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Short communication

Dielectric properties of $Ba(Ti_{1-x}Sn_x)O_3$ ceramics in the paraelectric phase

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Abstract

The outcomes of dilatometric, rentgenographic (XRD), microscopic (SEM) as well as dielectric measurements of polycrystalline $Ba(Ti_{1-x}Sn_x)O_3$ (BTS*x*) are described. These measurements were carried out within the range of para-ferroelectric phase transition and also for the high temperature paraelectric phase (from 300 K to 723 K). Within the range, where glass-like anomalies were noticed, the occurrences of electric properties peaks were recorded as well. Their occurrences are interpreted under the assumption of polar regions presence within the paraelectric phase. The size and dynamics of these polar regions influence the dielectric response at given temperatures and frequency of external electric field. Anomalies of dielectric losses and phase angle are pointing out on non-homogeneity and thermal evolution of polar regions.

Keywords: Dielectric properties; Diffused phase transition; Polar regions; Ceramics

1. Introduction

The $Ba(Ti_{1-x}Sn_x)O_3$; (BTS*x*) is a solid solution of ferroelectric $BaTiO_3$ (BT) and non-ferroelectric $BaSnO_3$ (BS). BTS*x* was a subject of many investigations involving temperature induced phase transitions (up to ≈500 K) [1,2]. The further broadening of measurements temperatures up to ≈700 K revealed the occurrence of "cross-over" regions within paraelectric phase [3–6]. It involves the evolution from displacement type behaviour (at elevated temperatures) to order–disorder one near the para-ferroelectric (PF) phase transition (PT). The dilatometric measurements for BTS*x*, [2] (see Fig. 1) revealed changes of linear thermal expansion as being typical for relaxors and glasses [7–12].

These phenomena are interpreted in terms of nucleation of polar regions (clusters). These are also connected with the presence of dipolar polarization (P_d) within the paraelectric phase [13–15].

XRD investigations show that Sn concentration increase leads to freezing of the cubic paraelectric phase during cooling on the way to ferroelectric phase [16,17]. The X-ray pattern for BTS10 shows at room temperature the cubic structure. The temperature T_m (the temperature of maximum value of real part of electric permittivity ε') equals 329 K.

It was also stated that, there the structural PT is not taking place at the T_m.

The aim of this work was the determination of the influence of temperature, electric field frequency and Sn concentration on dielectric properties of the paraelectric phase in polycrystalline BTS*x*.

The lack of structural transition in BTS10 at T_m is connected with the presence of polar cluster evolution taking place in the paraelectric phase. The nature of this temperature induced evolution is still to be explained. Additional question to be answered to is the determination of the influence of non-ferroactive Sn substitutions on polar cluster structure and dynamics in the paraelectric phase.

Solid solutions contained barium titanate are widely applied as capacitor ceramic, electromechanical transducers, ferroelectric memory-FRAM, thermistors, and others [18–20].

2. Experimental

Polycrystalline BTS*x* samples were obtained by calcinations at 1620 K. XRD data were collected by Philips X'Pert Pro MD powder diffractometer using $K_{\alpha 1}$ radiation from Cu anode. The configuration was the standard Bragg–Brentano setup with Ge (1 1 1) monochromator at the incident beam. All measurements were performed with 0.008° step size at 15–90° scanning range and the 285 s of measurement time for each step. The full pattern fitting procedure for

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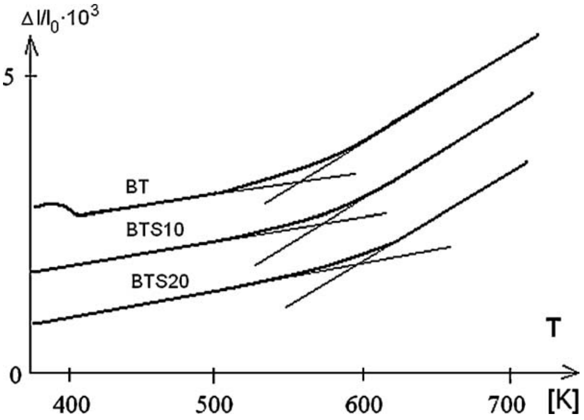

Fig. 1. The relative thermal linear expansion of polycrystalline BTS*x* samples [1].

quantitative analysis and determination of the structural parameters was carried out using Philips X'Pert HighScore Plus (PW3212) Release 2.1 software. The structure of BTS*x* was investigated by means of a Philips SEM 525 M electron microscope at room temperature. For dielectric measurements, a sample of diameter 10 mm and thickness 1.5 mm was covered with silver electrodes. The dielectric measurements were performed automatically (QUATRO KRIO 4.0 with Agilent type 4824A analyzer and BDS 1100). The measurements were carried out during cooling at a rate of 2 K/min, in the frequency range from 20 Hz to 1 MHz.

3. Results and discussion

The X-ray pattern for polycrystalline BTS10 sample (cubic phase) taken at room temperature T_r is presented in Fig. 2.

The T_r value is about 30 K lower then T_m. That means that at temperature $T_m = 329$ K no structural phase transition takes place.

A SEM micrograph of BTS10 sample (Fig. 3) shows rounded crystallites of a few to about 16 μm in size.

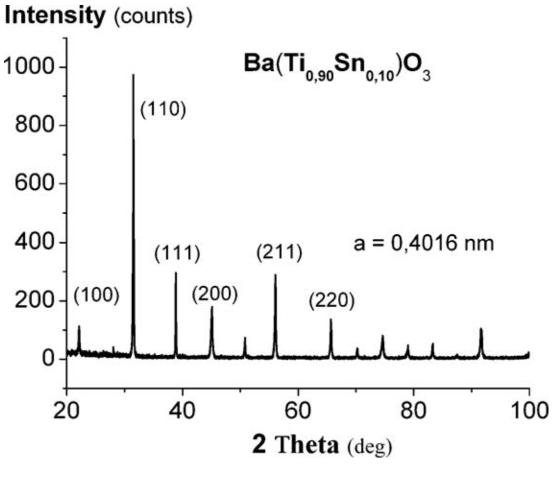

Fig. 2. X-ray pattern for BTS10 sample at room temperature (cubic phase, *a* = 4.02 Å).

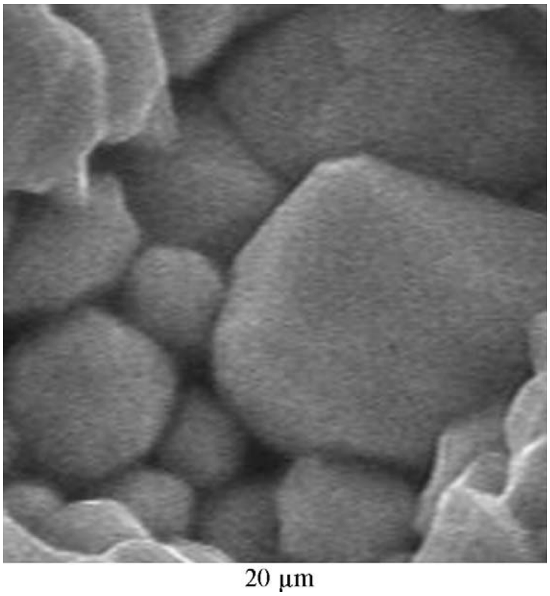

Fig. 3. SEM image of BTS10 crystallites on the sample surface at room temperature.

It is connected with the destructive influence of Sn ions substituents on dipoles interaction. In the $(A'A'')(B'B'')O_3$ solid solutions with statistical distribution of A/B ions, the decrease of the correlation length of inter-dipole interaction is observed. This phenomenon disturbs a creation of the periodic structure (especially for large crystallites surfaces-curvatures). This leads to creation rounded boundary of crystallites.

The dependences of the real part of dielectric permittivity (ε') on temperature and frequency (20 Hz to1 MHz) are presented in Figs. 4–6.

Sn concentration increase induces T_m lowering as compared with pure BT. Simultaneously small local shifts of $\varepsilon'_{\max}(T)$ were noticed for the paraelectric phase. It can be ascribed to small clusters sizes at high temperatures of paraelectric phase.

In the initial state of polar clusters nucleation, the Sn substituents do not enter into clusters structures and Sn

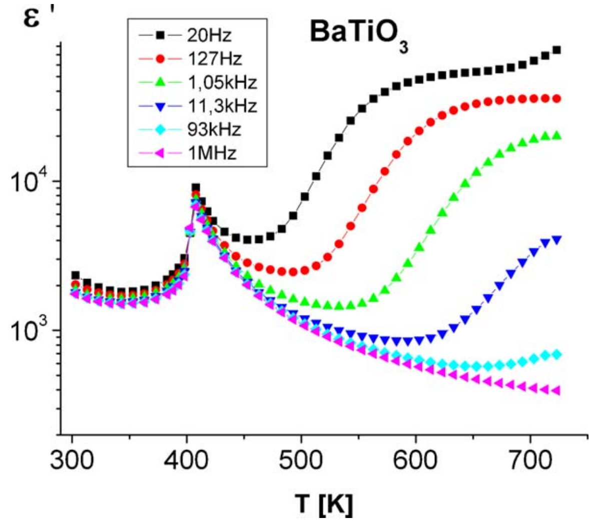

Fig. 4. Real part of electric permittivity for BT sample as a function of temperature and frequency.

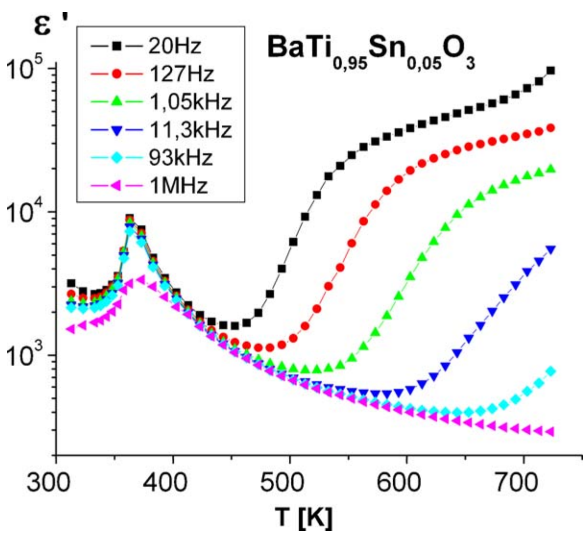

Fig. 5. Real part of electric permittivity for BTS05 sample as a function of temperature and frequency.

presence has no influence on clusters behaviour. Substitutions influence becomes visible in the range of the para-ferroelectric phase transition. During this transition ferroelectric domains are being created and we observed a rapid increase of the electric interaction correlations length.

The Sn ions presence disturbs this process. This leads to limitation of clusters size growth and to their labile behaviour. As an outcome, the increase of maximum value of ε' takes place in the BTS20, (see Fig. 7) and T_m lowering.

Practically, T_m value independent on frequency (see Fig. 7), points out that for concentration $x \approx 20\%$, BTSx materials undergoes a diffused phase transition. This transition is of the dielectric nature only and not accompanied by structural transition.

The dielectric loss tangent as a function of temperature and frequency for undoped BaTiO$_3$ is presented in Fig. 8.

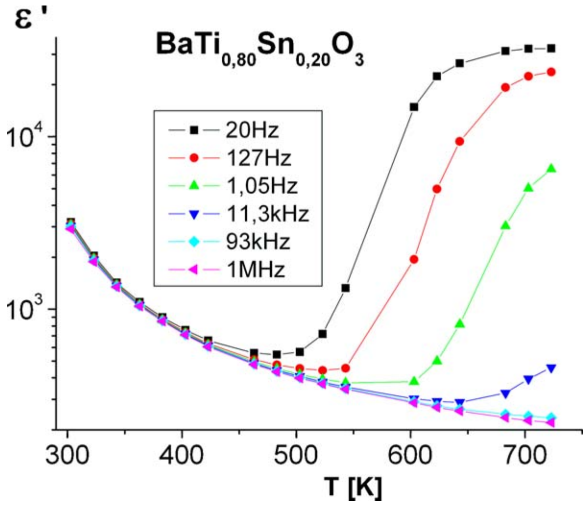

Fig. 6. Real part of electric permittivity for BTS20 sample as a function of temperature and frequency.

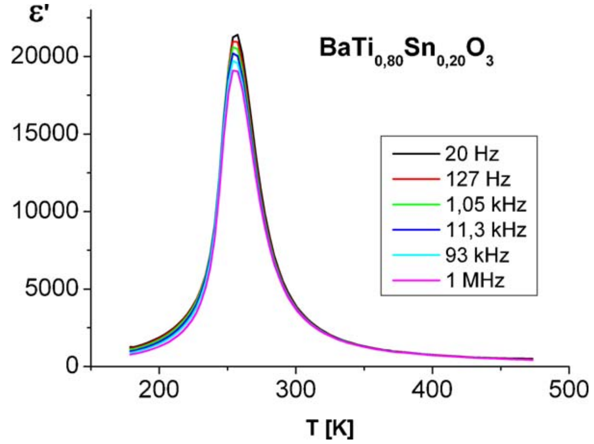

Fig. 7. Real part of electric permittivity for BTS20 sample as a function of temperature.

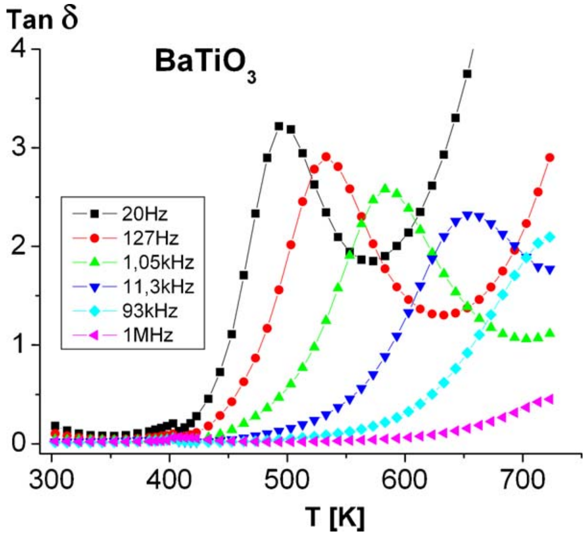

Fig. 8. The dependence of tan $\delta(T,\nu)$ for BT sample.

The maximum of energy losses undergoes a shift towards higher temperature and frequencies with simultaneous lowering of losses intensity. The temperature and frequency dependence is similar for BT and BTS10 (Figs. 8 and 10). In the case of BTS5 (see Fig. 9) peak values of energy losses remains almost constant within the T range from 450 K to 720 K and frequency range ~20 Hz to ~10^4 Hz.

These peak values were also observed during glassy transition followed by dilatometric measurements (see Fig. 1).

The Vogel–Fulcher formula (Eq. (1)) describes a glassy transition character [21,22]. This formula can be applied to correlate T_m points with their frequencies on the $\varepsilon'_{m,\nu}(T)$ functions. Moreover, this formula was applied to the maxima of tan $\delta(T,\nu)$ dependence in paraelectric phase.

From the glass model one can write the following equation involving $T_{m,\nu}$ values for different frequencies:

$$\nu = \nu_0 \exp\left(\frac{E_a}{k_b(T_{m,\nu} - T_f)}\right) \qquad (1)$$

where ν and ν_0 are the relaxation frequency at temperature T_m and a sufficiently high temperature respectively, E_a is the

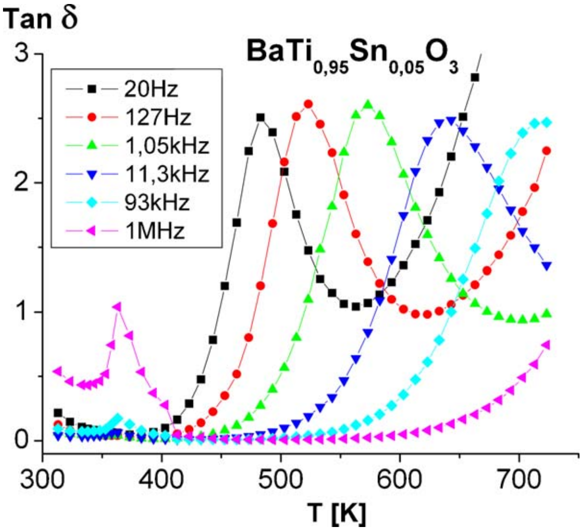

Fig. 9. The dependence of tan $\delta(T,\nu)$ for BTS05 sample.

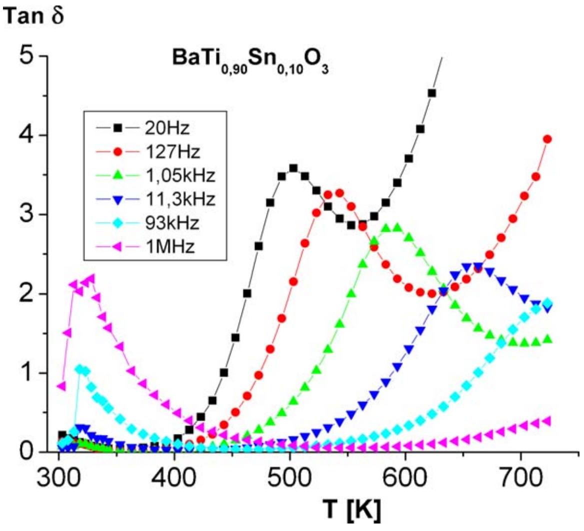

Fig. 10. The dependence of tan $\delta(T,\nu)$ for BTS10 sample.

activation energy of polar region, k_b is the Boltzmann constant and T_f is the freezing temperature of polar regions.

Fig. 11 presents the dependence of (ln ν) on $(1000/(T_{m,\nu} - T_f))$ for BTS10 sample. From this graph one can calculate a glassy temperature $T_f = 100$ K and activation energy $E = 0.8$ eV.

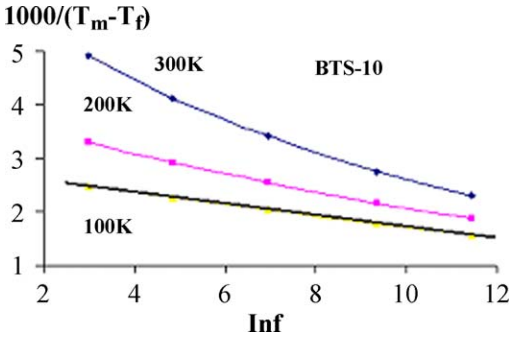

Fig. 11. The dependence of (ln ν) on $(1000/(T_m - T_f))$ for polycrystalline BTS10 ($T_f = 300$ K, 200 K, and 100 K, $E = 0.8$ eV).

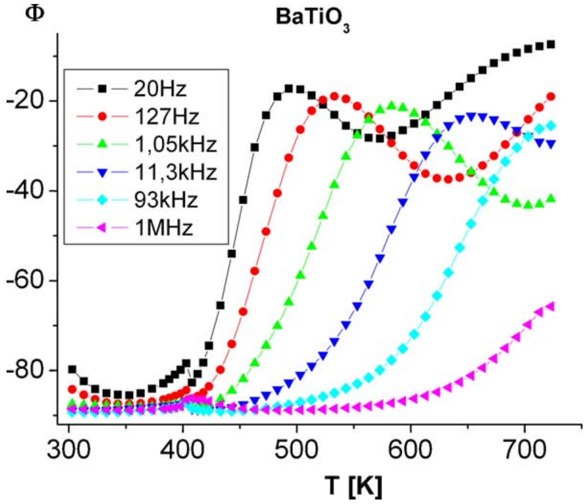

Fig. 12. The dependence of phase angle $\Phi(T,\nu)$ for BT sample.

The values of phase angle Φ for the ferroelectric phase are close to -90° (Fig. 12; within the T range 300 K to ~400 K). It is pointing on the polar character of the investigated material. For T above ~400 K, Φ values increase to almost 0 as well as the high values of tan δ are interpreted in terms of electronic conductivity increase for the paraelectric phase.

The comparison of temperature and frequency dependence of real part of the dielectric permittivity (ε') for undoped material (BT) as well as for BTS samples (BTS5 and BTS20) is presented in Figs. 13–15.

At a fixed temperature, the frequency of the measuring field was varied within the range 20 Hz to 1 MHz. For all investigated materials the T influence on $\varepsilon'(\nu)$ dependence can be separated into two T zones of $\varepsilon'(\nu)$ behaviour. In the low T range ($T \leq 423$ K for BT and BTS5; and $T \leq 523$ K for BTS20) the dielectric permittivity is almost frequency independent for all T-values applied in the experiment. Above these temperatures, the so called "cross-over" polarization behaviour is characterised by

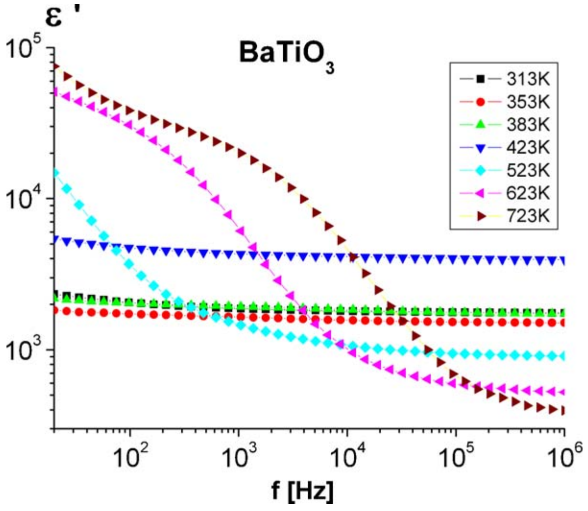

Fig. 13. Real part of electric permittivity for BT sample as a function of frequency and temperature.

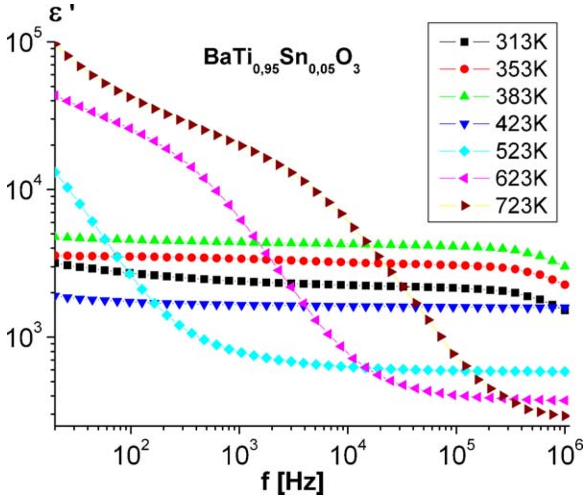

Fig. 14. Real part of electric permittivity for BTS05 sample as a function of frequency and temperature.

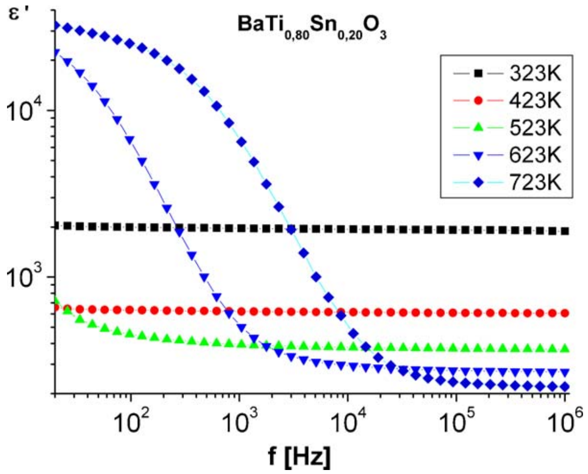

Fig. 15. Real part of electric permittivity for BTS20 sample as a function of frequency and temperature.

complex frequency dependence. The ε' values within low frequency range are about 1-order of magnitude higher as compared to low T quasi linear $\varepsilon'(\nu)/_{T = \mathrm{const}}$ dependence. Above about 10^4 Hz ε' values declined down and inflexion points undergo a shift towards higher frequencies with T increase. It can be interpreted in terms of dynamic properties of polarization clusters formed under T increase influence.

4. Conclusions

It was established, that Sn ions strongly modify the dielectric properties of polycrystalline BTSx ceramics especially within the temperatures range of the para-ferroelectric phase transition. This Sn influence was interpreted in terms of Sn ions disturbance of ferroelectric domains nucleation taking place in the ferroelectric phase. This influence is stronger for higher Sn ions concentration and also is manifesting itself more clearly at lower temperatures (LT). At LT, the larger polar clusters are being created with enhanced selectivity to translational symmetry disturbance as well as cooperative interaction of electric dipoles.

The local maxima of $\varepsilon'(T)$, $\tan\delta(T)$, $\Phi(T)$ are taking place within the range characteristic for dipole glass. Their occurrences confirm the polar regions (PR) presence in the paraelectric phase. The dynamic properties of the PR are T-sensitive by the correlation range change of inter-dipole interaction. The different T-values corresponding to the dielectric properties maximum values at different frequencies of the measuring electric field point out on the statistical distribution and T-sensitive character of the PR size.

The character of dielectric permittivity dependence on frequency ($\varepsilon'(\nu)$) confirms the "stiffening" of PR dipole correlation in the ferroelectric phase. The $\varepsilon'(\nu)$ dependence in the paraelectric phase confirms the PR existence. In the range of high temperatures, the ε' is strongly dependent on frequency. For low temperatures, the ε' is independent on frequency. It is connected with micro-domains nucleation inducting the strong electric interaction.

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