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Peculiarities of dielectric response of 1:1 family relaxors

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Abstract. A mixed ferroglass phase with coexistence of long and short range order was proposed as the model for quantitative description of the 1:1 family relaxors. Calculations of dielectric response of these relaxors were performed in the random field theory framework. Four and three groups of maxima were obtained in the dielectric permittivity temperature dependence at several frequencies for less and more ordered samples respectively. The frequency dependence of maxima at the lowest temperatures was shown to obey the Vogel–Fulcher (V–F) law, whereas other maxima the Arrhenius law. The peculiar feature of more ordered relaxors was shown to be the proximity of freezing temperature T_g to the temperature of maximum position T_m .

Measurement of dielectric response of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$ (PSNT) single crystals revealed two groups of maxima, one at $T \approx 310$ K and another at $T > 330$ K. The frequency dependences of low temperature maxima and high temperature ones were shown to obey the V–F law with $T_g = 292.5$ K and the Arrhenius law with activation energy 0.49 eV. The comparison of obtained experimental data for PSNT as well as those for two samples of $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ exhibiting different levels of order with the theory have shown that a mixed ferroglass model with different ratio of long and short range order describes fairly well the main peculiarities of the dielectric response of the 1:1 family relaxors.

1. Introduction

The relaxor ferroelectrics $\text{PbSc}_{1/2}\text{Ta}_{1/2}\text{O}_3$ (PST) and $\text{PbSc}_{1/2}\text{Nb}_{1/2}\text{O}_3$ (PSN) are known to be the most intensively investigated systems of 1:1 type [1–4]. A peculiar feature of these systems in comparison with those of the 1:2 family (e.g. $\text{PbMg}_{1/3}\text{Nb}_{2/3}\text{O}_3$ (PMN)) is the dependence of the degree of their disorder on technological conditions up to their transformation into normal ferroelectrics (see e.g. [5]). With decreasing of the degree of disorder the main characteristic features of any relaxor, namely the Vogel–Fulcher (V–F) law for dynamic permittivity and occurrence of different physical property maxima in a wide enough temperature range near the permittivity maximum tend to disappear [6]. The investigation of the samples with different degree of disorder seems to be important to find out the nature of relaxor ferroelectric property anomalies. The anomalies were shown to exist in the relaxors of 1:1 and 1:2 families as well as in the relaxor $\text{Pb}_{0.92}\text{La}_{0.08}\text{Zr}_{0.65}\text{O}_3$ (PLZT 8/65/35) in two temperature regions, namely in the vicinity of the Burns temperature T_d and at several hundred K lower temperatures near the dielectric permittivity maximum [7–9].

A model for relaxor ferroelectric property description was proposed recently. In this model ferroelectric long range order (which appears at $T = T_d$) is destroyed by the random field induced by substitutional disorder and other lattice imperfections on temperature lowering [10]. This model made it possible to describe correctly the variation of positions of dielectric permittivity maxima with La concentration increase in PLZT, critical concentration of random field sources and freezing temperature value and predict the strong influence of nonlinear contribution of random field on the relaxor properties [10–12]. The calculations of linear dynamic permittivity frequency and temperature dependence for the parameters corresponding to dipole glasses had shown the existence of LT and HT maxima with V-F and Arrhenius laws, respectively [13]. The obtained data seem to fit fairly well the observed permittivity of the relaxors like PMN.

The randomness of internal field in the relaxors of the 1:1 family can be supposed to be less than that in 1:2 materials due e.g. to smaller difference between values of B cation charges and due to the possibility of technological improvement of the samples. This can result in the conditions of mixed ferroglass phase appearance with coexistence of long and short range order.

In this work we considered the frequency and temperature dependence of dielectric permittivity for the latter case. Measurements of dielectric response of $\text{PbSc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3}\text{O}_3$ (PSNT) single crystals are also performed. The comparison of calculated and observed data for PSNT (both new and earlier ones [14]) and PST [5] is carried out. It has been shown that the approach based on random field theory describes well enough the observed peculiarities of dielectric response of the aforementioned 1:1 family relaxors.

2. Theory

2.1. Peculiarities of random field in the relaxors of the 1:1 family

Random field sources in any relaxors of $\text{PbB}'_{1-x}\text{B}''_x\text{O}_3$ type are numerous. They are antisite ions which appear due to substitutional disorder, vacancies of lead and oxygen and random electric and elastic dipoles which are the result of ion displacements from their equilibrium position in ideal perovskite structure. It was shown recently by the NMR method (see [15] and references therein) that both the directions and dipole moment values of electric dipoles in the relaxors are random quantities. Random orientations of dipoles used to be the consequence of lattice symmetry whereas the distribution of dipole moment values is due to random field distribution [10] and in particular to the degree of substitutional disorder and the number of lattice vacancies which seem to be extremely important for lattice excessive charge compensation. It is obvious that changes of the considered ion surrounding have to influence the ion attraction and repulsion forces as well as the interaction between the unit cells. This results in central or off-centre positions of the ion, the value of ion displacement being dependent on the degree of disorder. Therefore the concentration of random site electric dipoles has to be dependent on the strength of random field in the system. Since in the relaxors of the 1:2 family the degree of disorder is independent of the sample technology, i.e. internal field randomness is the same in any sample, one can suppose that electric dipole concentration is constant in any sample of the considered relaxor. Contrary to this in a relaxor of the 1:1 family the field randomness depends on technology and thus concentration of random field sources, including electric dipoles, must be also dependent on technology. So the dipole concentration is a sample dependent quantity in the 1:1 family relaxors. Since in conventional ferroelectrics like PbTiO_3 (where field randomness must be small enough) values of electric dipole moments are almost not distributed [15], one can suppose that electric dipole concentration in the relaxors has to increase with field

randomness decreasing. Latter seems to be important for the lattice order. This is because the electric dipoles were shown to be the only constituent which tends to order a system (i.e. at sufficiently large concentration of these dipoles long range ferroelectric order appears in the system) whereas all other random field sources try to disorder it [16]. Ferroelectric long range order is known to exist under the condition when the mean field approximation is valid. For the relaxors this condition corresponds to inequality $nr_c^3 \gg 1$, where n is electric dipole concentration, r_c is host lattice correlation radius. The host lattice was supposed to be the Burns reference phase, Burns temperature $T_d = T_{cmf}$ being the transition temperature from this phase to the ferroelectric one [10]. The fulfilment of the aforementioned inequality in the vicinity of T_d is a consequence of the large value of r_c rather than that of n because large enough field randomness can decrease the n value. This statement is confirmed by the fact that the temperature T_d is independent of the sample technology for 1:1 relaxors [9] as well as of the concentration of La ions in the PLZT ($x/65/35$) system [7, 8].

On the other hand at $T < T_d$ when r_c decreases, the mean value of random field (mean field) can become larger than its dispersion due to increasing of electric dipole concentration in technologically improved samples with smaller concentration of other types of random field source (which try to disorder the system, see above). Moreover, the mean value of random field and its dispersion depend on host lattice parameters, e.g. r_c , dielectric permittivity and elastic constant [16], all these parameters being temperature dependent quantities. Therefore in technologically improved samples of 1:1 family relaxors one can expect the appearance of the second ferroelectric phase transition at $T < T_d$, whereas there can only be one ferroelectric transition at $T = T_d$ in 1:2 family relaxors. The latter fact is due to strong field randomness and relatively small electric dipole concentration. The coexistence of long and short range order, corresponding to mixed ferroglass phase, may occur in 1:1 family samples, where the degree of disorder (in other words field randomness) is large enough. This phase will appear when the product nr_c^3 exceeds its critical value (percolation threshold) so that the first infinite cluster appears. The observation of anomalies of small angle light scattering in PST [3] confirms this statement and speaks in favour of mixed phase realization in the system.

In what follows we shall consider the dielectric response of the relaxors in a random field theory framework and perform the numerical calculations for the parameters which correspond to a mixed ferroglass phase.

2.2. The equations for dielectric response

Let us consider the disordered ferroelectric as a system of electric dipoles, point charges and dilatational centres randomly distributed in the host lattice. Calculations of the distribution function of random field induced by these sources has shown [16] that the random field strongly influences the number of coherently oriented dipoles L (long range order parameter) and thus the dielectric response of the system because dielectric susceptibility $\chi \sim \partial L / \partial \varepsilon$ (ε is external field). The dynamic response was considered in supposition of simple Debye form with an Arrhenius law for the single dipole relaxation time. Since the barrier height U in the Arrhenius law depends on the actual barrier shape (determined by, e.g., substitutional disorder and vacancies in cation and anion sublattices, which are known to be the sources of random field [10]) we considered the influence of the field on the barriers of different shape. In particular we considered the simplest case of a rectangular barrier between two possible orientations of a dipole and obtained the barrier height renormalization by the random field E in the form $U(E) = U \pm d^* E$, as supposed earlier [17]. In such a model with $l_z = \pm 1$, $l_x = l_y = 0$, $l = d^* / |d^*|$ ($d^* = d\gamma(\varepsilon_0 - 1)/3$ is the effective dipole moment, γ is the Lorentz factor, ε_0 is the host lattice static permittivity) dynamic order parameter $L(\omega)$, where ω is frequency, can

be expressed in a self-consistent manner [17, 18]:

$$L(\omega) = \int_{-\infty}^{\infty} \frac{\tanh((\varepsilon_E)/kT) f(E, L) dE}{1 + i\omega\langle\tau\rangle} \quad (1)$$

$$\langle\tau\rangle = \bar{\tau} \frac{\cosh(2(E + \varepsilon)/kT)}{\cosh(E + \varepsilon)/kT} \quad (2)$$

$$\bar{\tau} = \bar{\tau}_0 \exp(U/kT). \quad (3)$$

Equation (3) is the Arrhenius law for a dipole reorientation between equivalent positions separated by energy barrier of the height U . It is seen that dynamic order parameter $L(\omega)$ transforms into the static one L at $\omega \rightarrow 0$.

One can see that equations (1), (2) include quantum statistical averaging over possible orientations of a dipole and self-consistent averaging over a random electric field with distribution function $f(E, L)$. Dielectric susceptibility can be represented as

$$\chi \equiv \chi_{zz} = nd^* \left(\frac{\partial L}{\partial \varepsilon_z} \right)_{\varepsilon \rightarrow 0} \quad (4)$$

where n is the electric dipole concentration.

In the Gaussian approximation for the distribution function of the electric dipole random field the linear dielectric susceptibility χ can be represented in the form [17] obtained by substitution of equation (1) into equation (4)

$$\frac{4\pi}{\varepsilon_0} \chi \equiv \chi' = \frac{Q}{1 - Q} \quad (5)$$

$$Q = \frac{2\lambda^2}{\pi} \int_0^{\infty} \int_0^{\infty} \tanh\left(\frac{x}{\eta}\right) \exp[-\mu y^{3/2} - \Delta y - y^2] \times \sin(\lambda xy) \frac{y \cos[\lambda y(\xi + L)]}{1 + i\nu\tau_1(x)} dx dy \quad (6)$$

$$\tau_1(x) = \bar{\tau} \frac{\cosh 2x/\eta}{\cosh x/\eta}. \quad (7)$$

Equation (6) is written for a general enough case when random field sources are electric dipoles, point charges and dilatational centres so that the distribution function was written as a convolution of Gaussian, Holtzmarkian and Lorentzian forms. In such a case the order parameter L has the form:

$$L(\nu) = \frac{2}{\pi} \int_0^{\infty} \int_0^{\infty} \tanh\left(\frac{x}{\eta}\right) \exp[-\mu y^{3/2} - \Delta y - y^2] \sin(\lambda xy) \frac{\sin(\lambda y L)}{1 + i\nu\tau_1(x)} dx dy. \quad (8)$$

We used the following dimensionless variables in equations (6), (7), (8)

$$\begin{aligned} x &= E/E_0 & y &= \rho\sqrt{C} & \eta &= kT/E_0 = T/T_{cmf} & \nu &= \omega\bar{\tau}_0 \\ \mu &= A/C^{3/4} & \Delta &= B\sqrt{C} & \lambda &= \sqrt{15\pi nr_c^3}. \end{aligned} \quad (9)$$

Here parameters E_0 and A, B, C characterize respectively the mean value and the dispersion of the random field induced by different sources so that they depend on the source concentrations and parameters, namely

$$A = \frac{32}{15} \left(\frac{\pi Ze}{2\varepsilon_0} \right)^{3/2} n_1 \quad B = \frac{\Omega_0}{9} \frac{1 + \theta}{1 - \theta} pn_2 \quad C = \frac{16\pi}{15} \left(\frac{d^*}{\varepsilon_0 r_c^3} \right)^2 nr_c^3 \quad (10)$$

$$E_0 = \frac{4\pi nd^{*2}}{\varepsilon_0} \equiv kT_{cmf} \quad (11)$$

where n_1 and n_2 are the concentrations of point charges and dilatational centres respectively, Ze and Ω_0 are the point defect charge and elastic moment and p and θ are the host lattice piezoelectric tensor component and Poisson coefficient, respectively. Equation (5) with respect to equations (6)–(11) describes the dependence of the system linear dielectric response (its real and imaginary parts) on frequency, temperature, parameters of the host lattice and random field sources.

2.3. Dielectric response in mixed ferroglass phase

The phase diagram of a disordered system, both magnetic and electric, is known to be defined by ratio of the mean field E_0 to random field dispersion ΔE (see e.g. [10], [19] and references therein). In particular, there has to be ferroelectric long range order ($L = 1$) and dipole glass short range order ($L = 0$) at $E_0 \gg \Delta E$ and $E_0 \ll \Delta E$, respectively. An intermediate case $E_0 \approx \Delta E$ leads to mixed ferroglass phase where only a fraction of the electric dipoles are coherently oriented ($0 < L < 1$). Critical values of parameters μ , Δ , λ which define the boundaries between the aforementioned phases were calculated recently [10, 16]. This made it possible to know which parameters values correspond to, e.g., mixed ferroglass phase. The results of dielectric susceptibility real part numerical calculations are depicted in figure 1, the values of λ and Δ being fairly close to the boundary between the mixed phase and glassy state [10]. One can see from figure 1 that there are four groups of maxima: two low temperature ones (LT₁, LT₂) and two high temperature ones (HT₁, HT₂). The position of any maximum T_m appeared to be frequency dependent. We analysed the $T_m(\omega)$ dependence with the help of the formula

$$T_m(\omega) = T_g - \frac{V}{\ln(\omega\tau_0)} \quad (12)$$

which corresponds to the Arrhenius law ($T_g = 0$) or to the V-F law ($T_g \neq 0$). Parameters τ_0 and V are, respectively, the preexponential factor and barrier height in the expression for the relaxor relaxation time temperature dependence.

It was shown that equation (12) fits fairly well the LT₁ maxima with $T_g/T_{cmf} = 0.11$, $V/T_{cmf} = 3.35$ whereas LT₂, HT₁ and HT₂ were fitted to an Arrhenius law ($T_g \approx 0$) with the barriers $V/T_{cmf} = 13.2$, 31 and 38 respectively. These numbers were obtained in supposition that $\tau_0 = \bar{\tau}_0 = 10^{-13}$ s, $U/T_{cmf} = 1.143$. Note that the change of τ_0 value influences the barrier value, namely a tenfold τ_0 increase decreases the V/T_{cmf} value approximately by 10%. So the barrier height in (12) is everywhere larger than that for single dipole reorientation. We have to draw attention to the fact that the considered case the temperature T_g is much less than the temperature T_m (see figure 1).

The dielectric response with four groups of maxima can be considered as a fingerprint of the mixed phase with coexistence of short and long range order. Really, the LT₁ maxima obeying the V-F law must be the contribution of polar clusters with small barriers separating their equilibrium positions. The LT₂ and HT maxima described by the Arrhenius law represent the contribution to dielectric response of long range order domains. Fairly sharp HT₂ maxima appeared due to ferroelectric long range order at the region of the Burns temperature whereas the LT₂ group can be the manifestation of long range order at lower temperature $T < T_d$, as discussed in section 2.1. The group of smeared HT₁ maxima may be the response of former short range order clusters which can become more correlated in the region of the Burns temperature. Since the barriers defining their reorientation can be smaller than those for the domains with long range order, the positions of smeared maxima are shifted towards lower temperatures and relatively sharper maxima of the HT₂ group.

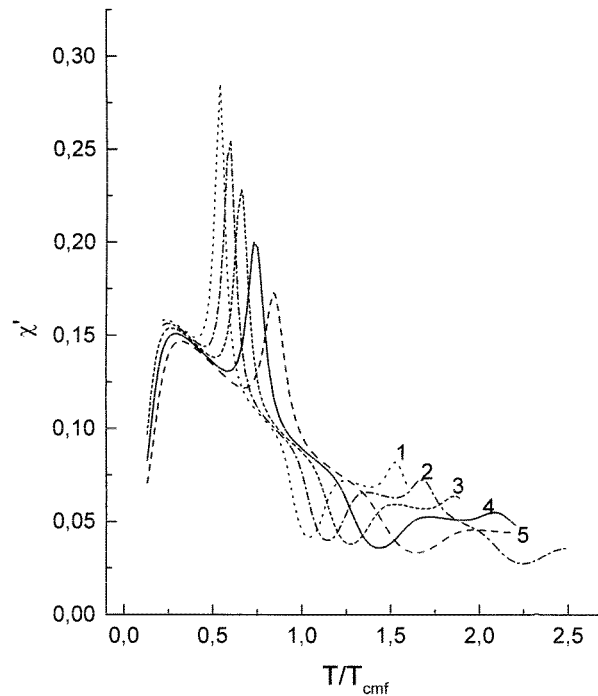


Figure 1. Temperature dependence of dielectric susceptibility for $\lambda = 5$, $\Delta = 8$ at the frequencies $\omega = 100$ Hz (1); 10^3 Hz (2); 10^4 Hz (3); 10^5 Hz (4); 10^6 Hz (5).

The considered case of $\lambda = 5$, $\Delta = 8$ is close to the boundary between mixed phase and dipole glass. For the sake of comparison of disordered and partly ordered relaxors let us proceed to another boundary between mixed and ferroelectric phases which corresponds to $\lambda = 5$, $\Delta = 2$ [10]. A general view of the real part of dielectric permittivity in a logarithmic scale is depicted in figure 2. It is seen that for the same (as in the previous case) single dipole parameters $U/T_{cmf} = 1.143$ and $\bar{\tau}_0 = 10^{-13}$ s, the shape of both LT maxima changed drastically, whereas the HT ones look like those in figure 1. To make the details clearer we depicted separately (in a normal scale) the behaviour of dielectric response in the regions of the LT₁, LT₂ maxima and IIT ones in the insets a, b and c, respectively. One can see that there is only one group of LT maxima with position close to that of the LT₂ group which corresponds to the lowest frequency. The height of these maxima is much larger than that of LT₂ in figure 1. One can see also the disappearance of the essential dispersion of the LT₂ maxima which transforms into small shifts of T_m towards lower temperatures with decreasing frequency (compare figures 1 and 2). The disappearance of the LT₁ group of maxima may be a consequence of the overlapping of LT₁ by very intensive LT₂ maxima because one can see some residual part of LT₁ maxima (like shoulders) in inset a. Both the HT maxima look like those in figure 1, but their heights are a little larger (see inset c). They were fitted to equation (12) with $T_g = 0$ (Arrhenius law), $V/T_{cmf} = 32.7$ and 38.6 for HT₁ and HT₂, respectively. The parameters of the fitting of LT maxima, depicted in inset b, are the following: $T_g/T_{cmf} = 0.37$, $V/T_{cmf} = 0.44$. We have to emphasize that T_g is very close to T_m values in contrast both to the previous case and to the pure dipole glass state [13]. Note that all theoretical calculations were performed for phase transitions of the second order.

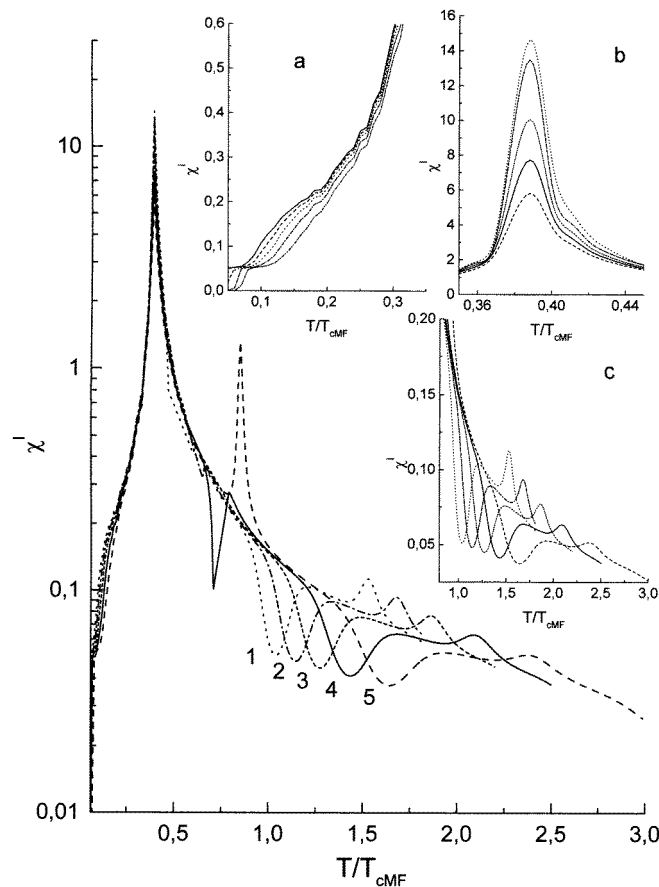


Figure 2. Temperature dependence of dielectric susceptibility for $\lambda = 5$, $\Delta = 2$ at the frequencies $\omega = 100$ Hz (1); 10^3 Hz (2); 10^4 Hz (3); 10^5 Hz (4); 10^6 Hz (5). Marks of the curves in the insets are the same as in the figure.

3. Experiment

3.1. Crystals and measurements

Single crystals of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$, abbreviated as PSNT, were grown from a flux mixture of weight ratio $\text{PSNT}/\text{PbF}_2\text{-PbO-B}_2\text{O}_3$: 0.15/0.40–0.40–0.05 in a covered platinum crucible. Powdered PSNT material was obtained by high temperature solid state reaction at 1273 K for 3 h in a homogeneous mixture of oxides in the weight ratio $1 \text{ PbO} + 0.25 \text{ Sc}_2\text{O}_3 + 0.125 \text{ Nb}_2\text{O}_5 + 0.125 \text{ Ta}_2\text{O}_5$. Cube-shaped crystals were extracted with hot dilute nitric acid and the chemical formula of the crystals was ascribed on the basis of the results of x-ray diffraction studies. As the ionic radii of Nb and Ta ions, possessing the same coordination in the case of BO_6 octahedra, are close to one another, the $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$ crystals can be treated as a solid solution of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.5})\text{O}_3$ and $\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$.

For dielectric studies the crystal surfaces were covered with silver electrodes and the dielectric properties were measured in the frequency range from 20 Hz to 6 MHz by using the computer-aided HP4192 and HP4284 LCR meters. The temperature of the crystals was

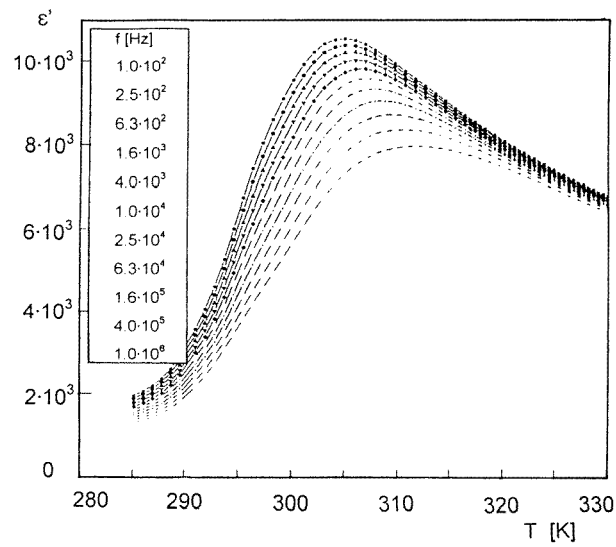


Figure 3. Temperature variation of dielectric permittivity of $\text{Pb}(\text{Sc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$ single crystals measured at various frequencies in the low temperature range.

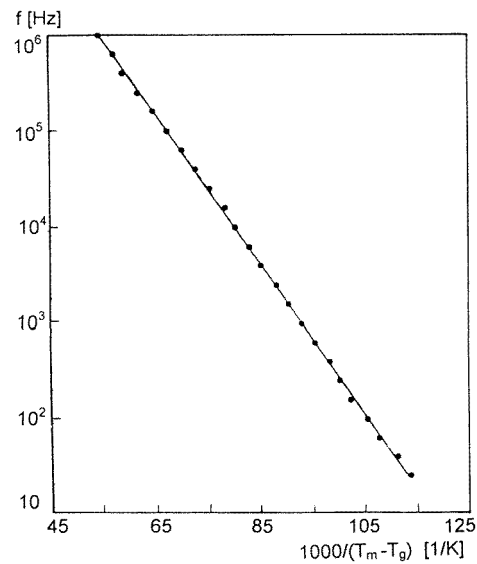


Figure 4. Vogel-Fulcher relationship for the frequency $f = \omega/2\pi$ of the permittivity maxima shown in figure 3.

changed at a rate of 0.02 K min^{-1} in the temperature range of 280 to 330 K and at a rate of 2 K min^{-1} in the high temperature range up to 500 K.

3.2. Results of the measurements

Figure 3 shows the temperature dependence of dielectric permittivity in the temperature range from 285 K to 330 K. The permittivity anomaly in this temperature range is characteristic

of ferroelectric relaxors: it is diffusive and strongly frequency dependent. Broad dielectric permittivity maxima are shifted towards higher temperature with the increase in measuring frequency and the frequency $f = \omega/2\pi$ of the permittivity maximum obeys the Vogel–Fulcher relation with freezing temperature $T_g = 292$ K. The dependence is shown in figure 4.

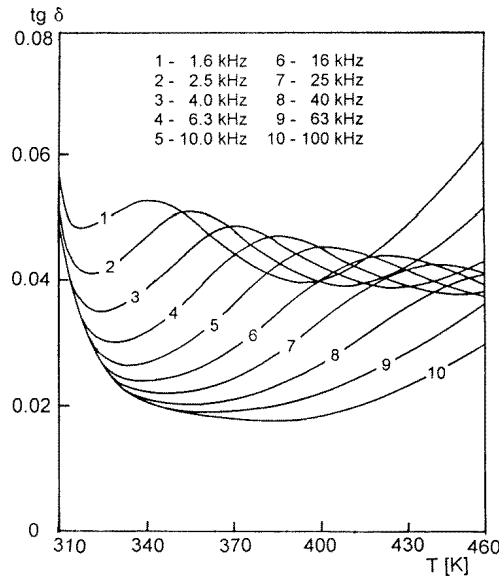


Figure 5. Temperature dependence of $\tan \delta$ in the high temperature range for $\text{Pb}(\text{Sr}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3})\text{O}_3$ single crystals.

In the high temperature range, above 330 K, other broad anomalies in dielectric behaviour are observed. The anomalies were found by us to be strongly frequency dependent [14] and were observed up to about 500 K. As the frequencies of $\tan \delta$ maxima are obtained with higher accuracy than that of the permittivity figure 5 shows the temperature variation of $\tan \delta$ and figure 6 the frequency of f of the absorption maximum versus the temperature T_m of the maximum. The relationship is described by an Arrhenius law with the activation energy of 0.49 eV.

4. Comparison with experiment. Discussion

4.1.

Maxima in the range of $T \approx (305\text{--}310)$ K which were observed in the PSNT dielectric response (see figure 3) could be compared with the calculated permittivity, namely with its LT maxima (see figure 2). One can see from figure 4 that this maximum frequency dependence obeyed the V–F law (see equation (12)) with $T_g \approx 292.5$ K. The proximity of measured T_g and T_m values was predicted theoretically for the case of the mixed ferroglass phase near the boundary with the ferroelectric phase. Really, allowing for the value calculated in section 2 $T_m - T_g \approx 0.03 T_{cmf}$ and $T_{cmf} = T_d \approx 670$ K [9] one obtains $T_m - T_g \approx 20$ K which is close to $T_m - T_g \approx 15$ K obtained from measurements of PSNT single crystals. Since in the high temperature region there were the experimental data only for $\tan \delta = \varepsilon''/\varepsilon'$, we calculated

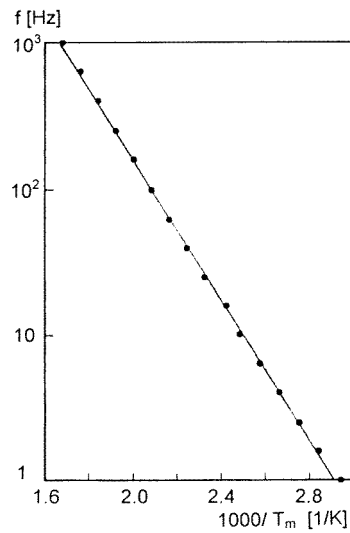


Figure 6. The frequency $f = \omega/2\pi$ of $\tan \delta$ maxima shown in figure 5 versus the temperature T_m .

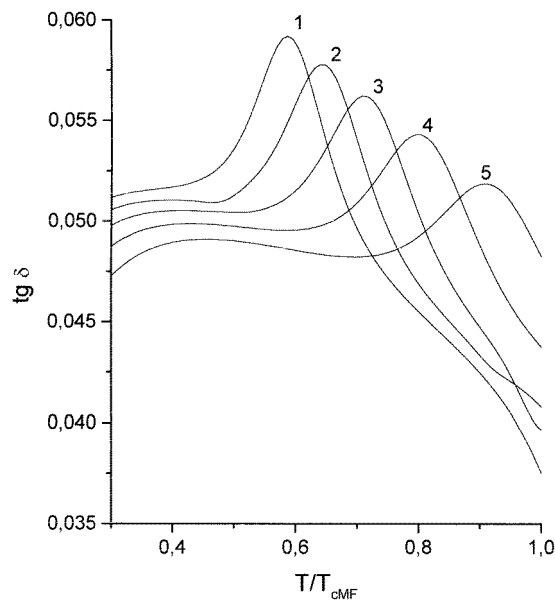


Figure 7. Temperature dependence of dielectric losses for $\lambda = 5$, $\Delta = 8$ at the frequencies $\omega = 100$ Hz (1); 10^3 Hz (2); 10^4 Hz (3); 10^5 Hz (4); 10^6 Hz (5).

this quantity, extracting both imaginary (ϵ'') and real (ϵ') parts of the dielectric susceptibility from equations (5)–(11). The results of $\tan \delta$ calculations for $\lambda = 5$, $\Delta = 8$ (boundary between FG and DG) in the temperature range $T_g < T < T_{cmf}$ for several frequencies are represented in figure 7. One can see the group of maxima with positions shifted towards higher temperatures with frequency increase. The values of $T_m(\omega)$ were fitted by the Arrhenius law, i.e.

by equation (12) with $T_g = 0$ and $V/T_{cmf} = 14.69$. These numbers were obtained for the same single dipole parameters as in the dielectric permittivity calculations. The obtained data lead to the barrier height $V = 0.85$ eV and maximum positions in the range $380 \text{ K} < T_m < 600 \text{ K}$ at $10^2 \text{ Hz} \leq \omega \leq 10^5 \text{ Hz}$. The calculations performed for the boundary between FG and ferroelectric phases ($\lambda = 5$, $\Delta = 2$) lead to larger values of $\tan \delta$ and sharper (than those represented in figure 7) maxima. But maximum positions $T_m(\omega)$ were the same (within accuracy of calculations) as in the previous case. This is because T_m values depend mainly on λ as shown in [13]. So, an Arrhenius law with the same (as for FG phase near the DG state) parameters should also describe the $T_m(\omega)$ dependence for FG in the vicinity of the ferroelectric phase boundary.

Therefore the existence of maxima in the $\tan \delta$ temperature dependence at $T_g < T < T_d$ obeying the Arrhenius law has to be the characteristic feature of the FG phase. The observed values of activation energy 0.49 eV in PSNT as well as the temperature range of maximum positions $360 \text{ K} < T_m < 500 \text{ K}$ at $10^3 \text{ Hz} \leq \omega \leq 10^5 \text{ Hz}$ (see figures 5, 6) are in reasonable agreement with calculated ones.

Note that the cases where the theoretical calculations were performed (mixed phase near the boundaries of the glassy state (figures 1, 7) and of ferroelectric phase (figure 2)) were taken for the sake of illustration rather than for quantitative comparison with experimental results. Keeping in mind also that the parameters of calculations, especially single dipole barrier height, can strongly influence the maximum positions, activation energy and the ratio of intensities of LT and HT maxima [13], one can see that the coincidence between the observed and calculated data is not bad at all.

4.2.

The dielectric responses of PST relaxor samples with different degrees of disorder were investigated experimentally in a wide range of temperatures and frequencies [5, 6]. The main features of the dielectric permittivity measured in two PST samples with smaller and larger degrees of disorder (PST-D and PST-DV respectively, the latter being with lead vacancies) look like those of LT_1 maxima in figure 1, and LT maxima in figure 2, respectively. Firstly, both the observed and calculated maximum frequency dependences were described by the V-F law. Parameters of this law for PST-DV and LT_1 maxima in figure 1 look like those for usual relaxor behaviour. The proximity of T_m and T_g was shown to be the characteristic feature of both calculated LT maxima in figure 2 and of the maxima observed in PST-D samples, the latter being close to 20 K in the considered frequency range [5]. The calculated barrier value ($V/T_{cmf} = 0.44$) appeared to be surprisingly close to the observed one: $V_{obs} \simeq 270 \text{ K}$, whereas $V_{cal} \simeq 295 \text{ K}$. The observed dielectric permittivity in PST-D appeared to be much larger than that in PST-DV which is in qualitative agreement with theoretical results. The shift of maximum position towards higher temperatures with the decreasing of the degree of disorder, observed both in [5] and [6], is also in agreement with the different in positions of the LT_1 (figure 1) and LT (figure 2) maxima. The remarkably strong dielectric dispersion in the vicinity of T_m , observed in strongly disordered PST samples, and a weak one in partially ordered samples [6], gives evidence of similarity of observed dielectric response in [6] and [5] and thus of the possibility to describe the data of both works by the proposed theory. Note that smaller dielectric dispersion in partially ordered samples speaks in favour of the proximity of T_m and T_g in these PST samples. Some experimental and theoretical data are collected in table 1 for the sake of their direct comparison. One can see that the agreement is not bad at all. Note that the experimental and theoretical data for LT and HT maxima were taken from the real part of the susceptibility and $\tan \delta$ respectively.

Table 1.

Experiment				
PSNT (present work)	PST		Theory	
	PST-D	PST-DV	Boundary of FG-F	Boundary of FG-DG
$T_m = 310$ K	$T_m = 280$ K	$200 \text{ K} < T_m < 270$ K	$T_m = 290$ K	$140 \text{ K} \leq T_m \leq 200$ K
V-F law	V-F law	V-F law	V-F law	V-F law
$T_m - T_g \approx 15$ K	$T_m - T_g \approx 20$ K		$T_m - T_g = 20$ K	$T_m - T_g \approx 90$ K
	$V = 270$ K		$V = 295$ K	
$340 \text{ K} \leq T_m \leq 460$ K	There are no data		$370 \text{ K} \leq T_m \leq 520$ K	$360 \text{ K} \leq T_m \leq 500$ K
Arrhenius law			Arrhenius law	Arrhenius law
$V = 0.5$ eV			$V = 0.9$ eV	$V = 0.85$ eV

A sharp drop of the permittivity observed both in [5] and [6] in partially ordered PST samples at $T \leq T_m$ seems to be the consequence of the first order phase transition in PST. To our mind this confirms our theoretical model in which the LT maxima of dielectric response in more ordered samples are connected mainly with ferroelectric long range order contribution. The disappearance of permittivity dispersion in the narrow temperature region of its sharp drop and the restoration of the dispersion at lower temperatures [5, 6] is known to be the characteristic feature of the first order ferroelectric phase transition rather than spontaneous relaxor-ferroelectric transition at temperature lowering.

5. Conclusion

The dielectric response of mixed ferroglass phase with coexistence of short and long range order was calculated in the random field theory framework. Several groups of maxima were obtained. The group at the lowest temperatures was shown to obey the V-F law, whereas other groups the Arrhenius law. The proximity of the freezing temperature T_g to the position of permittivity maximum T_m was obtained for more ordered relaxors. Measurements of dielectric permittivity of $\text{PbSc}_{0.5}\text{Nb}_{0.2}\text{Ta}_{0.3}\text{O}_3$ single crystals were performed. Frequency dependences of low temperature maxima at $305 \text{ K} < T_m < 310$ K were described by the V-F law with $T_g \approx 292.5$ K. At $T > 330$ K the group of maxima in dielectric absorption obeying the Arrhenius law with activation energy 0.49 eV was revealed.

The comparison of the theory with obtained experimental data for PSNT as well as for PST with different degrees of disorder [5, 6] have shown that relaxors of the 1:1 family can be described in the mixed ferroglass phase model. The proximity of T_g to T_m was shown to be a consequence of a large admixture of long range order in the mixed phase.

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References

- [1] Setter N and Cross L E 1980 *J. Appl. Phys.* **57** 4356
- [2] Viehland D, Wutting M and Cross L E 1991 *Ferroelectrics* **120** 71
- [3] Kamzina L S, Korgenevskii A L, Krainik N N and Sapognikova L M 1990 *Izv. Akad. Nauk* **54** 614

- [4] Bidault O, Licheron M, Husson E, Calvarin G and Morell A 1996 *Solid State Commun.* **98** 765
- [5] Chu F, Setter N and Tagantsev A K 1993 *J. Appl. Phys.* **74** 5129
- [6] Bogs M, Beige H, Pitzius A P and Schmitt H 1992 *Ferroelectrics* **126** 197
- [7] Burns G and Dacol F H 1988 *Phys. Rev. B* **28** 2527
- [8] Burns G and Dacol F H 1990 *Ferroelectrics* **104** 25
- [9] Korshunov O I, Markovin P A and Pisarev R V 1992 *Ferroelectr. Lett.* **13** 137
- [10] Glinchuk M D and Farhi R 1996 *J. Phys.: Condens. Matter* **8** 6985
- [11] Glinchuk M D, Farhi R and Stephanovich V A *J. Phys.: Condens. Matter* **9** 10237
- [12] Glinchuk M D, Farhi R and Stephanovich V A 1997 *Ferroelectrics* **199** 11
- [13] Glinchuk M D and Stephanovich V A 1999 *J. Appl. Phys.* **85** 1722
Glinchuk M D and Stephanovich V A 1998 *J. Korean Phys. Soc.* **32** 1100
- [14] Wolak J, Hilczler B, Caranoni C, Lampin P and Boulesteix C 1994 *Ferroelectrics* **158** 399
- [15] Glinchuk M D, Laguta V V, Bykov I P, Nokhrin S N and Jastrabik L 1997 *J. Appl. Phys.* **81** 3561
- [16] Glinchuk M D and Stephanovich V A 1994 *J. Phys.: Condens. Matter* **6** 6317
- [17] Glinchuk M D and Stephanovich V A 1995 *Ferroelectrics* **169** 281
- [18] Glinchuk M D and Stephanovich V A 1997 *Ferroelectr. Lett.* **22** 113
- [19] Binder K and Young A P 1986 *Rev. Mod. Phys.* **58** 801