DIELECTRIC PROPERTIES OF $Pb(Zr_{1-x}Ti_x)O_3$ SOLID SOLUTIONS WITH $PbTiO_3$ CONTENT UP TO 5%

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Temperature changes of electric permittivity and spontaneous polarization have bean investigated with differential analysis being applied for the solid solution of $Pb(Zr_{1-x}Ti_x)O_3$ containing up to 5% of $PbTiO_3$. The results obtained brought the authors to the conclusion that the observed ferroelectric phase occurs rather spontaneously and without any external electric field being applied.

1. *Introduction*

Solid solutions of $Pb(Zr_{1-x}Ti_x)O_3$ for $x > 0.05$ show only ferroelectric properties below the Curie point [1-3]. Solutions containing $PbTiO_3$ up to 5% show two phase transitions [3]. According to Sawaguchi [3] one of those transitions appears as a transformation from the paraelectric to antiferroelectric state A_β, the other one being another transformation from the latter state to the second antiferroelectric phase A_α. This fact resulted from *X*-ray, dilametric and dielectric examinations. Sawaguchi maintains that phase A_β is transformed into a metastable ferroelectric state when a sufficiently strong external electric field (approx. 20 kV/cm) is applied. Simultaneously a pseudotetragonal symmetry changes into a rhombohedral one.

The existance of ferroelectric phase even in pure $PbZrO_3$ has been proved by some investigations [4-6] as well as by our own results [7, 8]. Thus one might also expect the existance of the ferroelectric phase in $Pb(Zr_{1-x}Ti_x)O_3$ for $x \leqslant 0.05$ solid solutions which exhibit such close similarity to the pure lead zirconate. The authors of [9, 10] have proved it but they used samples containing different oxides (e. g. WO_3, Nb_2O_5, ThO_2, NiO). It has not been proved yet whether the ferroelectric phase exists in these solutions without the admixtures mentioned above.

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The authors of this paper have carried out experiments in order to investigate the nature of the phase transitions in PZT solutions containing $PbTiO_3$ up to 5% without any admixtures introduced on purpose. The temperature changes of the electric permittivity and spontaneous polarization were investigated and differential thermal analysis was used.

2. *Experimental results*

The samples used in tests were prepared from pure components: PbO, ZrO_2, TiO_2 and they were suitably thermally and mechanically treated. After they were ground to the same thickness their surfaces were polished and gold electrodes were applied. The electric permittivity was investigated at a measuring field frequency of 1 MHz for samples 1 mm thick.

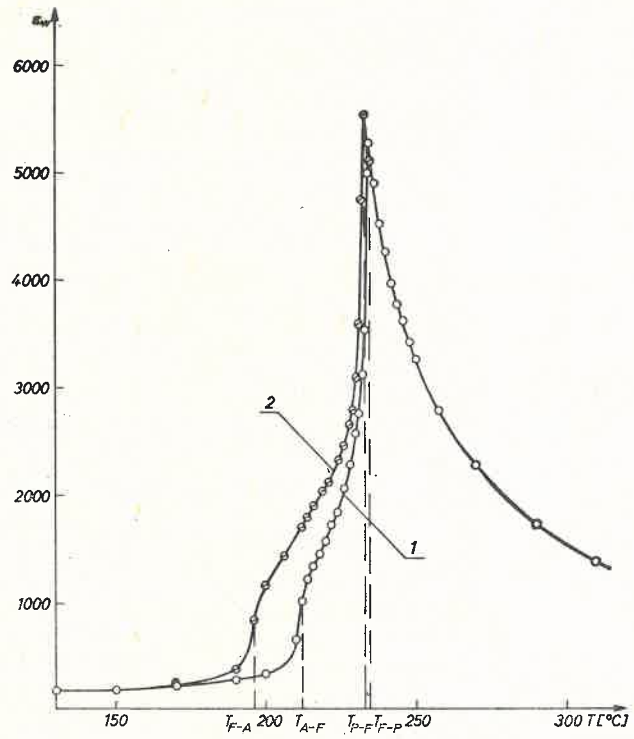

Fig. 1. Temperature changes of relative electric permittivity of $Pb(Zr_{0.99}Ti_{0.01})O_3$ in heating (curve *1*) and cooling (curve *2*)

Fig. 1 presents the temperature dependence of the electric permittivity of the solution containing 1% molar $PbTiO_3$. Besides the maximum taking place at the points T_{F-P} and T_{P-F} there is also a region of anomaly in the temperature range between T_{F-A} and T_{A-F}. Samples of other compositions exhibited similar dependences of $\varepsilon(T)$. These dependences are shown in Fig. 2 in the heating process. A clear region of anomaly at the temperatures of T_{F-A} and T_{A-F} takes place only for samples with a smaller ammount of $PbTiO_3$ (up to 2%). For

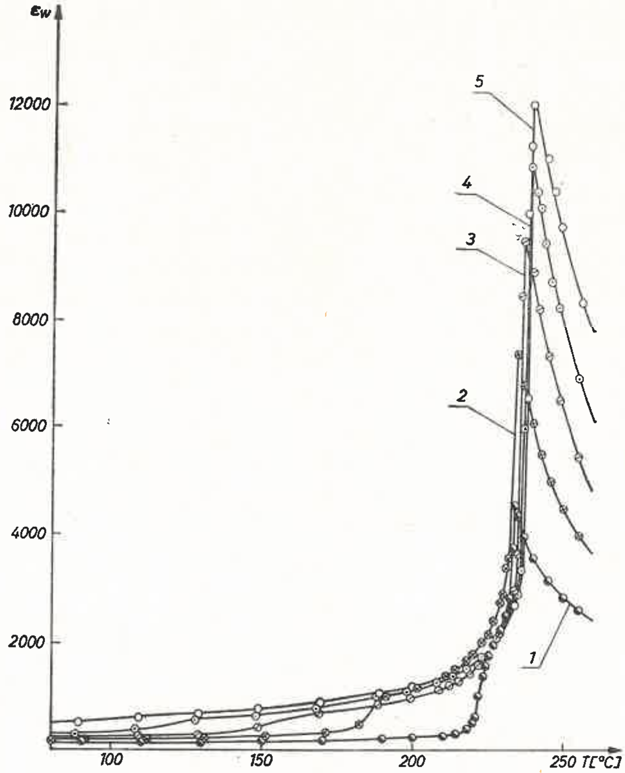

Fig. 2. Temperature changes of relative electric permittivity in heating of solid solution of $Pb(Zr_{1-x}Ti_x)O_3$ with $PbTiO_3$ content of *1* — 0.5%; *2* — 2%; *3* — 3%; *4* — 4% *5* — 5%; respectively

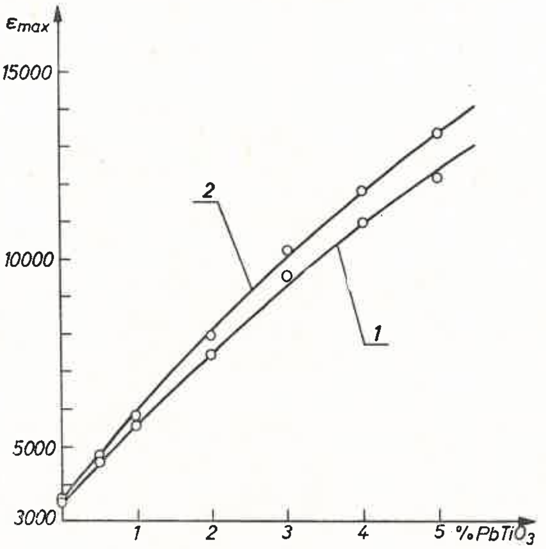

Fig. 3. Dependence of maximum relative electric permittivity at T_{F-P} (curve *1*) and T_{P-F} (curve *2*) points on $PbTiO_3$ percentage

a larger ammount of $PbTiO_3$ the anomalies are also visible but they are "broadened up" in a wider range of temperature.

The maximum values of the electric permittivity at the T_{F-P} and T_{P-F} points (Fig. 3) and the temperature values T_{A-F} and T_{F-A} (Fig. 4 curves *1, 2*) clearly depend on the $PbTiO_3$ content. Because of $\varepsilon(T)$ being "broadened up" as it was mentioned above the temperature values of T_{F-A} were determined only for samples containing up to 2% molar $PbTiO_3$.

In order to determine particular phase transitions more precisely and to investigate their nature a differential thermal analysis was introduced. An example of the DTA curve for the $Pb(Zr_{0.99}Ti_{0.01})O_3$ sample is presented in Fig. 5. Sharp maximum points can be seen on DTA curves at T_{F-P} and T_{P-F} temperatures both during the heating and cooling process. This proves the existance of endothermal phase transition. Also at T_{A-F} and T_{F-A}

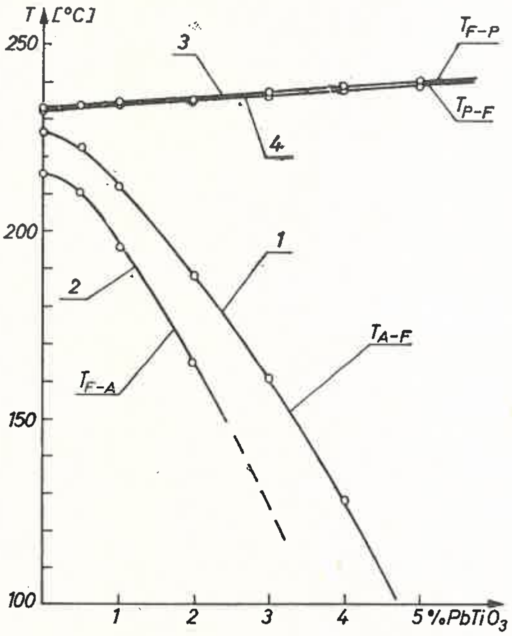

Fig. 4. The phase transition dependence on $PbTiO_3$ percentage in the solution

there are local maximum points on DTA curves which indicate that the endothermal phase transitions take place at these temperatures. It can be seen that the latter shows a much larger temperature histeresis loop, (Fig. 5 curves 1, 2).

Similar changes on the DTA curve are seen for the samples with different content being tested. The DTA investigations allowed to determine precisely the phase transition temperatures for all tested samples. The temperature dependence of particular phase transitions for different $PbTiO_3$ content determined that way reveal good conformability with data presented in Fig. 4.

Together with the increase of the $PbTiO_3$ content the values of T_{A-F} and T_{F-A} decrease. Thus the range of temperature values at which the post paraelectric state phase ap-

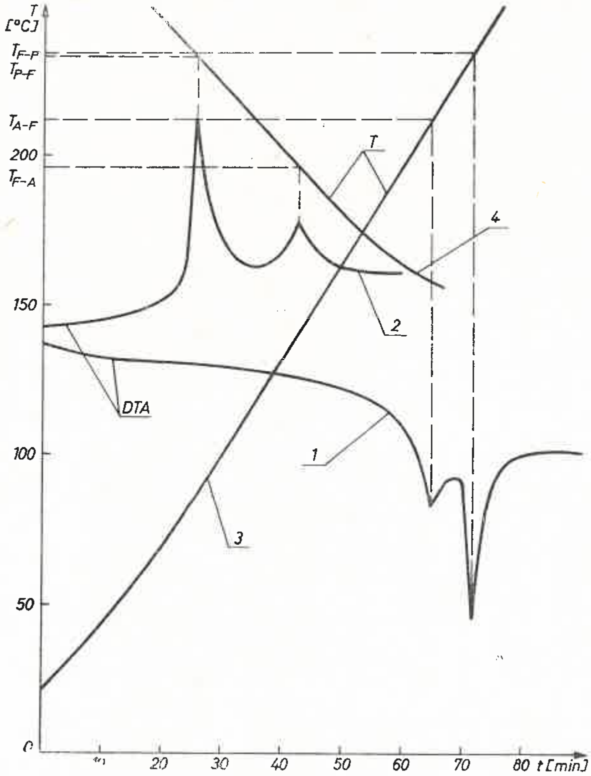

Fig. 5. DTA curve for $Pb(Zr_{0.99}Ti_{0.01})O_3$

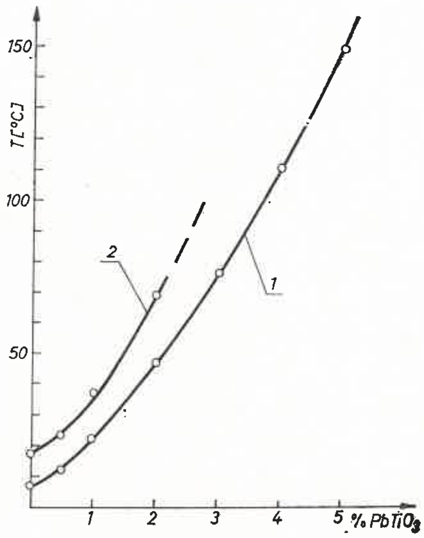

Fig. 6. Dependence of $T_{F-P} - T_{A-F}$ and $T_{P-F} - T_{F-A}$ temperture range on $PbTiO_3$ percentage in solid solution

pears is being enlarged. The temperature range at which this phase appears in the dependence of the $PbTiO_3$ content is presented in Fig. 6 in the heating (curve *1*) and cooling (curve *2*) process.

In order to confirm that the transition phase mentioned above possesses ferroelectric properties it is necessary to prove that the electric histeresis takes place here. The known

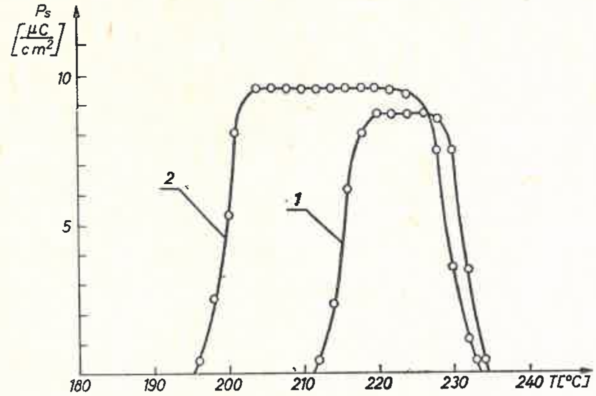

Fig. 7. Temperature dependence of spontaneous polarization of $Pb(Zr_{0.99}Ti_{0.01})O_3$ in heating (curve *1*) and cooling (curve *2*)

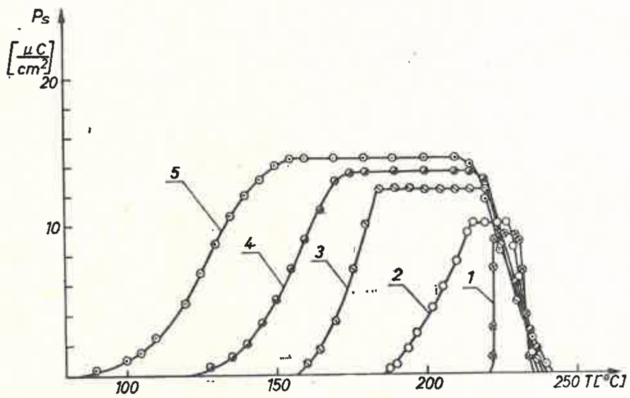

Fig. 8. Temperature dependence of spontaneous polarization in heating of $Pb(Zr_{1-x}Ti_x)O_3$ solid solutions for $PbTiO_3$ percentage equal to: *1* — 0.5%; *2* — 2%; *3* — 3%; *4* — 4%; *5* — 5%; respectively

method of Sawyer-Tower with the modification described in [11, 12] was used and proved in fact the existance of electric histeresis in that phase. The spontaneous polarization dependence on temperature was determined on the basis of the temperature changes of the histeresis loops. Fig. 7 presents the dependence of $P_s(T)$ in heating and cooling (curves *1* and *2* respectively) for the $Pb(Zr_{0.99}Ti_{0.01})O_3$ sample. Similar results were obtained for the other tested samples. Fig. 8 presents these dependences for the heating process. It can be seen from Fig. 7, 8 that as the molar content of $PbTiO_3$ increases in ceramic PZT, the range where ferroelectric phase appears at lower temperatures increases as well as does the value of spontaneous polarization (Fig. 9).

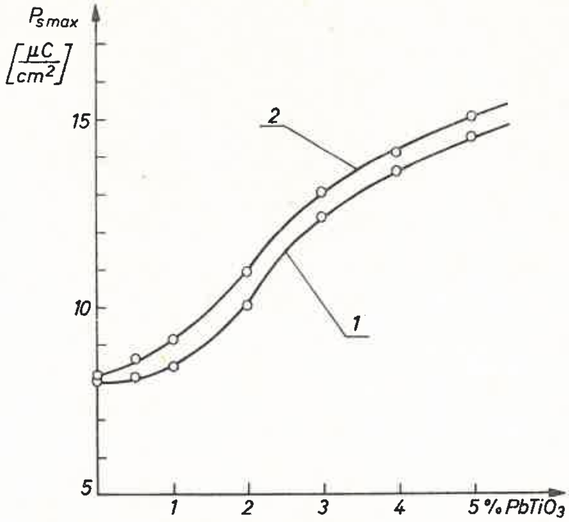

Fig. 9. Maximum value of spontaneous polarization in heating (curve *1*) and cooling (curve *2*) process versus $PbTiO_3$ percentage in solid solution

3. Discussion of results

Two phase transitions can be observed on the plots of the investigated temperature dependences $\varepsilon(T)$, $P_s(T)$, $DTA(T)$ in the solution of Pb $(Zr_{1-x}Ti_x)O_3$ containing $PbTiO_3$ $0 < x \leqslant 0.05$. The histeresis loop in the range of $T_{A-F} < T < T_{F-P}$ indicates the undoubtful presence of the ferroelectric phase.

On the basis of the investigations being carried out one can not explicitly state whether the observed ferroelectric phase is a metastable one caused by the previously external electric field applied, as Sawaguchi believes [3], or whether this phase appears without that factor.

Indirect arguments in favour of the latter hypothesis results from the analysis of investigated dependences. In the case of $\varepsilon(T)$ and $P_s(T)$ investigations a measuring field was applied to the sample. Thus it could influence the data obtained. The measurements of the electric permittivity were carried out for the measuring field of small intensity, whereas a relatively strong field ($E \cong 5$ kV/cm) was required in order to obtain fully saturated histeresis loops. If the A → F transition were "forced" by the electric field then one might expect a distinct phase transition temperature dependence on the field intensity. Especially, it should have appeared on $\varepsilon(T)$ and $P_s(T)$ curves. In fact the temperature values of phase transitions are very close to each other as can be seen in Fig. 2 and Fig. 8. Similarly the "broadening up" of $\varepsilon(T)$ and $P_s(T)$ dependences can be noticed in samples with $PbTiO_3$ $0.02 < x \leqslant 0.05$. Still a more convincing argument out of the differential temperature analysis data. Here samples were used which had not been treated with an external electric field. Also the measurements themselves do not require the use of that field. From DTA curves, however, the same temperature values of phase transitions were obtained as from the other remaining temperature dependences. Thus one can conclude that the observed ferroelectric phase appears rather spontaneously and without the presence of the external electric field.

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