

## Dielectric spectra and Vogel-Fulcher scaling in $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ relaxor ferroelectric

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1999 J. Phys.: Condens. Matter 11 4899

(<http://iopscience.iop.org/0953-8984/11/25/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.214

The article was downloaded on 15/05/2010 at 11:54

Please note that [terms and conditions apply](#).

# Dielectric spectra and Vogel–Fulcher scaling in $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ relaxor ferroelectric

A A Bokov<sup>†</sup>§, M A Leshchenko<sup>‡</sup>, M A Malitskaya<sup>†</sup> and I P Raevski<sup>†</sup>||

<sup>†</sup> Institute of Physics, Rostov State University, 194 Stachki Avenue, Rostov-on-Don 344090, Russia

<sup>‡</sup> Microelectronics Department, Kiev Polytechnic Institute, 37 Pobedi Avenue, Kiev 252056, Ukraine

E-mail: abokov@sfu.ca and smotr@ip.rsu.runnet.ru (I P Raevski)

Received 6 July 1998, in final form 19 March 1999

**Abstract.** Dielectric dispersion in disordered  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals was studied. Two dispersion regions were found at  $10^3$ – $10^5$  Hz and  $10^8$ – $10^9$  Hz at room temperature. The low-frequency relaxation process, which has a very wide distribution of relaxation times, shifts to higher frequency (up to about  $10^9$  Hz) and becomes narrower in frequency with increasing temperature. It is this relaxation process that is responsible for the temperature shift of the diffused  $\varepsilon(T)$  maximum with increasing frequency. At low frequencies ( $f < 10^6$  Hz) the temperatures of  $\varepsilon'$  and  $\varepsilon''$  maxima follow the Vogel–Fulcher law and the entire  $\varepsilon''$  data set can be scaled using a scaling variable related to frequency by the Vogel–Fulcher law. At  $f > 10^6$  Hz the Vogel–Fulcher law and scaling are also valid, but with different fitting parameters. The results can be described in terms of a phenomenological model implying a wide and smooth spectrum of relaxation times which broadens with decreasing temperature rather than be explained by freezing into the glass state.

## 1. Introduction

Dielectric relaxation in relaxor ferroelectrics has become a topic of considerable interest (Cross L E 1987, Cheng *et al* 1998, Tagantsev and Glazounov 1998). To account for the relaxation phenomena in these materials two different approaches are commonly used. The traditional one, first appearing in the works of Isupov (1963, 1964), considers clusters of polar phase located in non-polar phase to be responsible for the unusual relaxation behaviour. It was proposed that the relaxation polarization was attributed to the thermoactivated reorientation of dipolar moments of clusters or the motion of the boundaries of clusters (Smolensky *et al* 1984, Bovtoun and Leshchenko 1997, Tagantsev and Glazounov 1998). The second approach implies the existence of a structural (dipolar) glass state in relaxors. The observation of some properties typical of structural glasses is commonly considered to provide the experimental background in this case. In particular, the permittivity in glasses can be scaled using a temperature-independent distribution of activation energies linked to the relaxation times by a Vogel–Fulcher-type law (Courtens 1986). Viehland *et al* (1991a) found that the same scaling could be fulfilled in a  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  relaxor.

Studies of the glass-like behaviour of permittivity in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and some other relaxors have been performed in the comparatively narrow frequency range of  $10^2$ – $10^7$  Hz

§ Present address: Department of Chemistry, Simon Fraser University, Burnaby, British Columbia V5A 1S6, Canada.

|| To whom correspondence should be addressed.

(Viehland *et al* 1990, 1991a, b, Bokov and Emel'yanov 1991, Chu *et al* 1994, 1995). In this work we measured the permittivity of  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals in the range  $10^2$ – $10^9$  Hz.

Lead indium niobate  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  has a perovskite-type structure like most other relaxor ferroelectrics (Smolensky *et al* 1984). The interesting feature which makes  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  an excellent subject for studying relaxor properties is the possibility of changing (by special heat treatment) the degree of disorder in the arrangement of In and Nb cations on equivalent lattice sites (compositional disorder) (Bokov *et al* 1984, Bokov 1996). Compositional disorder is one of the main factors determining relaxor behaviour and changes of the degree of disorder lead to dramatic changes in relaxor properties of a crystal (Bokov *et al* 1984, Bokov 1996).

We studied  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals in a completely disordered state and found that the data obtained could be interpreted in terms of the glassy approach only at low frequencies ( $10^2$ – $10^6$  Hz), not over the whole frequency range  $10^2$ – $10^9$  Hz.

## 2. Experimental procedure

Flux-grown  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals were used in the present study; the details of crystal growth have been reported elsewhere (Smotrakov *et al* 1983). Samples of size about 1 mm were electroded with Aquadag or sputtered Pt. At frequencies of  $10^2$  to  $10^5$  Hz the complex permittivity  $\varepsilon^* = \varepsilon' - i\varepsilon''$  was studied using a P5083 AC bridge. Measurements were taken with a field applied along the (001) direction while increasing the temperature at a rate of  $0.5 \text{ K min}^{-1}$  or lower. High-frequency studies ( $10^6$  to  $1.1 \times 10^9$  Hz) were performed with the help of coaxial transmission line. The specimen was considered to be a distributed parameter system.

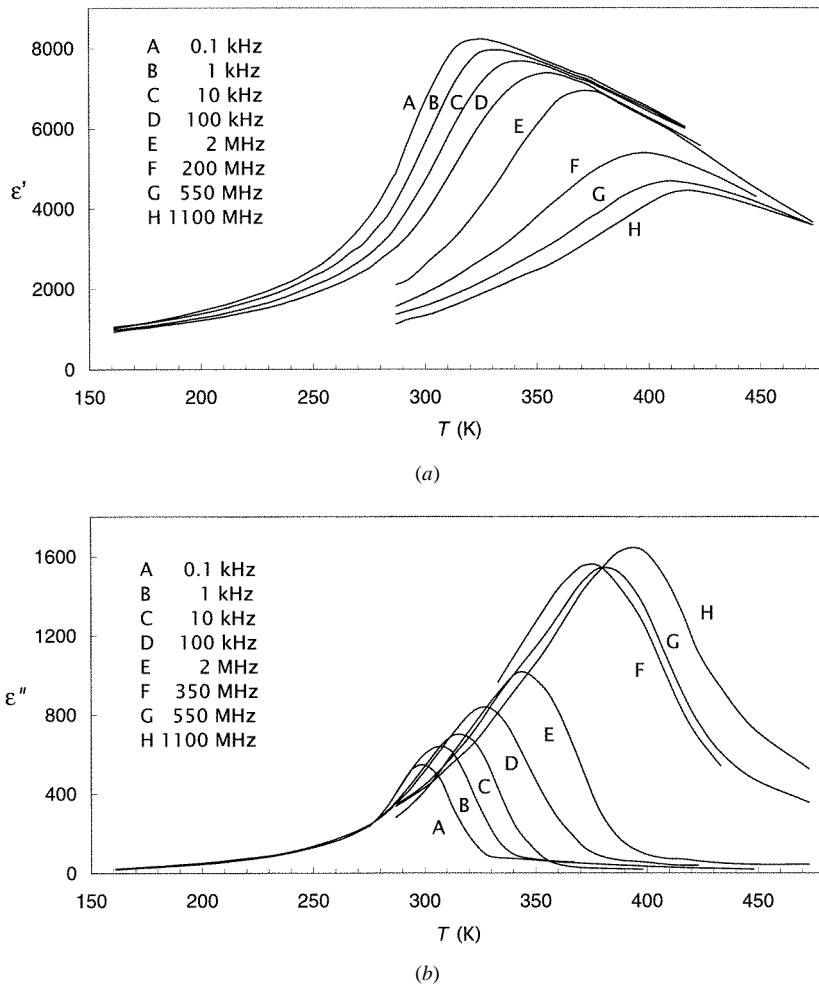
Prior to the measurements the crystals were annealed at 1300 K for 20 min. Such a treatment leads to complete compositional disordering of the structure (Bokov *et al* 1984, Bokov 1996).

## 3. Results and discussion

The temperature dependencies of the real ( $\varepsilon'$ ) and imaginary ( $\varepsilon''$ ) parts of permittivity at several selected measurement frequencies are shown in figures 1(a) and (b) respectively. In both sets of curves, broad maxima which shift towards a higher temperature with increasing frequency due to the strong frequency dispersion are among the main features of relaxor ferroelectrics (see, e.g., Smolensky *et al* 1984). These maxima are associated with the diffuse ferroelectric phase transition. Figure 2 shows  $\varepsilon'$  and  $\varepsilon''$  as a function of frequency at various temperatures. At low temperatures  $\varepsilon''$  is almost independent of frequency over the whole frequency range, suggesting a wide distribution of relaxation times. At higher temperatures two regions of dispersion can be resolved, with frequencies ranged around  $10^3$ – $10^5$  Hz and  $10^8$ – $10^9$  Hz. These regions can be associated with two different polarization mechanisms. At  $T > 350$  K only one dispersion region is observed.

Cole–Cole diagrams were obtained by plotting  $\varepsilon''$  versus  $\varepsilon'$  at constant temperature. Two dispersion regions visible in  $\varepsilon''(\nu)$  dependencies at low temperatures and one region at high temperatures are also clearly distinguished in the Cole–Cole diagrams. The spectra in each of these regions can be approximated by an empirical relation which is often used when describing Cole–Cole plots in materials with a wide distribution of relaxation times (Poplavko 1980)

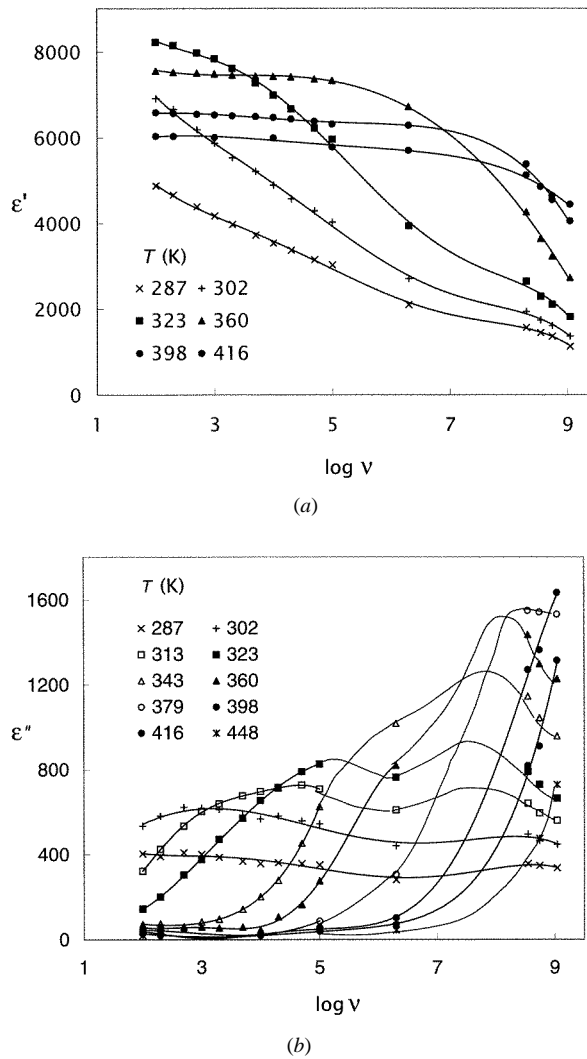
$$\varepsilon^* = \varepsilon' - i\varepsilon'' = \varepsilon_\infty + \frac{\varepsilon_0 - \varepsilon_\infty}{1 + (i\nu/\nu_p)^{1-\alpha}}$$



**Figure 1.** Temperature dependences of (a) the real and (b) imaginary part of the permittivity measured at various frequencies.

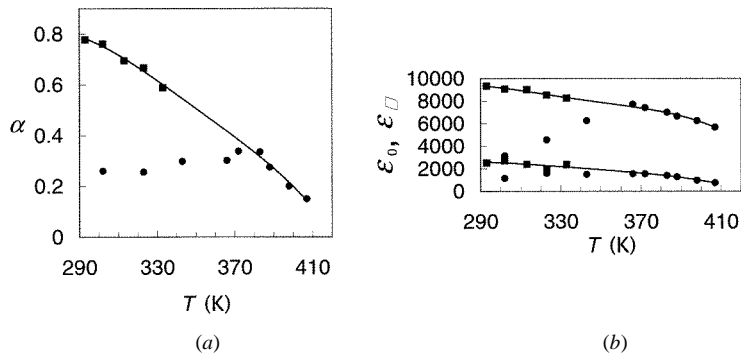
where  $\nu_p$ ,  $\alpha$ ,  $\varepsilon_0$  and  $\varepsilon_\infty$  are the average dispersion frequency, the parameter of relaxation frequency distribution and the low-frequency and high-frequency limits of  $\varepsilon$  in the dispersion region respectively. Figure 3 shows the temperature dependences of some of these parameters determined at  $T$  exceeding room temperature. At lower temperatures the spectra were too broad for these parameters to be reliably evaluated. It can be seen that the parameter  $\alpha$ , which represents a measure of the width of the relaxation time distribution, is much higher for a low-frequency than for a high-frequency relaxation process. When the temperature increases the part of the dielectric spectrum concerned with the low-frequency process becomes narrower, while the high-frequency part remains almost unchanged in width.

Dielectric relaxation in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  ceramics (but not crystals) has been studied in several works (Yasuda and Inagaki 1992, Chu *et al* 1994, Elissalde *et al* 1997). Relaxation in approximately the same frequency ranges as in our research was observed. However, comparison between the results is inappropriate because the high-temperature annealing step before measurements to disorder the structure was not carried out in the works mentioned



**Figure 2.** Frequency dependences of (a) the real and (b) imaginary part of the permittivity measured at various temperatures.

above. It is known (Bokov 1996) that in this case the structure of ceramic sample remains incompletely ordered. Comparison of our results with known data on a model relaxor ferroelectric  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (Kirillov and Isupov 1971, Bovtoun *et al* 1984, Viehland *et al* 1991a, b, Bovtoun and Leshchenko 1997) shows certain similarities in dielectric spectra. In  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  two dispersion regions (at  $10^5$ – $10^7$  Hz and  $10^8$ – $10^9$  Hz) were also observed at low temperatures and one high-frequency region remained at higher temperatures. Such behaviour was explained by the disappearance of the low-frequency polarization process at high temperatures. In the case of  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  another explanation is possible. Considering the low-temperature data in figure 2(b) one can see that with increasing temperature the dispersion frequency of the low-frequency process increases rapidly (much more rapidly than in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ). Thus, at high temperature the low-frequency process may appear



**Figure 3.** Temperature dependences of Cole–Cole parameters (a)  $\alpha$  and (b)  $\varepsilon_0$  and  $\varepsilon_\infty$  measured at low (squares) and high (circles) frequency.

shifted to high frequency about  $10^9$  Hz and becomes predominant there. If this is correct, it is easy to understand the results in figure 3. That is, the results at high temperature in figure 3 are related to the extrapolation of the low-frequency process at low temperature (this extrapolation is shown by the full curves in figures 3(a) and 3(b)).

When analysing glassy systems with a broad spectrum of relaxation times, Lundgren *et al* (1981) and Courtens (1984) found the fundamental relation between  $\varepsilon'$  and  $\varepsilon''$  to be valid in the temperature range of relaxation:

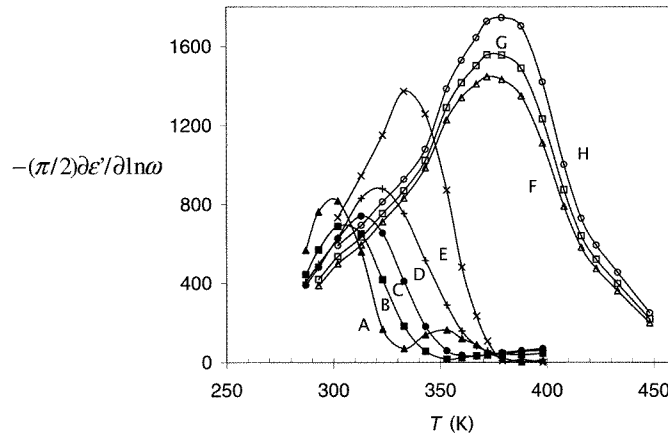
$$\varepsilon'' = -\frac{\pi}{2} \frac{\partial \varepsilon'}{\partial \ln \omega} \quad (1)$$

where  $\omega = 2\pi\nu$  is the angular frequency. We checked the validity of relation (1) in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ . To calculate the values of  $\partial \varepsilon' / \partial \ln \omega$ , the experimental isothermal frequency dependences of  $\varepsilon'$  (some of these dependences are shown in figure 2(a)) were approximated by polynomials using a least-squares fit. For best fitting, high-frequency ( $\nu > 1$  MHz) and low-frequency data were treated separately. The derivatives of the polynomials were then calculated for several values of  $\ln \omega$ . The results obtained are presented in figure 4 in the form of temperature dependences. Comparison of these curves with experimental  $\varepsilon''(T)$  curves in figure 1(b) shows that relation (1) is fulfilled quite well except at boundary frequencies. It should be noted however that the deducing of equation (1) does not require an assumption of freezing, and fulfilment of this equation only indicates a distribution of relaxation times  $\tau$  broad in  $\ln \omega$ .

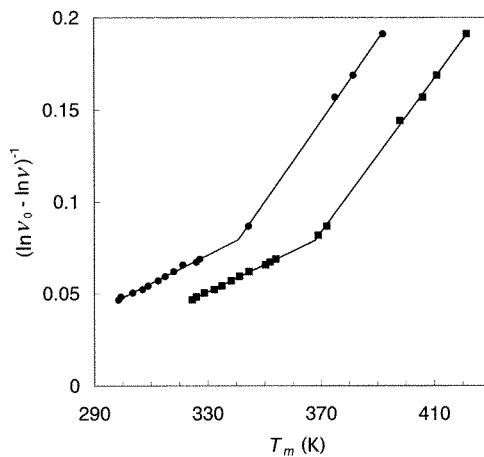
It is well known that in relaxor ferroelectrics the frequency dependence of the temperature of the permittivity maximum  $T_m$  cannot be described by an Arrhenius law which is to be expected for Debye relaxation process. Recent studies of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  and some other relaxors showed (Viehland *et al* 1990, 1991a, b, Bokov and Emel'yanov 1991, Chu *et al* 1994, 1995) that, like in spin and structural glass, this dependence obeys the empirical Vogel–Fulcher law

$$\nu = \nu_0 \exp\left(\frac{-E_a}{k(T_m - T_0)}\right) \quad (2)$$

where  $\nu$  is the measurement frequency and  $\nu_0$ ,  $E_a$  and  $T_0$  are phenomenological parameters. Our attempts to fit experimental  $T_m(\nu)$  dependences in the whole range of data by the Vogel–Fulcher law (2) as well as by an Arrhenius law failed. But when studying the high-frequency ( $\nu > \nu_b \approx 10^6$  Hz) and low-frequency ( $\nu < \nu_b$ ) areas separately, we found that the Vogel–Fulcher law was perfectly fulfilled in each of these areas with different values of  $T_0$  and



**Figure 4.** Temperature dependences of  $-(\pi/2)\partial\epsilon''/\partial\ln\omega$  values calculated at various frequencies. The curves are identified by the same letters as in figure 1(b). Full curves are guides to the eye.



**Figure 5.** Temperature  $T_m$  at which real (squares) and imaginary (circles) parts of the permittivity pass through maximum as a function of measurement frequency ( $\nu$ ) according to the Vogel–Fulcher law (2) with  $\nu_0 = 2 \times 10^{11}$  Hz.

$E_a$  and practically the same value of  $\nu_0$ . The fitting was performed with a linear least-squares routine.  $T_m$  was considered as a function of  $(\ln \nu_0 - \ln \nu)^{-1}$ . The square deviations were minimized by varying  $\nu_0$ . The results of fitting are presented in table 1 and in figure 5. When constructing the plots in this figure the average value  $\nu_0 = 2 \times 10^{11}$  was used.

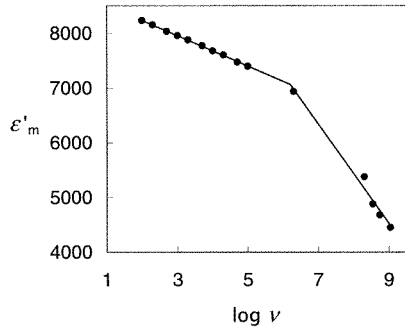
The frequency  $\nu_b$  is a peculiar frequency not only for  $T_m(\nu)$  dependences. The value of the real part of the permittivity maximum (i.e. at  $T_m$ ) was found to be a linear function of  $\log \nu$  and the slope of this function changes at  $\nu_b$  (see figure 6).

Studies of some structural glasses (Courtens 1984) and relaxor ferroelectrics (Viehland *et al* 1991a) have shown that not only the maximum value of permittivity, but the entire  $\epsilon''$  data set could be scaled onto a single curve. We applied the procedure developed in these other studies to  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals. The scaling was made with the equation

$$\epsilon''(\nu, T) = h(\nu, T)R(u) \quad (3)$$

**Table 1.** Parameters  $\nu_0$ ,  $E_a$ ,  $T_0$  and  $d$  determined in high-frequency ( $\nu > \nu_b \approx 10^6$  Hz) and low-frequency ( $\nu < \nu_b$ ) ranges from Vogel–Fulcher fitting of different experimental data: (1, 4) temperature of  $\varepsilon'$  maximum; (2, 5) temperature of  $\varepsilon''$  maximum; (3, 6) the entire  $\varepsilon''$  data.

Parameter	$\nu < \nu_b$			$\nu > \nu_b$		
	1	2	3	4	5	6
$\nu_0 \times 10^{-11}$ (Hz)	2.6	3.1	3.8	1.78	0.77	1.62
$E_a$ (eV)	0.120	0.118	0.129	0.040	0.029	0.033
$T_0$ (K)	260	236	237	331	313	317
$d$ (eV $^{-1}$ )	—	—	41	—	—	52



**Figure 6.** Maximal value of the real part of the permittivity as a function of measurement frequency.

where

$$R(u) = 0.5[1 + \tanh(du)] \quad (4)$$

is a scaling function,  $d$  is a constant and  $u(\nu, T) = E_a - E$  is a scaling variable which is related to frequency by the Vogel–Fulcher-like law

$$\nu = \nu_0 \exp\left(\frac{E}{k(T - T_0)}\right).$$

At low temperature the value of  $R$  should be close to 1, and  $\varepsilon'' = h(\nu, T)$  is an increasing function of  $T$ . At higher temperatures  $R$  tends to zero and the product of  $h$  and  $R$  passes through a maximum at a certain intermediate temperature, replicating the temperature behaviour of  $\varepsilon''$ .

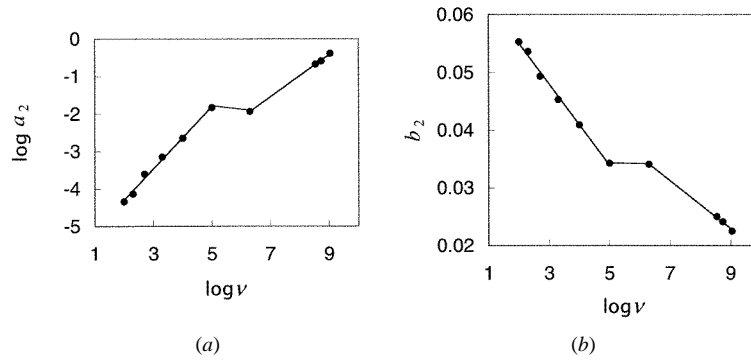
The temperature dependences of  $\varepsilon''$  measured at ten various frequencies (0.1, 0.2, 0.5, 2, 10 and 100 kHz and 2, 350, 550 and 1100 MHz) were used for the scaling. In the first stage of scaling procedure,  $h(T)$  functions were determined for each frequency independently. Each  $\varepsilon''(T)$  dependence was approximated at temperatures considerably lower than the temperature of the maximum by the function

$$h(T) = a_1 \exp(b_1 T) + a_2 \exp(b_2 T). \quad (5)$$

The first term in this relation helps in fitting at the lowest temperatures and was chosen to be the same for all frequencies with  $a_1 = 3.836$ ,  $b_1 = 0.010619$ . The values of  $a_2$  and  $b_2$  found from fitting at various frequencies are presented in figure 7.

In the second stage the high-temperature part of the data was scaled with the least-squares routine. As in the case of  $T_m$  fitting, the high-frequency ( $\nu > \nu_b \approx 10^6$  Hz) and the low-frequency ( $\nu < \nu_b$ ) data were considered separately. Deviations between the measured values of  $\varepsilon''$  and those calculated using expression (3) with various values of fitting parameters  $\nu_0$ ,





**Figure 7.** The parameters used for fitting with equation (5): (a)  $a_2$  and (b)  $b_2$  as a function of frequency.

$E_a$ ,  $T_0$  and  $d$  were obtained. The mean-square deviations were minimized by varying these parameters for a total of 90 points (15 temperatures at six frequency values) in the low-frequency case and 60 points (15 temperatures at four frequency values) in the high-frequency case. It should be emphasized that all the parameters  $\nu_0$ ,  $E_a$ ,  $T_0$  and  $d$  were varied independently in the course of fitting.

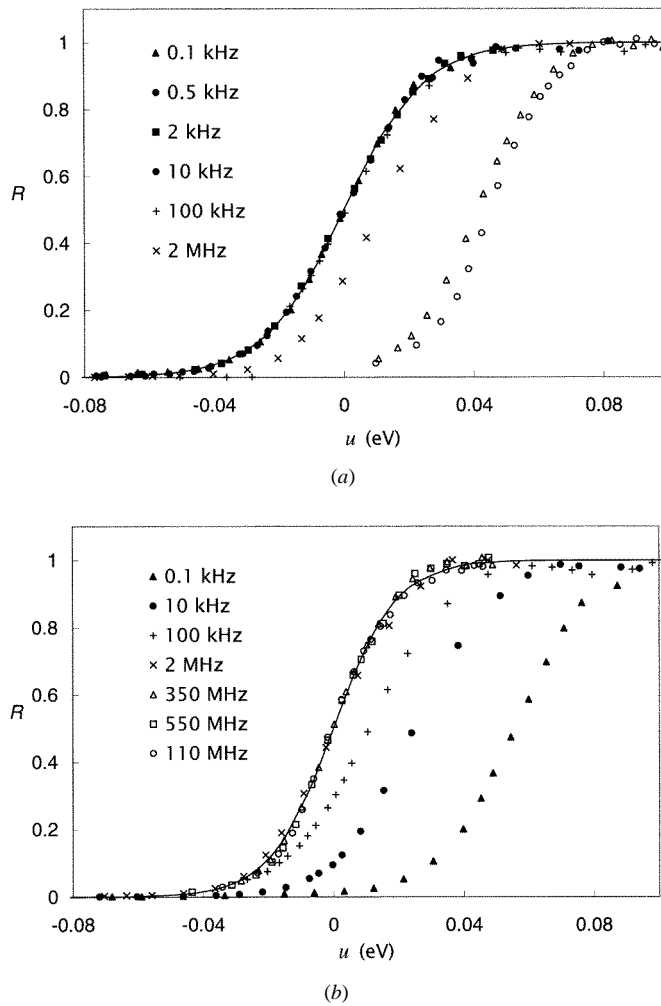
The best-fit values of  $\nu_0$ ,  $E_a$ ,  $T_0$  and  $d$  are presented in table 1 (in column 3 for ( $\nu < \nu_b$  and in column 6 for ( $\nu > \nu_b$ )). Figures 8 and 9 illustrate the quality of scaling. Figures 8(a) and 8(b) were constructed with the low-frequency set of parameters (given in column 3 of table 1) and the high-frequency set of parameters (column 6 of table 1) respectively. The scaling function  $R$  is depicted by the full curves. The points are the values of  $h^{-1}\varepsilon''$  which should be equal to  $R$  in the case of exact fitting. It is evident that high-frequency data cannot be scaled with the low-frequency set of parameters and vice versa. When plotting phenomenological  $\varepsilon''(T)$  curves in figure 9 the low-frequency set of parameters for scaling low-frequency data and high-frequency set of parameters for scaling high-frequency data were used. The scaling is quite good. Considerable departures only occur at temperatures greatly exceeding  $T_m$ . Apparently this is due to the contribution of another relaxation process to  $\varepsilon''$  (scaling describes one of the processes only).

Thus all phenomenological parameters describing  $\varepsilon(T)$  curves, except  $\nu_0$ , have different values at low and high frequencies. This means that the characteristics of dielectric relaxation responsible for the temperature shift of the diffused  $\varepsilon(T)$  maximum with increasing frequency change at a certain temperature. However, the invariability of  $\nu_0$  confirms the assumption discussed above, i.e. that the nature of this relaxation is the same within the whole frequency range  $10^2$ – $10^9$  Hz. The change of other parameters at about 350 K can be attributed to the variation of dimensions of polar clusters or to interactions in the system, which should also change with temperature.

The possibility of Vogel–Fulcher scaling in relaxors is often considered, by analogy with other glassy systems, to provide evidence of a true phase transition into a polar glass state. It is proposed in this case that the Vogel–Fulcher behaviour of permittivity arises from the critical temperature dependence of the characteristic (maximal in the spectrum) relaxation time

$$\tau_c^{-1}(T) = 2\pi\nu_0 \exp\left(\frac{-E_a}{k(T - T_0)}\right) \quad (6)$$

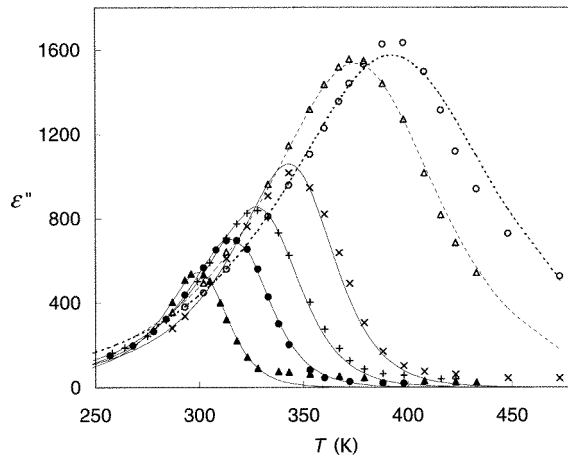
where  $\nu_0$  is the attempt frequency,  $E_a$  is the activation energy and  $T_0$  is the freezing temperature at which the relaxation time should diverge, signalling a phase transition. In other words, the system becomes frozen at  $T_0$  but not at  $T = 0$  as the Arrhenius' law prescribes.



**Figure 8.** Scaling of  $\varepsilon''$  data using (a) low-frequency ( $\nu < \nu_b$ ) and (b) high-frequency ( $\nu > \nu_b$ ) set of fitting parameters  $T_0$ ,  $E_a$ ,  $\nu_0$  and  $d$ . The full curves are the scaling functions  $R(U)$  calculated from equation (4) and the points are the experimental values of  $\varepsilon''$  divided by  $h(\nu, T)$ .

When discussing Vogel–Fulcher scaling in  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ , Viehland *et al* (1991a, b) used a model in which deviation from Debye behaviour and freezing arose due to a correlation between phase separated polar clusters (superparaelectric moments) at low temperatures. At high temperatures the moments are decoupled, and thus the high-frequency relaxation should exhibit Debye-type behaviour. This is not so in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ . Our results cannot therefore be explained in terms of this model.

Although Vogel–Fulcher behaviour in relaxors is usually attributed to the critical temperature dependence of the relaxation time, this is not the only possible approach. In the recent work of Tagantsev (1994), who considered a model describing the dielectric response of relaxor ferroelectrics, it was shown that the Vogel–Fulcher relationship for  $T_m$  could be obtained as a direct consequence of gradual broadening of the spectrum with decreasing temperature and did not necessarily imply fulfilment of relation (6) or any other kind of freezing in the

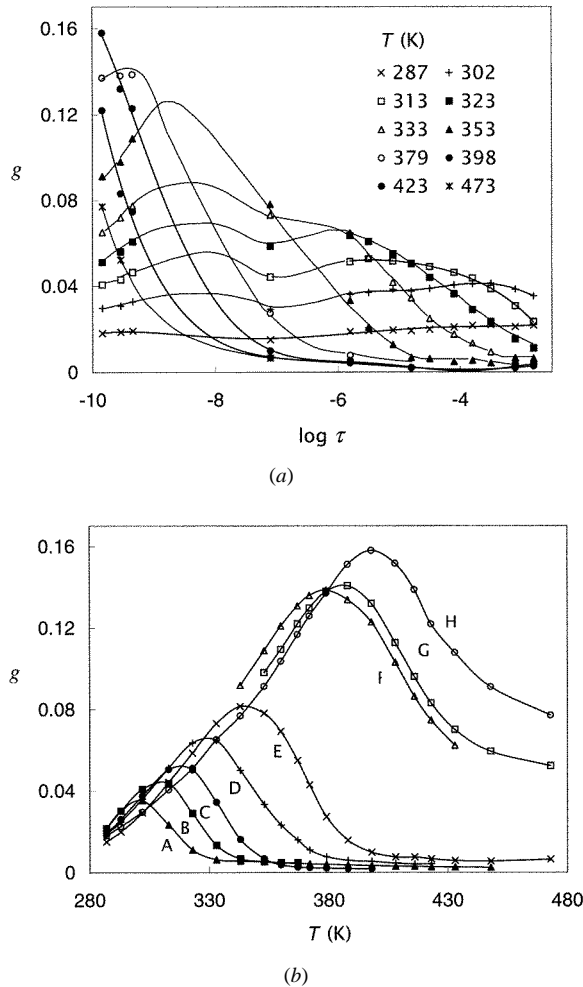


**Figure 9.** The imaginary part of the permittivity fitted with equation (3). The points represent experimental data. The curves are the results of fitting at  $10^2$ ,  $10^4$ ,  $10^5$ ,  $2 \times 10^6$ ,  $3.5 \times 10^8$ , and  $1.1 \times 10^9$  Hz. Curves are identified by the same symbols as in figure 8. Not all the experimental data points are shown.

system. Under the conditions that the smooth and wide spectrum  $g(\tau, T)$  gradually shrinks with increasing temperature due to a strong but non-singular decrease of  $\tau_{\max}$  and an insignificant variation of  $\tau_{\min}$  ( $\tau_{\max}$  and  $\tau_{\min}$  are characteristic maximal and minimal times of the spectrum respectively) and  $\varepsilon'(0, T)$  is a non-singular function of temperature having a maximum at some temperature  $T_A$ , it was found that relation (2) could hold both for real and imaginary parts of the permittivity. In this model the parameter  $T_0$  found with the temperature of  $\varepsilon'$  maximum merely equals  $T_A$ , and  $\nu_0$  equals  $(2\pi\tau_{\min})^{-1}$ . To investigate the applicability of this approach for  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals we tried to determine the relaxation time probability distribution function  $g(\tau, T)$ . This parameter can be estimated from experimental data using an approximate formula derived for broad spectra of relaxation times (Lundgren *et al* 1981, Courtens 1984):

$$g(\tau, T) \approx \frac{2\varepsilon''(1/2\pi\tau, T)}{\pi\varepsilon_0(T)} \quad (7)$$

where  $\varepsilon_0(T) \equiv \varepsilon'(0, T)$ ,  $\tau \gg \tau_{\min}$ . Unfortunately the value of  $\varepsilon_0(T)$  is unknown and its measurement in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ , as well as in other relaxors, is difficult. In several works (Yushin *et al* 1987, Viehland *et al* 1990)  $\varepsilon_0(T)$  was assumed to be  $\varepsilon'(T)$  measured at some low frequency (e.g. 100 Hz). But at a temperature lower than  $T_m$  these values can be greatly different. Furthermore, in glassy systems divergence of  $\varepsilon_0(T)$  at  $T_0$  can be expected (Courtens 1984). In our crystals the real part of the permittivity is almost independent of frequency at high temperatures (figures 1(a) and 2(a)), thus when calculating  $g$  at these temperatures we considered  $\varepsilon_0$  to be equal to  $\varepsilon$  measured at 100 Hz (the lowest frequency used). The linearity of  $\varepsilon'_m(\log \nu)$  (figure 6) made it possible to extrapolate this function to the lower frequencies and then to calculate  $\varepsilon'_m(T)$  dependence for temperatures lower than  $T_m$  at 100 Hz using relation (2). As can be seen in figure 1(a), the values of  $\varepsilon'_m(T)$  differ slightly from the values of  $\varepsilon$  measured at 100 Hz at the same temperature. Thus when calculating  $g$  at low temperatures we considered  $\varepsilon_0(T) = \varepsilon'_m(T)$ . The results of calculations of the relaxation time spectrum using formula (7) are presented in figure 10. Because of the above mentioned uncertainty of  $\varepsilon_0(T)$ , calculation of  $g$  at lower temperatures makes no sense and the curves shown in this figure do not pretend



**Figure 10.** The relaxation time probability distribution function versus (a) relaxation time at various temperatures and (b) temperature at various frequencies. Curves are identified by the same letters as in figure 1. Full curves are guides to the eye.

to hold a high degree of precision. However, some qualitative conclusions can be drawn. Two parts of the spectrum, responsible for high-frequency and low-frequency relaxation processes, are clearly seen in figure 10. The decrease of  $\tau_{\max}$ , which should lead to shrinkage of the spectrum with increasing temperature, is observed.

Unfortunately, the phenomenological model of Tagantsev is too simple to describe the dielectric properties of  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  quantitatively, but qualitative agreement between theory and experiment can be found. The shape and temperature evolution of the spectrum are similar to those considered in the model. As predicted by the theory, the temperature maxima of  $\varepsilon'$  and  $\varepsilon''$  follow the Vogel–Fulcher relationship, the  $T_0$  parameter for  $\varepsilon'$  is smaller than for  $\varepsilon''$ , the  $E_a$  parameters are positive and the  $\nu_0$  parameters for  $\varepsilon'$  and  $\varepsilon''$  are practically the same. On the other hand, the model deals only with a rather narrow temperature interval abutting on  $T_0$  and deviation from Vogel–Fulcher behaviour can be expected at higher temperatures. In  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  such deviation occurs in the form of changing some Vogel–Fulcher

parameters. Although the possibility of scaling the entire  $\epsilon''$  data set (not only the peak position) was not mentioned by Tagantsev in his work, this possibility is not in contradiction with his model.

#### 4. Conclusion

The temperature and frequency dependences of complex dielectric permittivity in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  crystals were measured at  $10^2$ – $10^9$  Hz and analysed. Before measurements the crystals were disordered by special heat treatment. As in other relaxors, broad peaks in the temperature dependences of the real and imaginary parts of the permittivity associated with diffuse ferroelectric phase transition were observed. These peaks shift to higher temperatures with increasing frequency. Investigations of the frequency dependences of permittivity and Cole–Cole diagrams revealed two dielectric dispersion regions. At room temperature they are located at  $10^3$ – $10^5$  Hz and  $10^8$ – $10^9$  Hz. The low-frequency relaxation process, which has a very wide distribution of relaxation times, shifts to higher frequency (up to about  $10^9$  Hz) and becomes narrower in frequency with increasing temperature. It is this relaxation process that is responsible for the temperature shift of diffused  $\epsilon(T)$  maximum with increasing frequency. The width of the high-frequency dispersion region remains almost unchanged with increasing temperature. Relation (1) between  $\epsilon'$  and  $\epsilon''$ , which is valid in systems with a broad spectrum of relaxation times, was experimentally confirmed to be valid in the whole investigated frequency range.

The problem was to find out if Vogel–Fulcher behaviour, typical of glassy systems, can be observed in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$ . The data obtained by measuring the imaginary part of the permittivity at different frequencies in a wide temperature interval can be scaled to a single curve using a scaling variable related to frequency by the Vogel–Fulcher law. As for the position of the temperature of maximum permittivity, it follows the Vogel–Fulcher law for both real and imaginary parts. All the parameters (except  $\nu_0$ ) used for the Vogel–Fulcher fitting differ considerably at high ( $\nu > \nu_b \approx 10^6$  Hz) and low ( $\nu < \nu_b$ ) frequency. The observed change of fitting parameters with frequency is unusual for glassy systems.

It has been shown that fulfilment of the Vogel–Fulcher law by the permittivity in  $\text{Pb}(\text{In}_{0.5}\text{Nb}_{0.5})\text{O}_3$  relaxor can hardly be explained by freezing into the structural glass state. It can be qualitatively described in terms of the phenomenological approach proposed by Tagantsev (1994) and implies a wide and smooth spectrum of relaxation times which broadens with decreasing temperature without any freezing-related singularity.

#### References

- Bokov A A 1996 *Ferroelectrics* **183** 65–73  
 Bokov A A and Emeliyanov S M 1991 *Phys. Status Solidi b* **164** K109–11  
 Bokov A A, Raevski I P and Smotrakov V G 1984 *Sov. Phys.–Solid State* **26** 1708  
 Bovtoun V P, Krainik N N, Markova L A, Poplavko Y M and Smolenskii G A 1984 *Fiz. Tverd. Tela* **26** 378–81  
 Bovtoun V P and Leshchenko M A 1997 *Ferroelectrics* **190** 185–90  
 Cheng Z-Y, Katiyar R S, Yao X and Bhalla A S 1998 *Phys. Rev. B* **57** 8166–77  
 Chu F, Reaney I M and Setter N 1994 *Ferroelectrics* **151** 343–8  
 ——— 1995 *J. Appl. Phys.* **77** 1671–6  
 Courtens E 1984 *Phys. Rev. Lett.* **52** 69–72  
 ——— 1986 *Phys. Rev. B* **33** 2975–8  
 Cross L E 1987 *Ferroelectrics* **76** 241–67  
 Elissalde C, Villesuzanne A, Ravez J and Pouchard M 1997 *Ferroelectrics* **199** 131–42  
 Isupov V A 1963 *Fiz. Tverd. Tela* **5** 187  
 ——— 1964 *Izv. Akad. Nauk. SSSR Ser. Fiz.* **28** 653

- Kirillov V V and Isupov V A 1971 *Izv. Akad. Nauk. SSSR Ser. Fiz.* **35** 2602–6
- Lundgren L, Svedlindh P and Beckman O 1981 *J. Magn. Magn. Mater.* **25** 33–8
- Poplavko U M 1980 *Physics of Dielectrics* (Kiev: Visha Shkola)
- Smolensky G A, Bokov V A, Isupov V A, Krainik N N, Pasynkov R E, Sokolov A I and Yushin N K 1984 *Ferroelectrics and Related Materials* (New York: Gordon and Breach)
- Smotrakov V G, Bokov A A, Raevski I P, Malitskaya M A and Zaytsev S M 1983 *Izv. Akad. Nauk. SSSR, Ser. Neorgan. Mater* **19** 1172–5
- Tagantsev A K 1994 *Phys. Rev. Lett.* **72** 1100–3
- Tagantsev A K and Glazounov A E 1998 *Phys. Rev. B* **57** 18–21
- Viehland D, Jang S, Cross L E and Wuttig M 1990 *J. Appl. Phys.* **68** 2916
- 1991a *Phil. Mag.* **64** 335–44
- Viehland D, Wuttig M and Cross L E 1991b *Ferroelectrics* **120** 71–7
- Yasuda N and Inagaki H 1992 *Ferroelectrics* **126** 115–20
- Yushin N K, Smirnova E P, Dorogovtsev S N, Smirnov S I and Guljamov G 1987 *Fiz. Tverd. Tela.* **29** 2947–52