

concentration over 3%, and the samples have a structure typical for homogeneous ferroelectrics. The authors of [10] noted that substitution of sodium ions by lithium ions in the 10% ratio makes it possible to obtain ceramics with ferroelectric properties.

Since most high-temperature studies of sodium niobate-based ceramics are dedicated to structural peculiarities, it is interesting to analyze the temperature dependences of complex permittivity of these materials. The goal of the present paper was to use the dielectric spectroscopy method to study the relaxation processes in samples of sodium niobate-based ceramics: pure NN and with addition of 10 mass % of LiNbO_3 (LNN).

The samples of sodium niobate and sodium–lithium niobate ceramics were obtained at the sintering temperature of 1100°C and studied using the equipment of the Core Shared Research Facility of Tver State University. Solid-phase synthesis of the material for the making of NN ceramics was performed by three different methods: single synthesis at 650°C (NN650) or 700°C (NN700); and double synthesis, both at 700°C (NN700-700). Materials LiNbO_3 and NaNbO_3 for LNN ceramics were synthesized separately by double synthesis. LiNbO_3 at 700°C, NaNbO_3 at 650 and 700°C. The LiNbO_3 and NaNbO_3 powders were mixed in the 10:90 proportion before sample pressing.

Temperature dependences of complex permittivity were studied in the frequency range of 1 Hz to 30 MHz at temperatures from 30 to 600°C. Measurements were performed by the LCR method using a Vector-175 phase-

sensitive meter (Newtons4th Ltd). Vector-175 measures the signal amplitude and phase (i.e. complex impedance), which is used for program calculation of the main dielectric parameters read at the device output. In this measurement scheme, when inductivity prevails in the reactive component of resistance, capacitance is recorded as a negative quantity. The simplest physical interpretation of negative capacitance is in that polarization is in antiphase to the controlling electric field [11]. Since the real part of complex permittivity is calculated using the plane capacitor formula, we in fact have a negative permittivity. Its meaning in this situation is the presence of resonance processes in the dielectric response [12]. Discussions of negative capacitance in literature note, first of all, the presence of conduction currents, presence of a time delay in their progress and an increasing current — time dependence [13–15]. While the author associates the resonance processes in the dielectric response, considered in detail in [11,12], with elastic ionic polarization, which occurs at optical frequencies, the processes which lead to a negative capacitance due to a time delay in current flow, are explained in [14,15] by the capture of charge carriers on traps of different nature and by a conduction mechanism similar to the Schottky barrier. The latter can occur only at relatively low frequencies.

2. Experimental results

A significant difference in the temperature dependences of permittivity of the NN samples (Fig. 1, *a–c*), synthesized by different technologies, was observed in the temperature range of 350–450°C which corresponds to the *R*-phase, according to [1]. Thus, the temperature dependence of permittivity for samples NN650 and NN700 (Fig. 1, *a, b*) has a pronounced maximum which is identical to the permittivity maximum at the Curie point of ferroelectric materials. For the NN650 material it is at $T \sim 360^\circ\text{C}$, for NN700 it is more blurred at $T \sim 370^\circ\text{C}$ (temperature of transition to the *R*-phase [1]). Thus, we can naturally assume the existence of a structural transition from the ferroelectric *Q*-phase to the *R*-phase at this temperature. This maximum occurs at the frequencies of 1 Hz to 5 MHz.

Sample NN700-700 which has antiferroelectric properties at room temperature, as demonstrated earlier [8], does not have a maximum upon transition to the *R*-phase. Consequently, a *P*-phase \rightarrow *R*-phase transition takes place in this case. An insignificant blurred maximum is observed for the given compound only at frequencies from 10 kHz to 5 MHz (Fig. 1, *c*) at 400°C which corresponds to the *R*-phase.

Apparently, the NN ceramics in the *R*-phase does not ferroelectric properties, even though the symmetry class at the given temperature allows for the presence of a polar direction in a unit cell. The disappearance of macroscopic manifestation of ferroelectric properties during heating is indicated by the temperature measurements of dielectric hysteresis loops performed by the oscillographic method.

Thus, beginning from the temperature of 200°C, a voltage drop is observed in the sample, which means a conductivity increase. When temperature approaches 300°C, the dielectric hysteresis loop smoothly changes its shape and becomes an ellipse of dielectric losses. This effect is more noticeable beginning from 370°C.

The implantation of 10% of lithium niobate into NN ceramics causes a considerable change of the temperature dependence of permittivity of LNN ceramics (Fig. 1, *d*). Up to the frequency of 60 Hz there is a constant increase (its run is close to an exponential dependence) of permittivity with temperature rise. Starting from the frequency of 60 Hz, there is a „break“ at 300–310°C, which becomes a rather blurred maximum during measurement at frequencies above 1 kHz. Starting from the frequency of 200 kHz (curve 6, Fig. 1, *d*) up to 4 MHz, there is a sudden change of permittivity at 305°C. The position of the second maximum (the sharper one), observed in the frequency range of 60 Hz–4 MHz, depends on frequency. Up to 1 kHz at 455, in the frequency range of 10 kHz–1 MHz it is observed at 425°C, and then the maximum gradually shifts towards the region of higher frequencies, similarly to ferroelectrics with relaxor properties [16,17]. At the same time, the literature contains no information the a material may have relaxor properties only in a certain frequency range.

One more anomaly makes itself conspicuous in the temperature dependences of permittivity — a minimum with negative permittivity values at the frequencies of 9–20 MHz for NN ceramics (regardless of material synthesis condition) and 10–15 MHz for LNN ceramics. The reason for this minimum becomes clear after plotting of frequency dependences of permittivity (Fig. 2).

Two experimental facts are distinguished in the frequency dependences of permittivity. Firstly, the presence of a resonance in NN ceramics in the frequency range of 9–20 MHz, which occurs at temperatures above 360°C, i.e. in the *R*-phase. The permittivity minimum is observed exactly at these frequencies, in the range of the antiresonance peak, in the temperature dependences of permittivity. LNN ceramics has only an „antiresonance“ minimum observed starting from the temperature of 300°C, which corresponds to the first temperature anomaly.

The second „anomaly“ is a spread in the permittivity values at low frequencies, which has already been mentioned earlier [8,18]. Since such behavior is typical for piezoelectric ceramics, it was explained by the presence of migration polarization — i.e. motion of bulk charges on grain boundaries. At the same time, the temperature studies of frequency dependences of permittivity showed that sudden changes of permittivity at low frequencies in NN ceramics, which has ferroelectric properties at room temperature, are observed only up to temperatures of 240–260°C. In NN with antiferroelectric properties they are observed up to the temperature of 360°C; in LNN ceramics — up to 300°C. Thus, it can be naturally assumed that sudden changes of permittivity at low frequencies are chiefly caused not by migration polarization, but by vibrations of

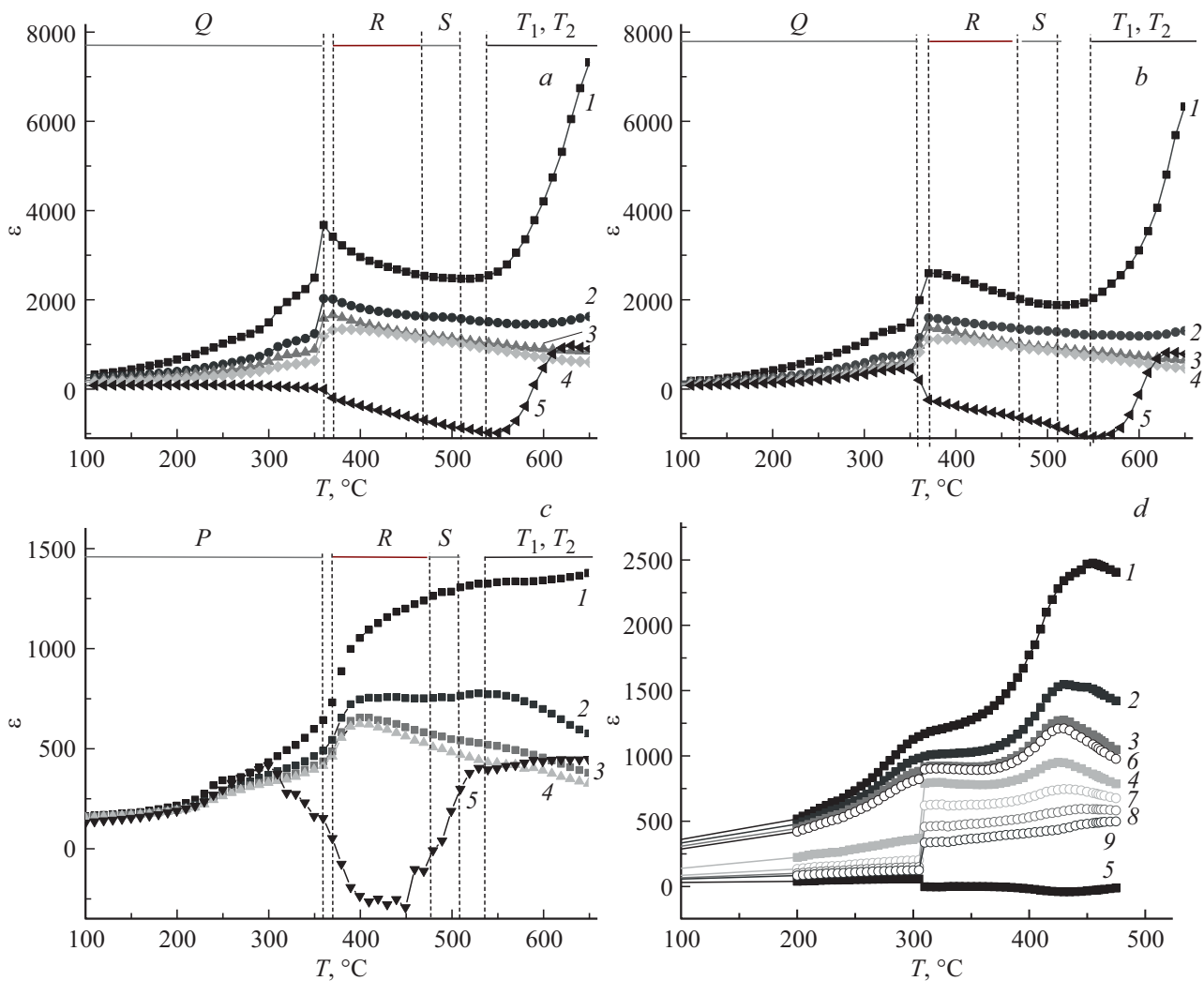


Figure 1. Temperature dependences of samples' permittivity: NN650 (a), NN700 (b), NN700-700 (c) and LNN (d). Curve 1 shows the measurement frequency of 1 kHz, 2 — 10 kHz, 3 — 100 kHz, 4 — 1 MHz, 5 — 10 MHz, 6 — 200 kHz, 7 — 2 MHz, 8 — 3 MHz and 9 — 4 MHz. Letters in the top (a, b, c) show the structural phases of NN as per [1].

a ferroelectric ion in a low-frequency electric field. Thus, in LNN ceramics they disappear at the first temperature anomaly at 305°C (Fig. 1, d); in NN ceramics, which exists at room temperature in the antiferroelectric phase, — upon a structural phase transition from the *P*- to the *R*-phase; in the ferroelectric phase — upon conductivity occurrence in the sample.

3. Analysis

The plotted dispersion diagrams of complex permittivity have shown three different mechanisms of relaxation processes in the samples of NN ceramics (Fig. 3, a–d). The „classical“ one in the shape of a semicircle arc, which is described by the Havriliak–Negami equation (this mechanism is characterized by infinitely intense decay and absence of inertia effects [12]); linear dispersion (in the low frequency region) and resonance dispersion (at frequencies

above 1 MHz), the dispersion diagram of which is a circle. Resonance dispersion, according to [12], corresponds to the frequency area of resonance — antiresonance (Fig. 2, a–c), and strong inertia effects occur for it. When inertia effects decrease (they are absent for the Debye case — a semicircle), the dispersion diagrams smoothly transform from a circle arc into a circle (resonance dispersion).

Such a change in the nature of dispersion dependence, conditioned by an increase of inertia effects, is clearly seen in all the complex permittivity diagrams for the NN samples, plotted on the basis of the experimental results, with a temperature increase.

Sample NN650 obtained by single synthesis (the appearance of diagrams is identical for sample NN700) is distinguished by an abrupt change of the mechanism of relaxation processes in the frequency range above 150 kHz at the temperature of a transition from the *Q*-phase to the *R*-phase — while a semicircle arc is observed at 350°C,

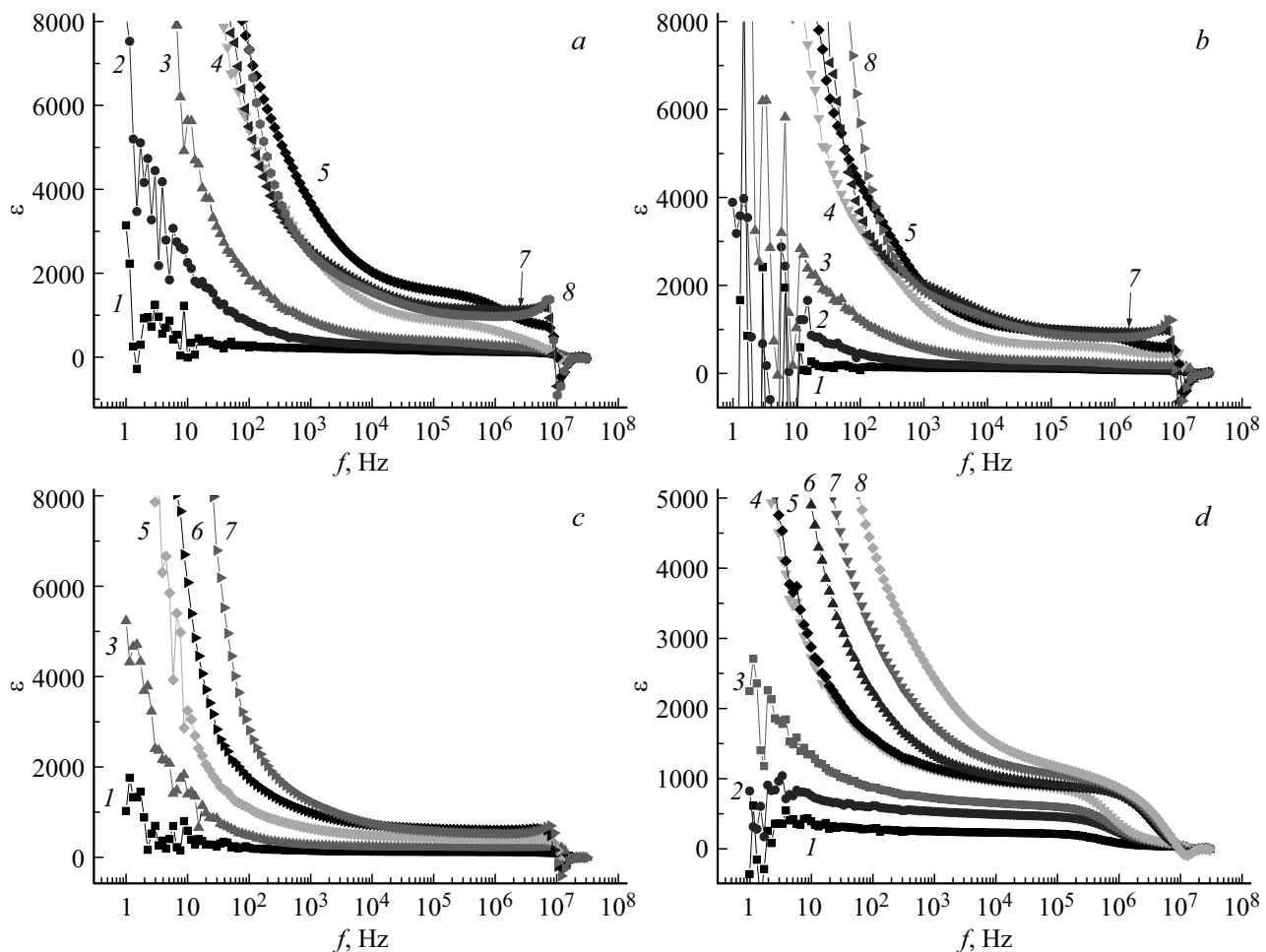


Figure 2. Frequency dependences of samples' permittivity: NN650 (*a*), NN700 (*b*), NN700-700 (*c*) and LNN (*d*). *a, b, c*: curves 1 — 30°C, 2 — 140°C, 3 — 230°C, 4 — 350°C, 5 — 360°C, 6 — 390°C, 7 — 470°C, 8 — 520°C; *d*: curves 1 — 30°C, 2 — 205°C, 3 — 250°C, 4 — 305°C, 5 — 310°C, 6 — 365°C, 7 — 400°C, 8 — 450°C.

a circle is observed at 360°C. When the sample is in the *Q*-phase, this frequency is, in fact, the upper limit of linear dispersion which characterizes slow relaxation processes. It is constant for the NN sample which exists in the *Q*-phase (Fig. 3,*a*), there is only an increase of the permittivity value (both the real and the imaginary parts). The frequency interval of existence of linear dispersion shifts to the frequencies of 600 kHz (*S*-phase) and 1 MHz (*T*₁- and *T*₂-phases) upon a transition to the *R*-phase (Fig. 3,*b*), and then to the *S*- and *T*₁-, *T*₂-phases (Fig. 3,*c*). Since slow relaxation processes, which characterize linear dispersion, in ceramic materials are identified with migration (bulk charge) polarization induced by charge motion on grain boundaries, this result can be logically explained by activation of this process with a temperature rise. In all probability, an increased contribution of migration polarization with an increase of the thermal motion of charges causes the conduction in the samples at high temperatures, which is indicated by the studies of dielectric hysteresis loops.

The appearance and transformation of the dispersion diagrams for samples NN700-700, obtained by double

synthesis, with a temperature increase in the *R*-, *S*-, *T*₁- and *T*₂-phases are identical to those for samples NN650 and NN700. A significant difference is observed only in the relatively low-temperature phase (existing up to 360°C). In the NN650 sample this is the *Q*-phase (Fig. 3,*a*), where two circle arcs smoothly transform into one arc by the temperature of the structural phase transition (360°C). In the NN700-700 sample this is the *P*-phase. In this case the high-frequency region features only one circle arc which becomes a circle already by 250°C (Fig. 3,*d*).

At the same time, attention must be paid to the fact that the authors of survey papers on dielectric spectroscopy, when speaking of the resonance polarization mechanism, mean elastic ionic polarization and associate it with the frequency of 10¹³–10¹⁴ Hz. A resonant response in our experiments was observed at 10⁷ Hz. Consequently, elastic ionic polarization cannot be meant. On the other hand, Jonscher in [13] notes that an intense increase of the real part of permittivity at low frequencies implies a finite and reversible charge accumulation on interfaces. The negative capacitance in this case, which is accompanied by resonance

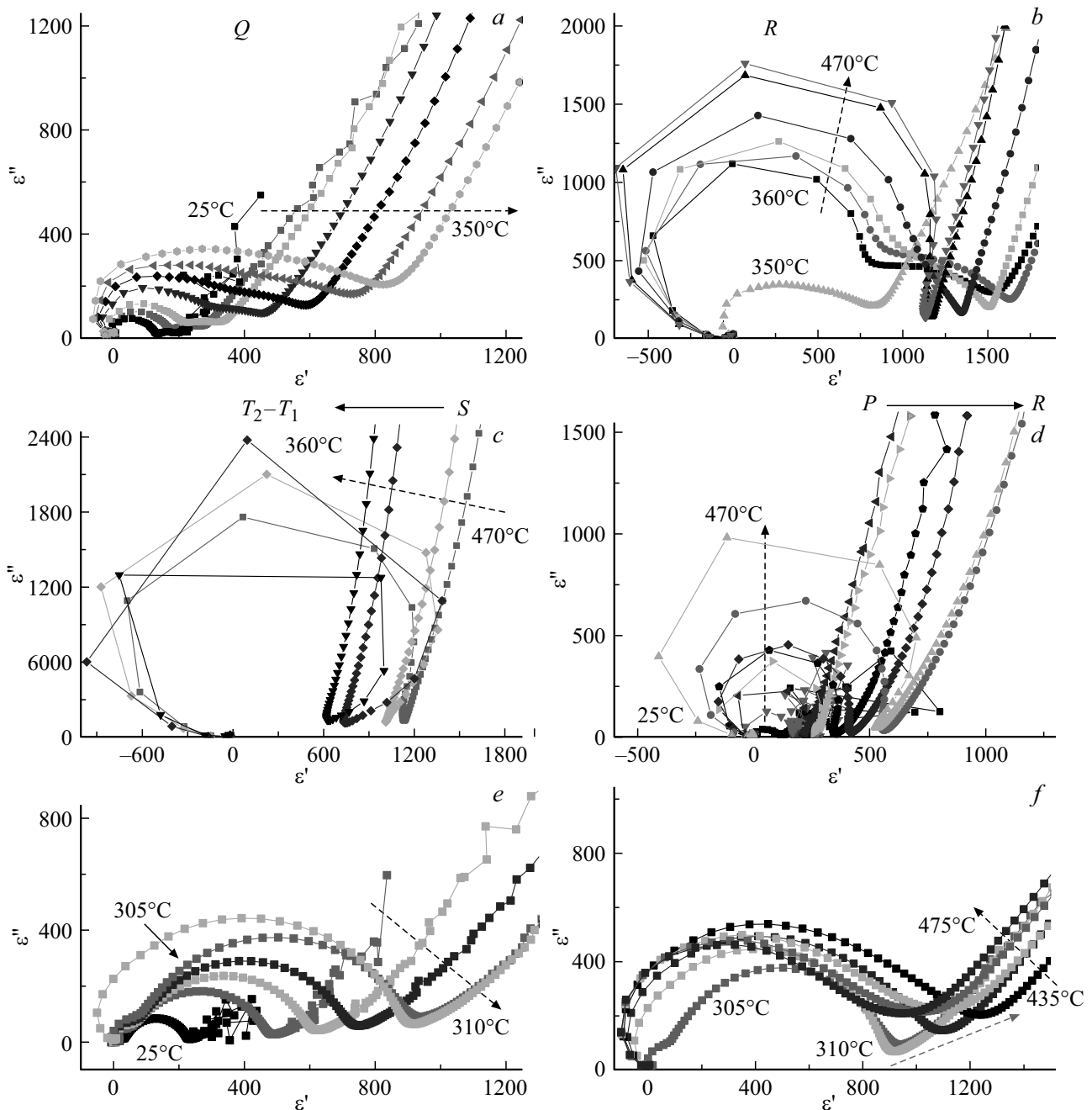


Figure 3. Dispersion diagrams of permittivity of the NN650 (*a–c*), NN700-700 (*d*) and LNN samples (*e,f*). Structural phases were noted for the NN samples; according to [1], they correspond to the temperature ranges shown in the plot. Broken arrows show the direction of transformation of dispersion diagrams with a rise of sample temperature.

dispersion, can be explained as follows: according to [14], the potential barrier decreases with a temperature increase, and this leads to a conductivity increase at relatively low frequencies. As a result, a heterocharge passes through the sample with a time delay. Thus, current oscillations arise in an alternating electric field in a certain frequency range; they are in antiphase with the controlling electric field and make a contribution to the overall dielectric response. This process is recorded as resonance dispersion when the dielectric response is measured.

In ceramic samples, grain boundaries act at interfaces where electric charge can be accumulated. The presence of jump processes at low frequencies (Fig. 2), which disappear with a temperature rise upon a sharp increase of the real part of permittivity and occurrence of conduction in the sample, confirms this conjecture.

Implantation of 10% of lithium niobate into NN ceramics leads to „exclusion“ of resonance dispersion. The temperature anomaly observed at 305–310°C (Fig. 1, *d*) in the dispersion diagram of complex permittivity of the LNN

sample (Fig. 3, *e*) corresponds to an abrupt transition from two circle arcs to a „bent“ arc which corresponds to an intermediate state between resonance dispersion and Debye dispersion [11]. The frequency, which is the upper limit of linear dispersion, increases continuously with temperature rise from 6 kHz at room temperature to 30 kHz at the temperature anomaly of 310°C, 90 kHz at the permittivity maximum and further up to 300 kHz. This is considerably lower than in pure NN ceramics.

At the same time, the question of whether the maximum, observed in LNN ceramics at 425–455°C, indicates a structural phase transition from the ferroelectric to the paraelectric phase, or this is a transition to the relaxor state where polar region are still present, according to [19], remains open at this time.

4. Conclusion

According to [12], peaks of the resonance–antiresonance type in frequency dependences of permittivity occur when there are strong inertia effects (the perfect „Debye behavior“ of permittivity diagrams corresponds to absence of inertia effects), and we can assume that resonant polarization takes place in the samples. Thereat, while discussing in detail the cases of strong inertia effects and their absence, the author of two survey monographs on relaxation in solids [11,12] only mentions the possibility of an „intermediate“ case, which we observed for LNN ceramics — the presence of an antiresonance peak with negative permittivity values and absence of a resonance peak. That is, when permittivity values at certain frequencies smoothly decrease to zero with frequency increase. We can assume that such behavior is typical in the paraelectric phase for ferroelectrics which have relaxor properties, since this material class is not considered in principle in Jonscher’s papers [11,12]. At the same time, the authors of [17], while describing the dispersion dependences of permittivity in ferroelectrics — relaxors, note the existence of non-linear effects with similar behavior of dielectric susceptibility. The authors of [17] also mention the fact that the presence of a spontaneous (ferroelectric) dipole moment in a sample hinders the transition of permittivity to negative values.

Since a negative (antiresonance) response in the samples of NN ceramics occurs in the experiment only above certain temperature between the *Q*- and *R*-phases, we can assert that the structural transition from the *Q*-phase to the *R*-phase for NN650 and NN700 ceramics is a ferroelectric phase transition.

The occurrence of a negative dielectric response in LNN ceramics may indicate a transition from the ferroelectric to the state with relaxor properties at the temperature of 305°C.

Conflict of interest

The authors declare that they have no conflict of interest.

References

- [1] R.H. Mitchell, B.J. Kennedy, K.S. Knight. *Phys. Chem. Mineral.* **45**, 1, 77 (2018).
- [2] K.E. Johnston, C.C. Tang, J.E. Parker, K.S. Knight, P. Lightfoot. *J. Am. Chem. Soc.* **132**, 8732 (2010).
- [3] H.D. Megaw. *Ferroelectrics* **7**, 1–4, 87 (1974).
- [4] Yu.I. Yuzyuk, P. Simon, E. Gagarina, L. Hennet, D. Thiaudiere, V.I. Torgashev, S.I. Raevskaya, I.P. Raevskii, L.A. Reznichenko, J.L. Sauvajol. *J. Phys: Condens. Matter.* **17**, 33, 4977 (2005).
- [5] V.S. Bondarev, A.V. Kartashev, M.V. Gorev, I.N. Flerov, E.I. Pogoreltsev, M.S. Molokeev, S.I. Raevskaya, D.V. Suzdalev, I.P. Raevsky. *FTT* **55**, 4, 752 (2013).
- [6] N.N. Krainik. *Izv. AN SSSR. Ser. fiz.* **28**, 4, 643 (1964) (in Russian).
- [7] O.V. Malyshkina, M. Ali, A.I. Ivanova, I.A. Chernyshova, D.V. Mamayev. *FTT* **63**, 11, 1890 (2021) (in Russian).
- [8] O.V. Malyshkina, M. Ali, E.V. Barabanova, A.I. Ivanova. *Ferroelectrics* **567**, 1, 197 (2020).
- [9] I.P. Raevski, L.A. Reznichenko, V.G. Smotrakov, V.V. Eremin, M.A. Malitskaya, L.A. Shilkina, E.M. Kuznetsova. *Ferroelectrics* **265**, 1, 129 (2002).
- [10] O.V. Malyshkina, E.S. Tesnikova, N.E. Malysheva, A.I. Ivanova. *Fiziko-khimicheskiye aspekty izucheniya klasterov, nanostruktur i nanomaterialov* **11**, 198 (2019) (in Russian).
- [11] A.K. Jonscher. *Universal relaxation law*. Chelsea Dielectrics Press, London (1996). 415 p.
- [12] A.K. Jonscher. *Dielectric relaxation in solids*. Chelsea Dielectrics Press, London (1983). 380 p.
- [13] A.K. Jonscher. *J. Chem. Soc., Faraday Trans.* **2**, 82, 75 (1986).
- [14] A.A. Felix, M.O. Orlandi, J.A. Varela. *Solid State Commun.* **151**, 1377 (2011).
- [15] H.L. Kwok. *Phys. Status Solidi C* **5**, 2, 638 (2008).
- [16] L.E. Cross. *Ferroelectrics* **151**, 305 (1994).
- [17] W. Kleemann, J. Dec, S. Miga. *Phase Transitions: A Multinatl. J.* **88**, 3, 234 (2015).
- [18] O.V. Malyshkina, E.V. Barabanova, N.E. Malysheva, A. Kapustkin, A.I. Ivanova. *Ferroelectrics* **561**, 1, 114 (2020).
- [19] V.A. Isupov. *FTT* **45**, 6, 1056 (2003).