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DIELECTRIC AND THERMAL PROPERTIES OF RELAXATION FERROELECTRICS AT LOW TEMPERATURES

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1. Introduction

It has been shown that ferroelectric crystals serve as excellent samples for investigation of the glassy behaviour of solids at low temperatures /1/. Typical glassy anomalies are found in thermal and dielectric properties of relaxation ferroelectrics /1-6/, order-disorder type ferroelectrics /1/ and quantum paraelectrics /1,7,8/.

It appears that the glassy behaviour of ferroelectrics is an immediate consequence of its characteristic lattice properties /1/. Even at low temperatures the decisice excitations in these solids are strongly influenced or caused by the kinetics of the basic electric dipoles and the domain structure.

So dielectric measurements prove to be a very sensitive and effective tool for detailed investigations and for controlling any theoretical model explaining glassy anomalies. The present paper deals with a further analysis of dielectric and thermal properties of the relaxation ferroelectrics $Pb_{1-x}La_x(Zr_yTi_{1-y})O_3$ (PLZT) and $Sr_{1-x}Ba_x(Nb_2O_6)$ (SBN).

All details of sample properties, preparation, measuring method and accuracy are summarized in paper /1/.

2. Experimental Results

Thermal conductivity /3/ and dielectric dispersion were measured on a PLZT polycrystal with x = 0.085 and y = 0.65. The measurements indicated that their thermal conductivity was strongly affected by structure relaxation and ageing effects. However, after some thermal cycles by cooling from room temperature, the results were reproduced. The detailed report of these effects is given in /6/. The reproductive data of thermal conductivity λ are shown in fig.1. Over a
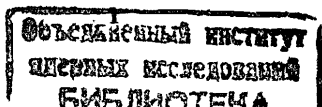
range of $0.1K < T < 0.7K$ the results obey:

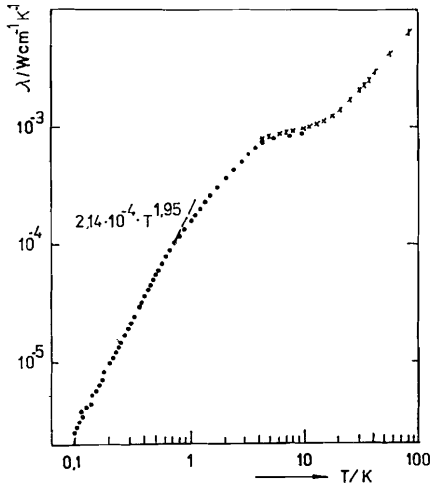$$\lambda = 2.14 \cdot 10^{-4} \cdot T^{1.95 \pm 0.05} \qquad (W/cm\ K) .$$

Fig.1. Thermal conductivity of PLZT 8,5/65/35. • , present data; x, data from Ref.6 .

Above 0.7K the slope decrease, and around 4K a plateau is observed with $\lambda \approx 9 \cdot 10^{-4}$ W/cmK. Above 11K λ shows a roughly linear temperature increase. The specific heat C of PLZT also exhibits the characteristic features of an amorphous solid both the roughly linear dependence for $T < 1K$ and the maximum in C/T^3 at temperatures close to the plateau in λ /9,10/.

The complex dielectric ac-susceptibility was measured on the same sample with a measuring frequency of f = 1.6 kHZ at $0.03K < T < 100K$.

Figure 2 shows the variation of the real part $\frac{\Delta\varepsilon}{\varepsilon} = \frac{\varepsilon'(T) - \varepsilon'(T_o)}{\varepsilon'(T_o)}$ and of the imaginary part ε'' with temperature.

Here and in further considerations $\varepsilon'(T_o)$ is always defined as the minimum in $\varepsilon'(T)$ at low temperatures. This proves to be advantageous for systematization and comparison of experimental results.
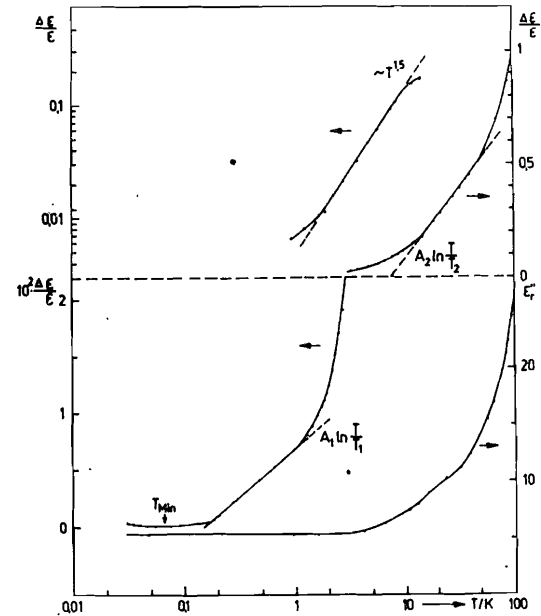

Fig.2. Variation of dielectric constant ε of polycrystalline PLZT 8,5/65/35 with temperature. Note the different scales for $\Delta\varepsilon/\varepsilon$.

With increasing temperature there are five different peculiarities. At the lowest temperatures one obtains a slight minimum (T_{min}= 90mk, ε'_{min}= 360, $\Delta\varepsilon/\varepsilon$ (30 mk) = $3 \cdot 10^{-4}$). The minimum is continued by a logarithmic increase of $\Delta\varepsilon/\varepsilon \sim ln\ T$. For $T > 1K$ the slope changes to $\Delta\varepsilon/\varepsilon \sim T^k$ (k = 1.5) and for $T > 10K$ a second logarithmic dependence is found. At $T > 50K$ the slope of $\Delta\varepsilon/\varepsilon$ rises again due to the lowest part of the broad maximum of the diffuse phase transition. The T^k-dependence is represented in an additional double logarithmic scale. Because of smaller sensitivity, ε'' does not reveal an analogous behaviour below 1K. There is only a smooth increase in ε'' with temperature. For T > 4K the slope gets stronger showing some curvature around 20K and it is determined for $T > 50K$ by the peak of the diffuse phase transition.

So the general behaviour of the complex dielectric susceptibility at low temperatures suggests the existence of two different processes with a cross-over in the range from 1K to 10K.

The same behaviour of ε is obtained for a second PLZT-sample with $x = 0.10$ and $y = 0.65$. At all temperatures the results of the two samples for ε'' agree within the measuring accuracy determined by geometry (5%). At $T > 1K$ the values of $\Delta\varepsilon/\varepsilon$ agree within 10%.

SBN is the first ferroelectric single crystal where glassy behaviour was observed /4/. This is important for excluding any effect of grain boundaries or analogous defects.

Figure 3 shows the thermal conductivity of two $Sr_{1-x}Ba_x(Nb_2O_6)$ crystals ($x = 0.39$ and $x = 0.55$) in the range from 60 mk to 80K /1,4,6/. For $T < 2K$:

$$\lambda = 2.1 \cdot 10^{-4} \cdot T^{1.7 \pm 0.05} \quad (W/cm\ K) \quad (x = 0.55)$$

and

$$\lambda = 1.7 \cdot 10^{-4} \cdot T^{1.7 \pm 0.05} \quad (W/cm\ K) \quad (x = 0.39).$$

In order to control the effect of ageing, the measurement was repeated for the second sample after being aged at room temperature for one year: $\lambda = 1 \cdot 10^{-4} \cdot T^{2.0 \pm 0.05}$ (W/cm K). At shorter times the values of λ monotonously change within the values reported.

The spacific heat C measured on such crystals at $T > 0.5K$ also displays the significant departures from the Debye behaviour known for amorphous solids /5/. However, for $T < 1.5$ K C should be described by $C = AT^{\alpha} + BT^3$ with $\alpha < 1$, unusual for glasses ($\alpha \geq 1$). Further investigations of the specific heat were extended down to 0.15K by a usual relaxation method /1/. The SBN(39% Ba) sample was the same one as taken for the thermal conductivity measurement. The results are shown in fig.4 ($C \approx 2.75 \cdot 10^{-5}T$ (J /cm³·K) at $T < 2K$.

The variation of the dielectric constant was measured on SBN($x = 0.5$). This single crystal shows similar peculiarities in

Fig.3. Thermal conductivity of $Sr_{1-x}Ba_x(Nb_2O_6)$ single crystal.

($\circ$, $x = 0.55$; $\times$, $x = 0.39$ (first measurement);

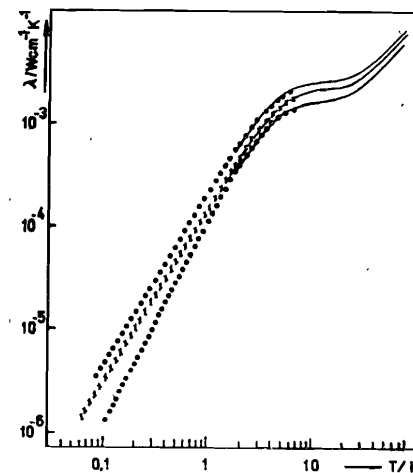$\bullet$, $x = 0.39$ (after ageing for 1 year);
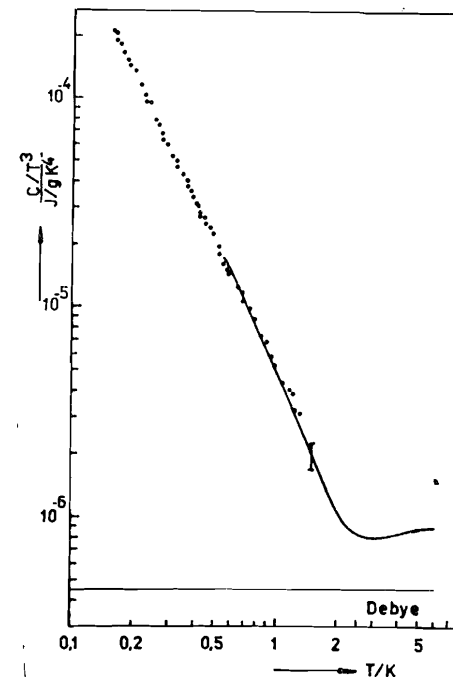
—— , data from Ref.4 and 6 .

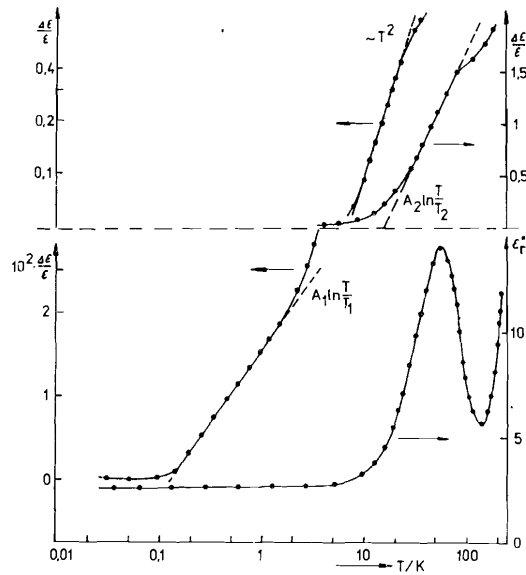Fig.4. Departure of the specific heat of SBN (39% Ba) from T^3– Debye behaviour (—— , data from Ref.5)

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Fig.5. Variation of dielectric constant $\mathcal{E}$ of $Sr_{0,5}Ba_{0,5}(Nb_2O_6)$ single crystal with temperature.
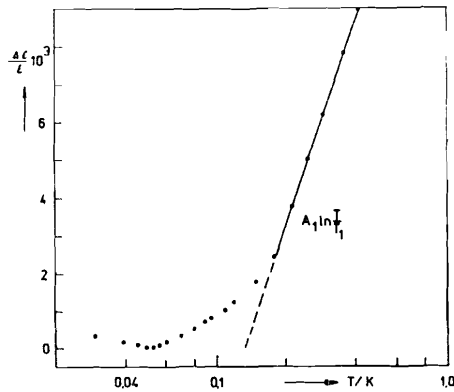
Fig. 6. Minimum in $\Delta\mathcal{E}/\mathcal{E}$ of SBN (50% Ba)

the variation of $\Delta\mathcal{E}/\mathcal{E}$ (T) as obtained for the PLZT polycrystal (fig.5). The smooth minimum is obtained at somewhat lower temperatures ($T_{min}= 55$ mK, $\mathcal{E}'_{min}= 123$, $\Delta\mathcal{E}/\mathcal{E}$ (25mK) = 3.7 · 10^{-4}), fig.6. Both the empirical coefficients A_1 and A_2 are larger for the single crystal. The cross-over in $\Delta\mathcal{E}/\mathcal{E}(T)$ from the first logarithmic dependence to the second one takes place at higher temperatures, where $\Delta\mathcal{E}/\mathcal{E} \sim T^2$ for 9 K < T < 25 K.

As seen in the imaginary part, the general behaviour of the dielectric constant, at least for T > 2 K, is determined by a process causing the broad peak in between 5K and 140K with $T_{max}= 60K$. The strong rise in the slope for T > 140K is also due to the phase transition just like in PLZT.

3. Discussion

The thermal and dielectric properties of PLZT and SBN obey all the glassy anomalies at low temperatures with comparable magnitudes for the poly- and single crystals.

At T < 2K the available specific heat results for PMN /2/, PLZT /10/ and SBN /1,5/ show an excess contribution due to localized excitations: $C_{ex} \approx A \cdot T^{\alpha}$ with $\alpha < 1$. For amorphous solids $\alpha > 1$ is usual. So the question arises if this difference between glasses and crystals is a general one and what conclusions regarding the origin of low excitation spectra should be made. The results suggest that the linear contribution in glasses may be caused by a superposition of a finite number of well defined Schottky terms /7,11,12/. The narrow range of energy splitting in the single crystal is broadened by the disorder in the amorphous solid.

As the glassy behaviour was found for a large range of various single crystals grain boundaries are ruled out of consideration. For ferroelectrics it is obvious that these effects are due to the presence of domains. This is confirmed by specific measurements on $NaNO_2$ in

single domain and polydomain polarization state /13/. Domain walls, however, amount to only a small part of the bulk, and the energy spectra due to dipole rearrangement, should be discontinuous. Thus, the localized excitations are suspected to occur within the domains. At present there is no microscopic theory explaining the glassy behaviour. Various phenomenological models invert finally some experimental results to certain assumptions for properties of low excitation spectra and leave the matter at that. Also the tunneling model /14,15/ successful in the correlation of various low temperature anomalies fails when a large amount of experimental results is regarded /1,16, 17/. Thus, an accurate analysis of any postulated attribute of the two-level excitations is needed.

The subsequent application of the tunneling model required an energy-dependent density $P(E)$ and a broad spectrum of thermal relaxation times τ for each tunneling-state energy E. As pointed out, primary attention in this paper is given to the dielectric results. Analogous to the acoustic case, the variation of the dielectric constant with temperature due to the resonant and relaxation scattering of electromagnetic waves with $\omega = E/\hbar$ by two-level systems is given by /18/:

$$\left(\frac{\Delta\varepsilon}{\varepsilon}\right)_{res} = B \cdot \int_0^{E_{max}} E \cdot P(E)\, dE \cdot \left[\frac{tanh(E/2K_B T)}{(\hbar\omega)^2 - E^2} - \frac{tanh(E/2K_B T_0)}{(\hbar\omega_0)^2 - E^2} \right]$$

$$\left(\frac{\Delta\varepsilon}{\varepsilon}\right)_{rel} = J(T,\omega) - J(T_0,\omega_0)$$

$$J(T,\omega) = -\frac{B}{4}\int_0^{E_{max}} \frac{dE \cdot P(E)}{K_B T cosh^2(E/2K_B T)} \int_0^{ln(\tau_{max}/\tau_{min})} \frac{ds(1-e^{-s})^{1/2}}{1 + A^2 tanh^2(E/2K_B T)e^{2s}(E/K_B)^{-6}}$$

$$A = 2\pi\hbar^4 \varrho\, v^2 \gamma^{-2}(K_B^3 \sum_i v_i^{-3})^{-1} \cdot \omega$$

$$B = (-2\pi/27)\mu_0^2 (\varepsilon'+2)^2/\varepsilon' \cdot \varepsilon_0 ,$$

where ε_0 is the dielectric constant of free space; μ_0, the average microscopic dipole moment of the two-level states and γ, the coupling constant.

In numerical calculations the quadratic form $P(E)=P_0(1+aE^2)$ was used. At measuring frequency $\omega = 10^4 s^{-1}$ the relation $\hbar\omega/K_B T \ll 1$ is fulfilled and so $P(E) = P_0$ produces a roughly logarithmic decrease with temperature:

$$\left(\frac{\Delta\varepsilon}{\varepsilon}\right)_{res} = B P_0 I_c \cdot ln(T/T_0).$$

For low measuring intensity $I_c \approx 1$. At higher temperatures the contribution of the relaxation process predominates, and $\Delta\varepsilon/\varepsilon$ increases again obeying also a logarithmic dependence:

$$\frac{\Delta\varepsilon}{\varepsilon} = A_1 ln T/T_1 .$$

So the characteristic minimum in $\Delta\varepsilon/\varepsilon$ can be explained by the competition of the resonant and relaxation scattering on the two-level system. The measuring intensity was $(0.1 \ldots 1)\cdot 10^{-6} W/cm^2$. Analogous to amorphous dielectrics, no saturation was obtained at these magnitudes. The saturation intensity is $I_s \sim \sqrt{\varepsilon'}$. Thus, saturation effects in ferroelectrics would require a larger intensity in consequence of a shorter relaxation time of the tunnel system due to stronger dipolar interactions. Above the minimum there are three characteristic empirical functions for $\Delta\varepsilon/\varepsilon$ with increasing temperatures:

$$\Delta\varepsilon/\varepsilon = A_1 ln T/T_1 \qquad (T \lesssim 1K) \qquad (1)$$
$$\Delta\varepsilon/\varepsilon \sim T^k \qquad (1\ldots 20K,\ k = 1\ldots 2) \qquad (2)$$
$$\Delta\varepsilon/\varepsilon = A_2 ln T/T_2 \qquad (10 \ldots 100K) \qquad (3) .$$

For simulation (1), $P(E) = P_0$ is sufficient. Assuming an energy-dependent density of states (a > 0), a more rapid increase in $\Delta\varepsilon/\varepsilon$ can be produced. An attempt to fit the dielectric data for PLZT and SBN in the (1) and (2) regions (with $\gamma = 1.92 \cdot 10^{-19}$ J, E_{max}/K_B =

= 100 K and $\tau_{max}/\tau_{min} = 5.5 \cdot 10^{12}$ /1/) shows similar results as known for glasses. However, owing to the more sensitive dielectric constant of ferroelectrics, it is clearly seen that the fit in the (2) region remains unsatisfactory. Using $B \cdot P(E) \approx 8 \cdot 10^{-2}(1 + 5 \cdot 10^{-4}(E/K_B)^2 \cdot K^{-2})$ and changing $B \cdot P_0$ and "a" within one order of magnitude, the dielectric results are fitted with a similar accuracy for the above-mentioned samples. Then an estimate of μ_0 yields $4.0 \cdot 10^{-30}$ Asm(SBN, $P_0 = 2.8 \cdot 10^{45}$ J^{-1} m^{-3}) and $1.4 \cdot 10^{-30}$ Asm(PLZT, $P_0 = 1.9 \cdot 10^{45} J^{-1} m^{-3}$) /1/. The values of $a \approx 10^{-4} \dots 10^{-3}$ K^{-2} are in the same range known for amorphous solids /16,19,20/. Extrapolation of the model to the second logarithmic dependence (3) does not give any reasonable fit.

4. Conclusion

A proof analysis of published acoustic and dielectric measurements in connection with the above results can be summarized as follows:

At lower temperatures (T $\lesssim$ 1K) the results are explained by a constant density of states.

At T $\gtrsim$ 1K, analogous to thermal conductivity and heat capacity, the treatment of the dielectric and acoustic results in the tunneling state model requires an energy-dependent density of states $P(E)$. However, even for a narrow range of temperature the fits to the experimental results are wrong. Thus, physical correctness of this procedure remains under discussion.

The upper logarithmic dependence (3) at T $\gtrsim$ 10K appears to be caused by a process other than that described in the tunneling model. This assumption is supposed by the behaviour of the imaginary part ε''. Figure 5 shows that one obtains $\Delta\varepsilon/\varepsilon \sim T^k$ just in the range where ε'' begins to rise up to the broad maximum with increasing

temperature. So it is reasonable to treat (2) as a cross-over from scattering at tunneling-states with $P(E) \approx P_0$ at lower temperatures to another physical process where the tunneling model is not applicable. The steep rise (2) is due to a growing number of excitations responsible for electrical field when the temperature increases. Just in this range (2) the thermal conductivity shows the plateau and specific heat - the C/T^3 - maximum. This supports the assumption that the peak in dielectric losses is thermally activated. Such peaks in dielectric losses and acoustic attention are known for a large amount of amorphous solids and have to be considered as characteristic features of the glassy behaviour. It was proposed that this anomalous absorption had its origin in the disorder itself /16/. Usually the phenomenon is assumed to adhere to Debye theory in which the losses χ'' vary with $\omega\tau$ as

$$\chi''(\omega) \sim \frac{\omega\tau}{1+(\omega\tau)^2} \quad , \qquad (4)$$

where the relaxation time τ is thermally activated and varies with temperature as $\tau = \tau_0 exp(\tilde{E}_a/K_B T)$, $\tilde{E}_a$ is an activation energy and τ_0 is some "attempt-to-jump" time. However, the peaks are much wider than predicted by (4). Similar to the tunneling model philosophy at lower temperatures, a distribution of activation energies $g(\tilde{E}_a)$ is postulated. For this formal description of the relaxation process no reasonable justification can be found, and the distribution of $\tilde{E}_a$ required to fit the data is often unphysical. Thus, it is not surprising that such a treatment of experimental results up to date is not very efficient for adding knowledge of glassy behaviour. In an alternative approach it has been shown that the understanding of the physical origin of these dielectric loss peaks is essential for the interpretation of the whole complex of glassy anomalies /1/. This question will be considered in the following paper.

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Фишер Э.   E8-86-98
Диэлектрические и тепловые свойства сегнетоэлектриков
релаксационного типа при низких температурах

Диэлектрическая восприимчивость, теплопроводность и удельная теплоемкость кристаллических сегнетоэлектриков релаксационного типа имеют такие же температурные зависимости как у аморфных диэлектриков. Анализ характерных аномалий в поведении диэлектрической восприимчивости на основе модели двухуровневых систем дает удовлетворительные результаты для T < 1 К. При этом требуется предположить постоянную плотность состояния. При более высоких температурах экспериментальные данные не указывают на существование двухуровневых систем с зависящей от энергии плотностью состояния.

Fischer E.   E8-86-98
Dielectric and Thermal Properties of Relaxation
Ferroelectrics at Low Temperatures

Changes in dielectric constant with temperature and the behaviour of thermal conductivity and specific heat in relaxation ferroelectric crystals are similar to glasses. The consideration of characteristic anomalies in dielectric constant using the tunneling state model gives reasonable results for T < 1 K with a constant density of states. No confirmation for the presence of any energy-dependent density of tunneling states at higher temperatures can be found.