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ELECTRIC PROPERTIES OF $PbZrO_3$ MONOCRYSTALS

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The temperature dependence of electric permittivity, spontaneous polarization and electric conductivity of $PbZrO_3$ monocrystals have been investigated. The monocrystals in question had been obtained by crystallization of a melted PbO–ZrO_2–PbF_2–B_2O_3 solution. All the characteristics indicate the existence of two phase transitions in $PbZrO_3$ monocrystals from the para- and ferro- to the antiferroelectric state. The results obtained are similar to those observed earlier for polycrystalline samples of that compound.

1. *Introduction*

In most of the papers published so far on the electric properties of $PbZrO_3$, results of tests carried out on polycrystalline samples have been presented because of difficulties in obtaining adequately pure and sufficiently large monocrystals [1, 2]. Tests carried out on polycrystalline samples of $PbZrO_3$ covered a wide range of their properties including the identification of phase transitions [3–8, 11, 12], temperature dependence of electric permittivity [9–10], spontaneous polarization [11–13], polarization of space charge [13–15] and electric conductivity [12, 16–18].

$PbZrO_3$ is an interesting material because of the two phase transitions which occur in it; one between the antiferroelectric and ferroelectric state $A \rightleftarrows F$ and the other between the ferroelectric and paraelectric state $F \rightleftarrows P$.

Many authors have shown the existence of two phase transitions in $PbZrO_3$ [4, 6, 7, 11, 12, 19], there are, however, some who have not noticed the ferroelectric phase in this compound [10, 20]. Perhaps these doubts will disappear after a series of experiments on monocrystalline samples have been carried out. Data obtained from tests carried out on nonmonocrystalline samples should be considered with full understanding of their specific properties which depend on their ceramic heat treatment. Different technological processes can result in a different crystalline to glassy phase quantity ratio, and in the change of electrical properties. It should be interesting to compare the results obtained from experiments carried out on polycrystals and monocrystals of this compound.

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In the present work results of the investigation of temperature influence on electric permittivity, spontaneous polarization and electric conductivity of monocrystalline $PbZrO_3$ are presented. This will make the comparison of investigated parameters possible.

2. *Preparation of $PbZrO_3$ monocrystals*

The crystallization method was used in order to obtain $PbZrO_3$ monocrystals from melted salt solutions [19]. As a solvent PbF_2 and B_2O_3 were used in adequate mole ratio. The optimum system of components in crystal pulling is as follows: 44–48% PbO — 14–20% ZrO_2 — 36–26% PbF_2 and 6% B_2O_3. Different ratios were used but the following were the final ones: 45% PbO, 17% ZrO_2, 32% PbF_2 and 6% B_2O_3 with an impurity percentage less than 10^{-2}%. The components were melted in a platinum melting pot of 100 cm^3 capacity in canthal furnace at a temperature 1200—1250°C maintained for about 18 hours. The mixture then was cooled at a constant rate of about 3°K/h to 900°C and then quickly cooled to the room temperature.

There is a difficulty in obtaining $PbZrO_3$ monocrystals from a PbO-ZrO_2-PbF_2-B_2O_3 mixture since intensive vapourization of the solvent takes place at high temperature. The temperature of crystal growth is very close to the boiling temperature of PbF_2 (1293°C). Therefore in order to protect the furnace chamber and the heating elements against contamination the pot was placed inside a corundum container. The crystals obtained were semitransparent with red-brown colour and were shaped as cubicoids with dimensions $1 \times 1 \times 0.5$ — 2 mm. A complex domain structure was observed in polarized light, the structure changing rapidly in the temperature range of 210—230°C.

3. *Experimental results and discussion*

Temperature values of phase transitions in $PbZrO_3$ crystals were determined by differential thermal analysis (DTA-system: F. Paulik, J. Paulik, L. Erdey). Endothermic phase transition was observed on heating at 222°C ± 1°C and 230°C ± 1°C and on cooling at 228°C ± 1°C and 212°C ± 1°C, all of them being of the first order. The temperatures given are the characteristic points of phase transitions. It is more difficult to determine them from the temperature dependence of electric permittivity, especially when $A \rightleftarrows F$ transition is concerned.

All the electric measurements presented here were carried out on samples coated with silver electrodes. Fig. 1 presents the temperature dependence of the electric permittivity at a field frequency of 1 MHz. Characteristic anomalies corresponding to phase transitions can be observed below the Curie point for both the heating (curve *1*) and the cooling (curve *2*). They are not so distinct at temperatures T_{A-F} and T_{F-A} as they are for polycrystalline samples [12]. The Curie–Weiss law $\varepsilon = C/T - T_0$ holds in the paraelectric region, where the Curie constant $C = 1.7 \times 10^5$ °C and the extrapolated Curie–Weiss temperature is $T_0 = 182$°C. These values differ from those obtained by some authors [3, 10] for polycrystalline samples ($C = 1.5 \times 10^5$ °C, $T_0 = 190$°C). Temperatures marked in Fig. 1 correspond to transitions from the antiferroelectric to the ferroelectric phase

T_{A-F} and T_{F-A} and from the ferroelectric to the paraelectric phase T_{F-P} and T_{P-F} on heating and cooling, respectively. It should also be noticed that ε takes the same values for both polycrystalline and monocrystalline samples in the investigated region [12, 19]. In the region between the phase transitions an electric hysteresis loop has been observed. A modified Sawyer–Tower [21, 22] system was used which made possible a direct reading of the spontaneous polarization value of the tested sample. Fig. 2 shows an electric hysteresis loops observed at different temperatures during the cooling process (along ⟨100⟩ direction). An electric field of $f = 50$ Hz and amplitude of 4 kV/cm was applied during the tests. The dependence $P_s(T)$ is shown in Fig. 3 with curve *1* plotted for the rising temperature and curve *2* for the falling temperature. The characteristic of these dependences is similar to the corresponding dependences observed for polycrystalline samples. The differences in values of P_s on heating and cooling are higher in this case than for ceramics [12]. It also seems that the polarization of the space charge and screening of the spontaneous polarization by free charge carriers and ionic lattice defects play a much more important part in polycrystalline samples [12–15]. It leads to the changes of spontaneous polarization described in [12, 13] which have not been noticed in monocrystals. It does not mean, however, that these processes are of no importance here. Two phase transitions are indicated also by the temperature dependence of electric permittivity. Fig. 4 shows $\ln \sigma = f(1/T)$ dependence for Ag-PbZrO$_3$-Ag system obtained in the heating process. A voltage of 2V was applied to the sample while the temperature was being changed at the rate of 2°K/min. The activation energy was $\varphi_1 = 0.9$ eV and $\varphi_2 = 1$ eV for the antiferroelectric and paraelectric phase, respectively, and in the ferroelectric region $\varphi_3 = 2.8$ eV. Both the nature

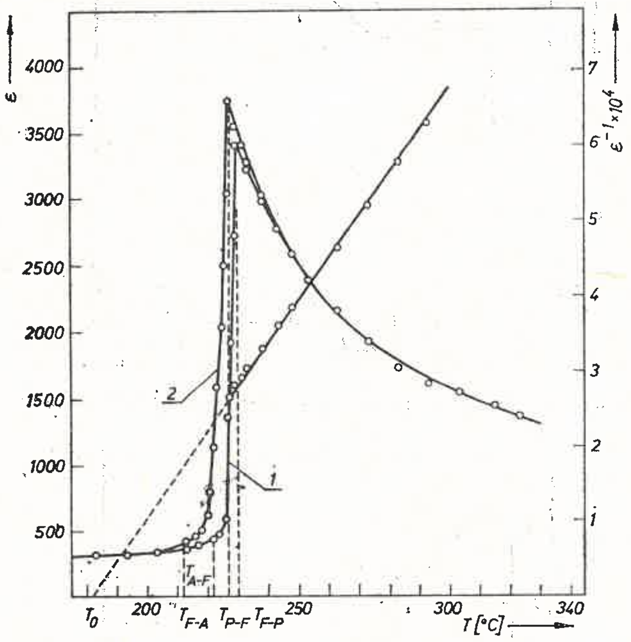

Fig. 1. Temperature dependence of electric permittivity during heating (*1*) and cooling (*2*)

of this dependence and the values of activation energy are identical to those observed for polycrystalline samples, which is somehow surprising since the electric conductivity responds specially to differences in the internal structure of the substance. The jump in σ value just before and after the Curie point is somewhat more distinct. Whereas a clear difference can be seen between the electric conductivity for poly- and monocrystalline samples. The temperature dependences shown on Figs 1, 3, 4 have been determined within a temperature measurement accuracy of 0.1°C and with errors in ε, P_s, σ of 1%, 3% and 5% respectively.

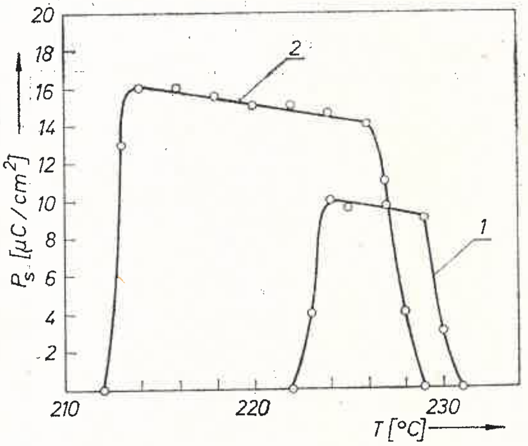

Fig. 3. Temperature dependence of spontaneous polarization during heating (*1*) and cooling (*2*)

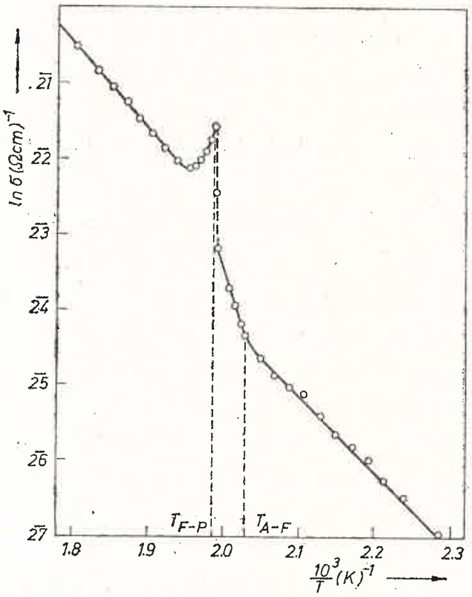

Fig. 4. $\ln \sigma = f\,(1/T)$ for Ag-PbZrO$_3$-Ag system

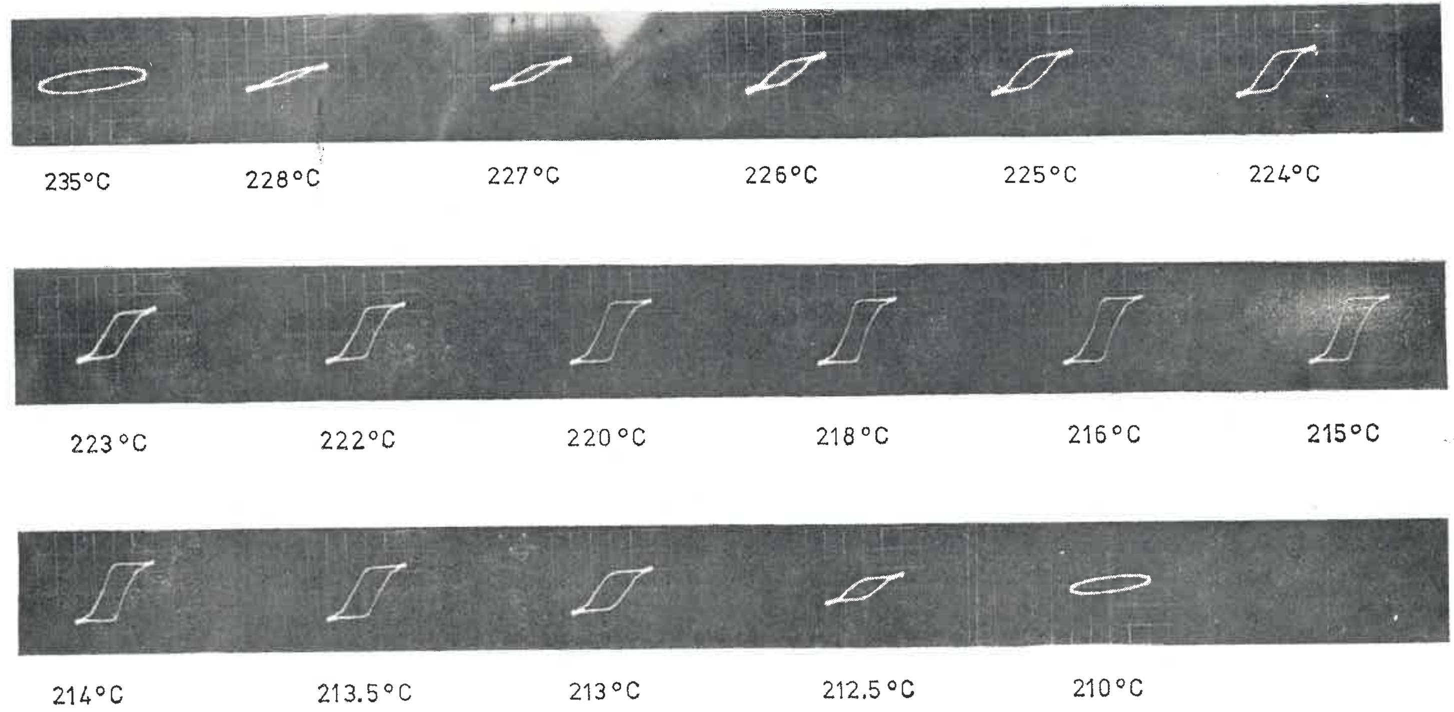

Fig. 2. Loops obtained by means of an oscillograph in an electric field of 4 kV/cm, 50 Hz. The smallest scale for the y-axis is 2 $\mu C/cm^2$ and for the x-axis is 400 V/cm

4. Summary

All the temperature characteristics investigated in this and earlier works of the authors [11–18] indicate two phase transitions in $PbZrO_3$. The first one between the antiferroelectric and ferroelectric phase with a significant temperature hysteresis and the second one between ferro-and paraelectric phase with a much less significant temperature hysteresis loop. Obtaining the same result for monocrystals makes the basis of theoretical analysis of these transitions more reliable.

Material which shows two basic phase transitions (A ⇄ F and F ⇄ P) at temperatures relatively high and close to each other is very convenient for investigating the influence of ferroelectric properties on transport phenomena and especially on electric conductivity and the thermoelectric effect.

An intensive increase in carrier activation energy in the temperature range where the spontaneous polarization occurs is especially interesting.

More complete experimental data will make the theoretical analysis of the mutual influence of free carriers on ferroelectric and antiferroelectric properties possible.

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