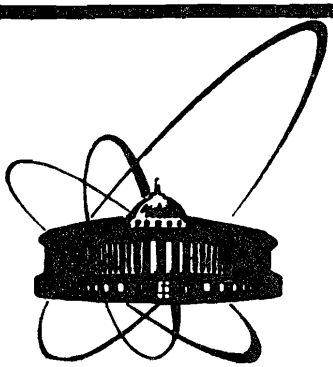

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# THERMAL CONDUCTIVITY AND DIELECTRIC PROPERTIES OF POLYCRYSTALLINE $(Pb_xSr_{1-x})TiO_3$ AT LOW TEMPERATURES

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Introduction

The results of the thermal conductivity $\lambda$ and dielectric measurements on a $SrTiO_3$ single crystal reveal the glassy behaviour of this quantum paraelectric at low temperatures /1,2/. It was suggested that the characteristic anomalies can be understood qualitatively on the basis of lattice dynamics. Thus analogous investigations are of interest in which the lattice dynamics can be changed within the same system.

On that account measurements on $Pb_xSr_{1-x}TiO_3$ solid solutions (PST) are promising.

The lattice of these crystals is of the perovskit - type and highly symmetric.

Phase transitions are characterized by only small deformations of the ideal cubic structure. These deformations are caused by the lattice instabilities due to soft modes characterizing, for instance, the rotation of $TiO_6$ groups about a symmetry axis. Consequently, the new phase can be represented as the ideal lattice structure with the frozen displacement of the atoms taking part in the soft mode.

In $SrTiO_3$ the structural phase transition at 105 K is generated by the softening of an optical mode at the zone boundary /3/. The further softening of an optical mode at the zone center is accompanied by its degeneration with the longitudinal acoustic branch and stabilized in a quantum paraelectric regime /4/.

The ferroelectric state can be forced by applying an electrostatic field or by impurities. Thus for such solid solutions the structural and ferroelectric phase transitions and the anomalies in

acoustic and dielectric properties caused by them, are strongly influenced by the concentration of impurities and sample preparations /5/. For the system $Pb_xSr_{1-x}TiO_3$ the phase diagram is shown in fig.1.

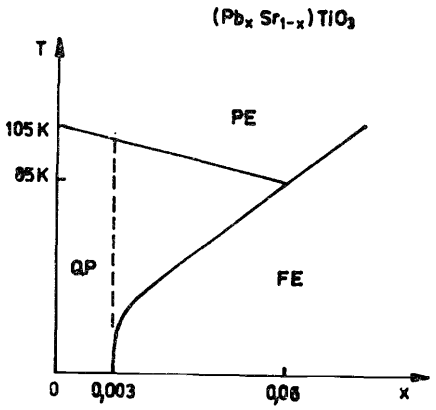



Fig.1. Phase diagram of $Pb_xSr_{1-x}TiO_3$ (according to ref./6/).

Three ranges of Pb - concentration should be distinguished; For concentrations $x < 0.3$ % the samples shew a structural transition at about 105 K and quantum paraelectric behaviour (Q.P.) at lower temperatures. For 0.3 % < x < 6 % in addition to the structural transition at 105 K > $T_o$ > 85 K there is a ferroelectric phase (F.E.) at the lowest temperatures.

With increasing Pb - concentration (x > 6 %) there occurs the ferroelectric phase transition from the paraelectric state (PE) when the temperature decreases. Consequently, for systematic investigations polycrystalline samples with x = 0; x = 0.005; x = 0.055; x = 0.12 and x = 1 were chosen.

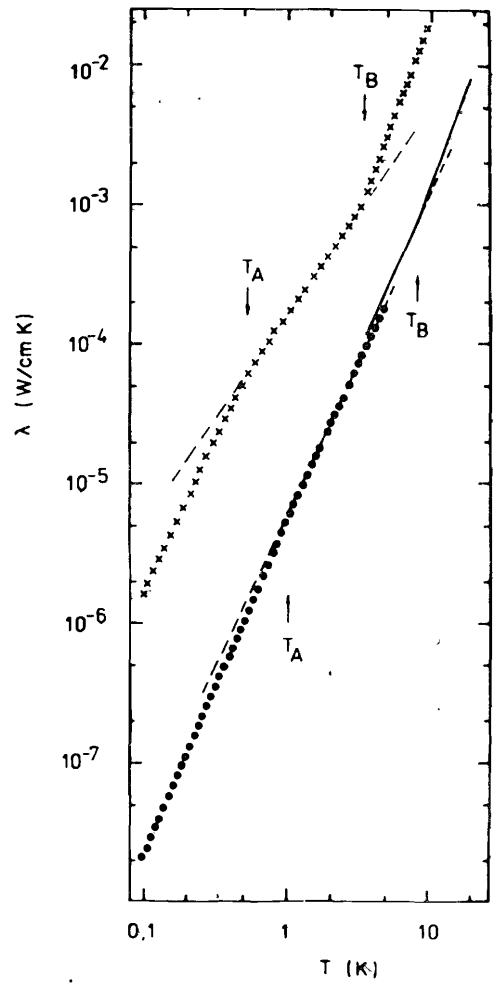
All details of the experiment are summarized elsewhere and will not be discussed here /1/.

Experimental Results and Discussion

For both the $SrTiO_3$ single crystal and ceramic sample (x = 0) the thermal conductivity $\lambda$ is shown in fig. 2.



Fig. 2. Thermal conductivity of $SrTiO_3$ ( x , single crystal; •, polycrystal; —— , from Ref. /7/; – –, $\lambda \sim T^{P_{min}}$ at $T_A < T < T_B$ )




In comparison with the single crystal the thermal conductivity of polycrystalline $SrTiO_3$ is reduced for about two orders of magnitude at the lowest temperatures. There is also only a slight change in slope ( $\lambda \sim T^P$) with increasing temperature at $T_A$ = 1 K from p = = 2.4 to p = 2.2 (= P min), A second curvature in $\lambda(T)$ is known at $T_B$ = 8.7 (p = 2.2 to p = 2.7) /7/. The general behaviour of $\lambda$ for both crystals is quite similar although there is only a slight reduction of temperature dependence in the intermediate range for the

polycrystal. It may be suggested that the main difference in the absolute values is due to additional defect scattering within the grain boundaries in the ceramics.

The dielectric results for the both samples are similar. Fig. 3 shows the imaginary part $\varepsilon''$ between 1 K and 200 K.

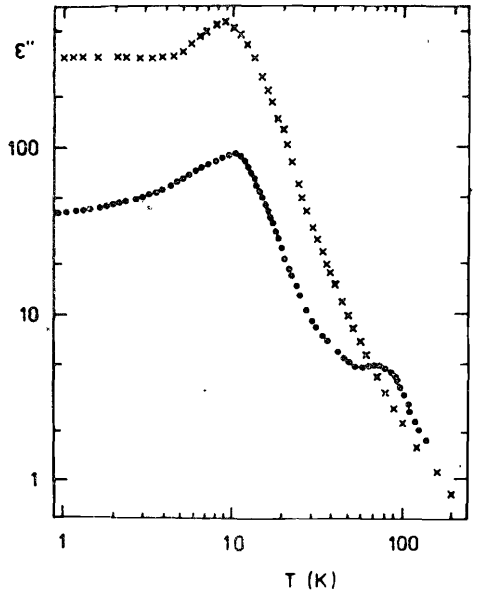



Fig. 3. Temperature dependence of the dielectric $\varepsilon''$ losses of $SrTiO_3$ (×, single crystal; •, polycrystal).

At 0.1 K < T < 1 K $\varepsilon''$ remains constant within the measuring accuracy. There is a distinct reduction in the magnitude of $\varepsilon''$ for the ceramic sample, however, the broad peak occurs also at $T_{max}$ = 10 K. The real part obeys a lineary temperature dependence for both the single crystal (at 0.4 < T < 1.4 K) and the polycrystal (at 0.2 K < T < 4 K), (fig. 4).

A new feature in $\varepsilon''(T)$ observed only for the polycrystal is the second maximum around 80 K. This maximum occurs for all the ceramic samples with $0 \leq x \leq 1$. The position of this peak does not change with Pb - concentration or sample preparation. This maximum shows



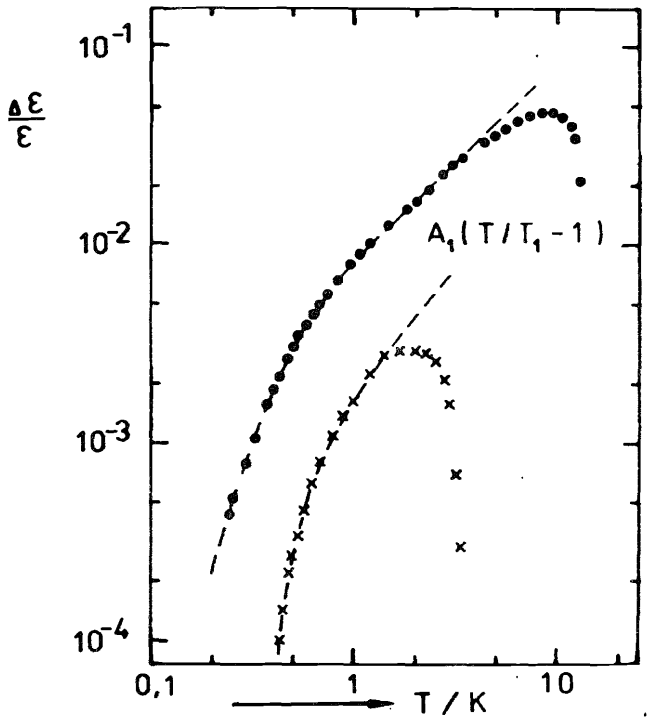



Fig. 4. Variation of the dielectric constant with temperature (×, single crystal; •, polycrystal; measuring frequency $f$ = 1,6 kHz). $A_1$ and $T_1$ are empiric constants, fitting the results according to $\Delta\varepsilon/\varepsilon = A_1(\frac{T}{T_1} - 1)$ (broken line).

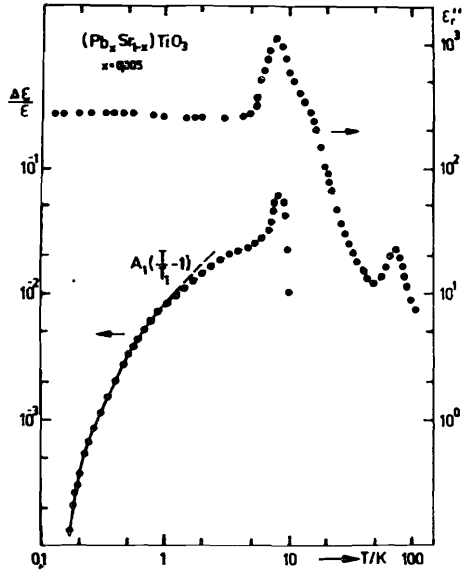



Fig. 5. Temperature dependence of the dielectric constant of PST (0.5 % Pb).

the presence of certain excitations independent of topological disorder or impurity concentrations.

It was suggested that this relaxation peak is caused by additional polarization units due to oxygen vacancies produced by burning the sample at 1800 K /5/.

For PST (x = 0.5 %) the phase diagram indicates a ferroelectric state at the lowest temperatures. However, ferroelectric and quantum paraelectric states are only weakly separated and nearly degenerated in energy. Therefore, a phase mixture caused by concentration fluctuation is expected. The dielectric results are in accordance with these considerations (fig. 5).

All the peculiarities of the $SrTiO_3$ sample are preserved. Nevertheless, a sharp peak is obtained around 8 K suggesting a partially ferroelectric phase transition although the quantum paraelectric behaviour

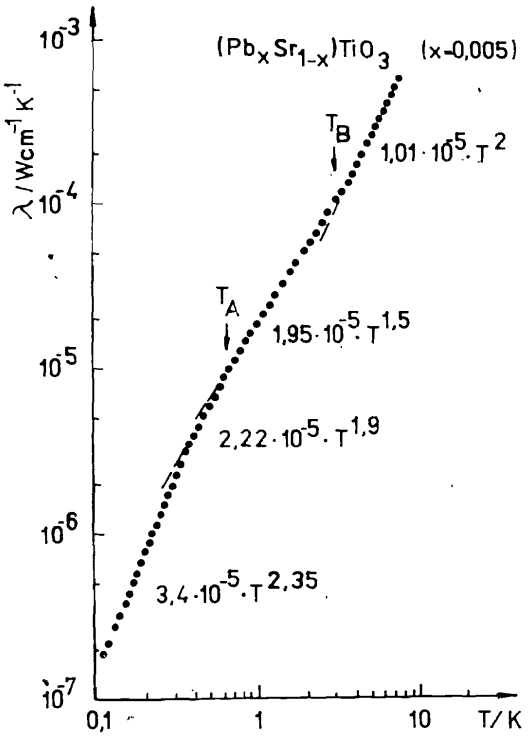



Fig. 6. Thermal conductivity of PST (0.5 % Pb).



remains deciding. Around 3K $\varepsilon''$ shows a slight minimum $\left(\frac{\Delta\varepsilon''}{\varepsilon''}(0{,}1K) \approx 10\ \%\right)$ and $\Delta\varepsilon/\varepsilon \sim T$ between 0.2 and 1 K.

The thermal conductivity of this sample (fig.6 ) is similar to glasses with a reduced temperature dependence at $T_A < T < T_B$ and a quadratic term at 0.4 K < T < $T_A$ = 0.7 K.

At low Pb-concentration the lattice dynamics of the PST - system is characterized by large instabilities. Their influence on thermal and dielectric results finishes with increasing x. At x = 5.5 % the structural and ferroelectric phase transition are close to one another and at x>6 % the only transition leads to a stable ferroelectric phase at $T < T_c$.

The thermal conductivity for PST (x = 5.5 %; $T_c$ = 90 K) and PST ( x = 12 %; $T_c$ = 130 K) at 0.1 K < T < 8 K is shown in fig.7.

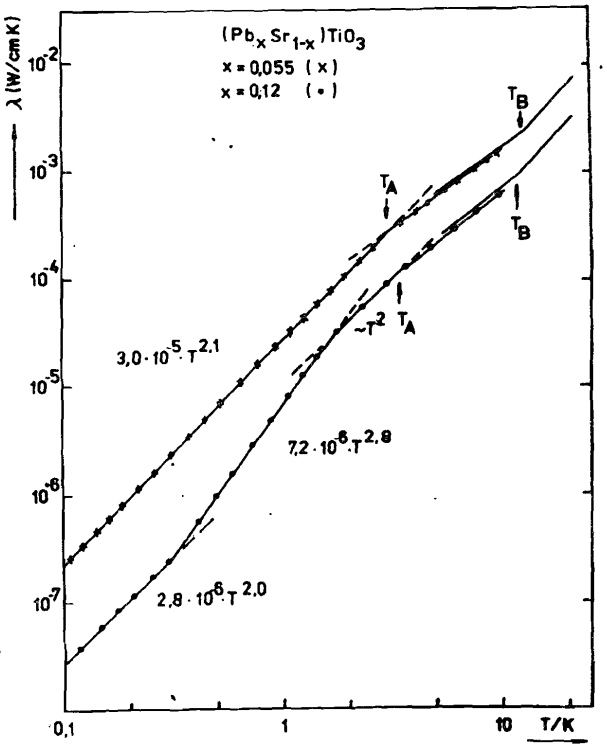



Fig. 7. Thermal conductivity of PST (5,5 % Pb;(-•-)), and PST (12 % Pb;(-•-)), solid line (at T > 5K) - data from Ref./8/.

The results are completed up to 20 K by ref. /8/. Again there is the characteristic feature in $\lambda(T)$ with the reduced plateau-like dependence ( $\lambda \sim T^{1.5}$ ) at an intermediate range shifted to somewhat higher temperatures (3 K < T < 12 K). For the x = 12 % sample the magnitudes of $\lambda$ are reduced about three times. This is supposed to be due to an additional scattering process seen in the distinct deviation from $T^2$ - dependence at 0.3 K < T < 1.7 K.

The dielectric results of these specimens are very interesting (fig. 8 and 9).

Quantum paraelectric behaviour rules out and considerable contributions due to the ferroelectric phase transition and the relaxation maximum (around 80 K) become apparent only above 30 K.

Nevertheless, the same additional loss peak as in $SrTiO_3$ is seen for x = 5.5 % although $T_{max}$= 1.7 K is shifted to higher temperatures analogous to the temperature range of the plateau-like slope in $\lambda(T)$.

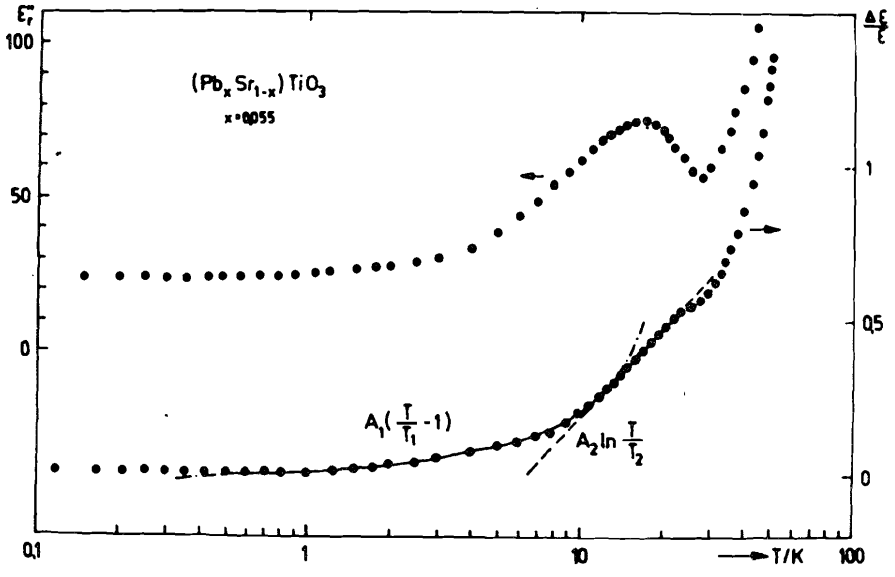



Fig. 8. Dielectric constant of PST (5.5 % Pb).



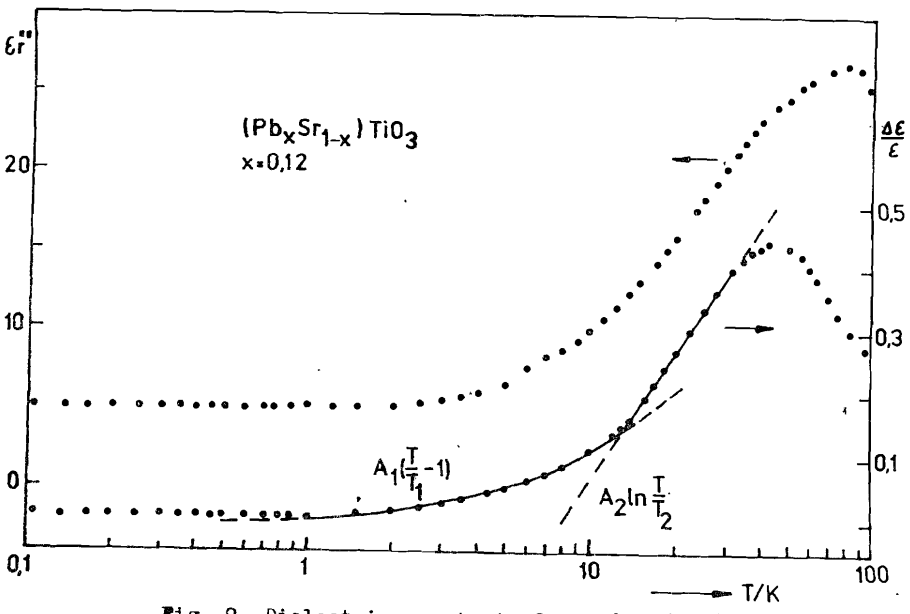



Fig. 9. Dielectric constant of PST (12 % Pb).

The correspondent maximum in ultrasound attenuation for this sample has been found recently /8/. Thus it is worthy to be conceived as the characteristic glassy anomaly. For PST x = 12 % this relaxation peak is superimposed at the high temperature side by the maximum in $\varepsilon''$ localized around 80 K. So one wide maximum is obtained. $\Delta\varepsilon/\varepsilon\,(T)$ obeys a lineary and logarithmic dependence (0.6 K < T < 13 K and 13 K < T < 23 K respectively) for x = 5.5 % and (0.9 < T < 13 K and 13 K < T < 30 K) for x = 12 %. It appears that $T_{max}$ of the discussed here additional relaxation peak, thought to be due to glassy behaviour, shifts by increasing Pb - concentration (or increasing $T_c$) to higher temperatures. Therefore it cannot be revealed for $PbTiO_3$ ($T_c$=763K), (fig.10).

There remains only the slight maximum around 80 K. However the behaviour of $\frac{\Delta\varepsilon}{\varepsilon}(T)$ suggests that in general the relaxation kinetics is similar to that of other samples. Above the well-defined minimum at

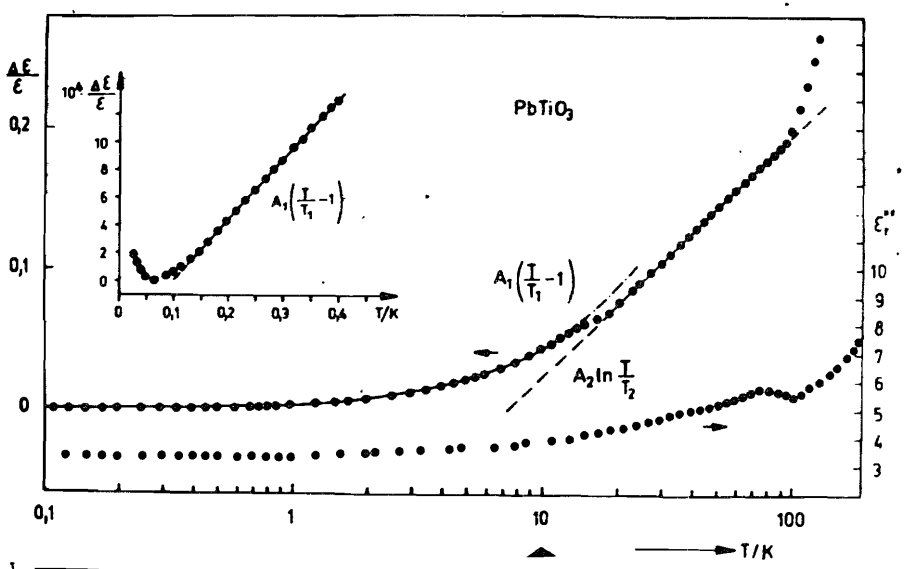



Fig. 10. Dielectric constant of $PbTiO_3$.

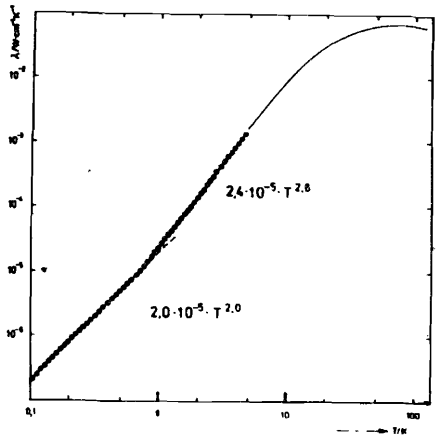



Fig. 11. Thermal conductivity of $PbTiO_3$, (for T > 5 K the results are from Ref. 7).

60 mK the lineary variation is suprisingly exact from 0.15 K to 15 K (two decades in temperature!) and the logarithmic dependence from 17 K to 100 K.

At T > 10 K the dielectric loss of $PbTiO_3$ is essentially lower than for the other PST - samples. It is noteworthy that this corresponds to analogous effects for the phonon scattering. The thermal conductivity of $PbTiO_3$ (fig. 11) obeys $\lambda = 2.0 \cdot 10^{-5} \cdot T^2$(W/cm·K) at T < 0.8 K.



However, at T > 0.8 K there is no plateau - like reduction in the temperature dependence of $\lambda(T)$ but a steep increase up to the broad maximum near 20 K. It is reasonable to consider $\lambda \sim T^{2,6}$ as a result of the beginning influence of the scattering process responsible for the characteristic $T^2$ - dependence by lowering the temperature. This is confirmed by the linearity of $\Delta\varepsilon/\varepsilon(T)$, as shown in /1/. The dielectric properties and thermal conductivity of $PbTiO_3$ at low temperatures are not unlike those found in order-disorder ferroelectrics /1/. Due to the weakness of the scattering process usually causing a plateau - like reduction in $\lambda(T)$ for amorphous solids, for $PbTiO_3$ only a reduction in the magnitude of $\lambda$ at the maximum is obtained. Another typical anomaly of glasses, the $C/T^3$-maximum in specific heat has been recently found for $PbTiO_3$ - polycrystal at 15 K/9/.

## Conclusions

The results of the thermal conductivity and dielectric measurements on a $SrTiO_3$ single crystal and polycrystalline samples of the system $Pb_xSr_{1-x}TiO_3$ show the glassy behaviour of these crystalline materials.

The characteristic anomalies ($\lambda \sim T^2$, plateau or reduction in temperature dependence of $\lambda$, $\frac{\Delta\varepsilon}{\varepsilon} \sim T$ and $\frac{\Delta\varepsilon}{\varepsilon} \sim \ln T$, minimum in $\frac{\Delta\varepsilon}{\varepsilon}(T)$ and a broad maximum in dielectric losses) are found for all samples though in particular case the singular effect can be masked by other excitations.

A correlation between the Curie-temperature $T_c$ of the ferroelectric phase transition and the anomalies in thermal conductivity and dielectric constant is observed. Thus the temperature $T_{max}$ of the dielectric loss peak, characteristic of glasses, increases with $T_c$. The results suggest a connection between magnitudes and temperature dependence of the process causing this dielectric loss peak and the strength of phonon scattering at low temperatures (plateau region). This supports the assumption that glassy behaviour is due to excita-

tions in the dipole system determined by lattice properties and by the disorder of the frozen domain structure.

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Фишер Э.



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Теплопроводность и диэлектрические свойства поликристаллов $(Pb_x Sr_{1-x})TiO_3$ при низких температурах


Представляются результаты измерения теплопроводности и диэлектрической восприимчивости поликристаллических образцов системы $(Pb_x Sr_{1-x})TiO_3$ для $0 \leq x \leq 1$ при низких температурах. Для каждого образца найдено аналогичное аномальное поведение как у аморфных веществ. Конкретные параметры обнаруженных аномалий коррелируют с сегнетоэлектрической температурой Кюри $T_c$.



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Препринт Объединенного института ядерных исследований. Дубна 1986



Fischer E.



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Thermal Conductivity and Dielectric Properties of Polycrystalline $(Pb_x Sr_{1-x})TiO_3$ at Low Temperatures


Measurements of the thermal conductivity and the dielectric constant at low temperatures have been made on polycrystalline samples of the system $(Pb_x Sr_{1-x})TiO_3$ with $0 \leq x \leq 1$. In each case the results show similar anomalies as known for amorphous materials. This glassy behaviour of the ferroelectric crystals is found to be correlated with the Curie - temperature $T_c$.



The investigation has been performed at the Laboratory of High Energies, JINR.

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