THE COMPLEX PHASE COMPOSITION OF SOLID $PbZr_xTi_{1-x}O_3$ SOLUTIONS FOR $x > 0.95$

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Temperature variations of the dielectric susceptibility ε and dielectric loss tan δ as well as of the piezoelectric module d_{31} for solid $PbZr_xTi_{1-x}O_3$ solutions with up to 4% mol titanium content have been investigated. The existence of a ferroelectric phase in the above mentioned materials was determined for the entire range of values $x > 0.95$. From piezoelectric module investigations, the dependence of the observed phase transitions as a function of titanium content in these compounds was obtained. From this dependence, the existence of a complex phase composition in solid $PbZr_xTi_{1-x}O_3$ solutions was determined for $x > 0.95$.

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1. Introduction

$PbZr_xTi_{1-x}O_3$ solid solutions for $x > 0.95$ have been, for a number of years, the subject of investigations. These investigations chiefly concerned their phase compositions. In one of the initial papers dealing with these compounds [1] the possibility of the existence of four phases was determined, i.e. antiferroelectric A_α and A_β, ferroelectric F and paraelectric P. In the opinion of Sawaguchi [1] the F phase for $x < 0.97$ appears spontaneously whereas for $x \geqslant 0.97$, its occurrence is due to external factors e.g. an electric field. A similar phase composition was presented in paper [2] where the F phase occured for $x < 0.98$. The presence of the ferroelectric F phase in the entire region $x \geqslant 0.95$ has been verified by the authors of [3, 4], who also underlined the strong dependence of the temperature range of existence of this phase on the titanium percentage. One should add that the existence of a ferroelectric state was also noted in pure $PbZrO_3$ [5–7].

The existence of A_α, A_β, F and P phases has also been observed by other authors investigating $PbZr_xTi_{1-x}O_3$ solid solutions for $x > 0.95$ with the addition of oxides of Nb, Th, V and W [8]. The phase composition obtained by them was attributed to the introduced doping substances. The existence of a complex phase composition in $PbZr_xTi_{1-x}O_3$

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compounds with small titanium content and without purposely introduced admixtures has also been observed neutronographically by Morozov et al. [9]. It is worth mentioning, that a complex phase composition has also been observed in $PbZr_xCa_{1-x}O_3$ solid solutions with $x = 0.88 \div 0.92$ [10].

In the present paper, information has been obtained regarding the existence of phase transitions in $PbZr_xTi_{1-x}O_3$ compounds. Information was obtained through investigations of the temperature dependence of the dielectric permeability ε, dielectric loss $\tan \delta$ and piezoelectric module coefficient d_{31}.

Investigations were conducted for $PbZr_xTi_{1-x}O_3$ ceramics with $x = 0.96 \div 0.99$, and for a $PbZr_{0.984}Ti_{0.016}O_3$ monocrystal. The composition of the investigated materials was determined by X-ray microanalysis.

2. *Experimental technique and results*

Measurements of dielectric permeability ε and of dielectric loss $\tan \delta$ were performed by an automatic capacitance bridge with a measuring frequency of 1 kHz. Samples with gold electrodes were used. The measuring-field intensity was 0.055 kV/cm.

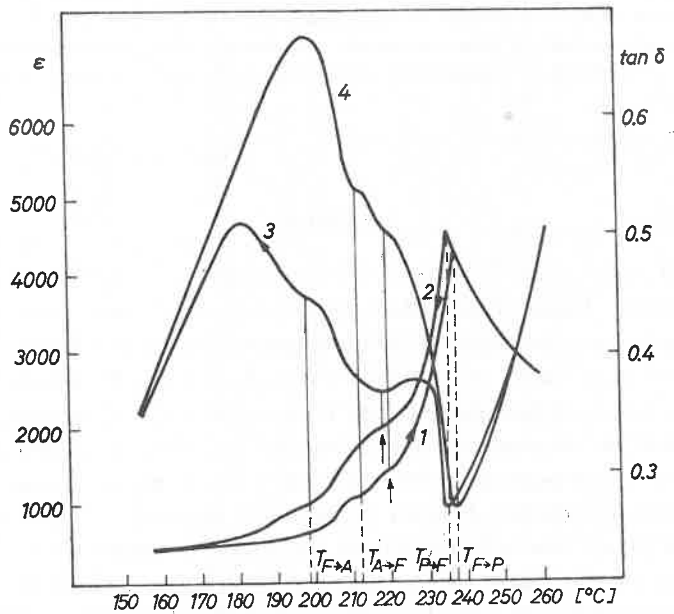

Fig. 1. Dielectric permeability ε *1, 2* and dielectric loss $\tan \delta$ *3, 4* as a function of temperature for a $PbZr_{0.99}Ti_{0.01}O_3$ solid solution

Fig. 1 shows the plot of $\varepsilon(T)$ and $\tan \delta$ (T) during heating and cooling for a $PbZr_{0.99}Ti_{0.01}O_3$ solid solution. Broken lines indicate the phase transition temperatures in accordance with the temperatures $T_{F\rightleftarrows A}$ and $T_{F\rightleftarrows P}$ obtained through the derivatograph investigations in paper [11]. Additional anomalies of $\varepsilon(T)$ and $\tan \delta$ (T), indicated by arrows, which could testify the existence of further phase transitions, are also visible. Similar results were obtained for the remaining materials investigated. As an example, Fig. 2 depicts the plot of $\varepsilon(T)$ during heating for $PbZr_{0.99}Ti_{0.01}O_3$ and $PbZr_{0.98}Ti_{0.02}O_3$ ceramics and for a $PbZr_{0.984}Ti_{0.016}O_3$ monocrystal. In the case of a $PbZr_{0.98}Ti_{0.02}O_3$ solid solution,

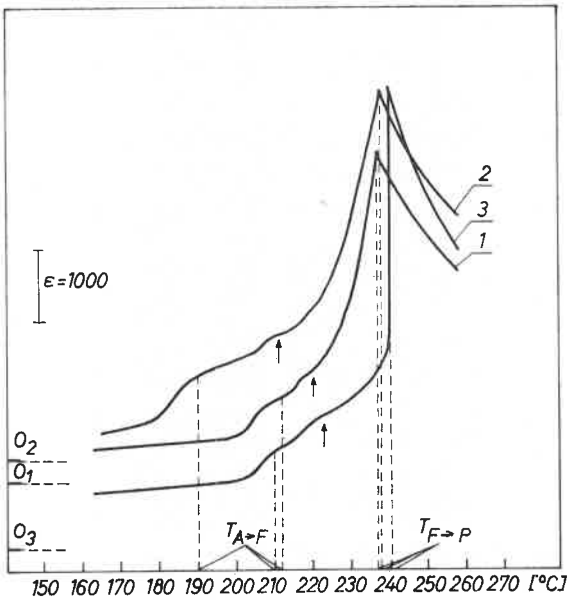

Fig. 2. Dielectric permeability ε during heating for $PbZr_{0.99}Ti_{0.01}O_3$ *1*, $PbZr_{0.98}Ti_{0.02}O_3$ *2* and for a $PbZr_{0.984}Ti_{0.016}O_3$ *3* monocrystal

the $\varepsilon(T)$ anomaly corresponding to the temperature $T_{F\to A}$ as a result of pre-polarizing shifts towards lower temperatures and moves into a clear local maximum and minimum on the $\varepsilon(T)$ curve (Fig. 3).

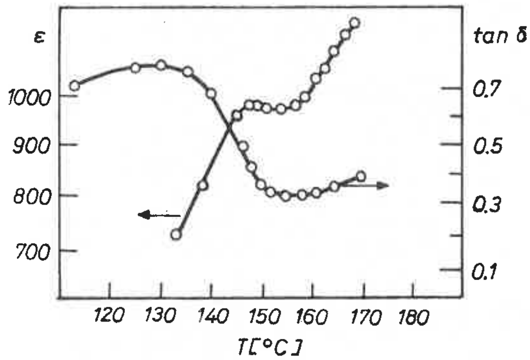

Fig. 3. $\varepsilon(T)$ and $\tan\delta(T)$ dependences in the neighbourhood of the transition to the antiferroelectric phase for a polarized $PbZr_{0.98}Ti_{0.02}O_3$ solid solution: $T_p = 255°C \to 180°C$, $E_p = 0.85$ kV/cm

The existence of a ferroelectric phase in a relatively narrow temperature range, in the investigated solutions, confirms the remnant polarization investigations on the well-known Diamant-Drenck-Pepinsky system. In addition to the disappearance of the hysteresis loop at temperatures corresponding to transitions to the A and P phases, additional singularities of the $P_r(T)$ plot, corresponding to the anomalies observed on the plots of $\varepsilon(T)$ and tan δ (T), have also been observed. In the case of a monocrystal, clear pyroelectric peaks have, in addition, been observed at the singularity points of $P_r(T)$.

Additional information regarding the phase transitions, occuring in the investigated solid solutions, have been obtained from measurements of temperature variations of the piezoelectric module d_{31}. In measuring d_{31}, the series impedance method described in paper [2] was employed. The intensity of the measuring field, applied to samples posessing the required geometry, was 0.055 kV/cm. Piezoelectric activity was obtained after the pre-polar-

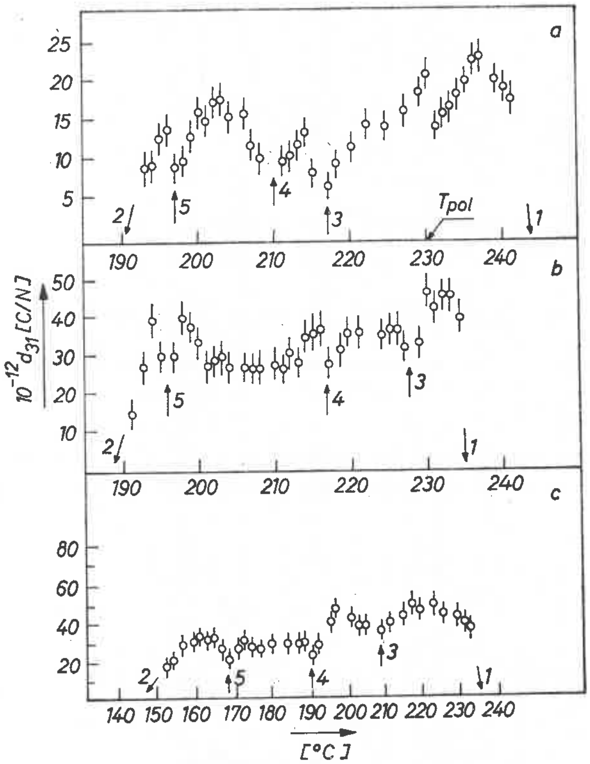

Fig. 4. Temperature variations of the piezoelectric module d_{31} for prepolarized materials: a. $PbZr_{0.984}Ti_{0.016}O_3$ monocrystal, b. $PbZr_{0.99}Ti_{0.01}O_3$, c. $PbZr_{0.98}Ti_{0.02}O_3$

ization process. With this aim, a constant electric field was applied to a sample, heated to a temperature in the paraelectric phase region, for 10 min. The sample was then cooled to a temperature below the Curie point with the electric field still on. In the individual polarization processes, the electric field intensity was changed.

Typical $d_{31}(T)$ plots for the investigated solutions are depicted in Fig. 4, in which the arrows indicate the temperatures at which piezoelectric vibrations and additional singularities of the $d_{31}(T)$ plot, possibly related to further phase transitions, disappear.

In the case of the solutions $PbZr_{0.99}Ti_{0.01}O_3$ and $PbZr_{0.98}Ti_{0.02}O_3$, the observed phase transitions and singularities as functions of the polarizing field intensity are shown in Fig. 5 and were obtained from the d_{31} (T) plots for the individual polarization processes.

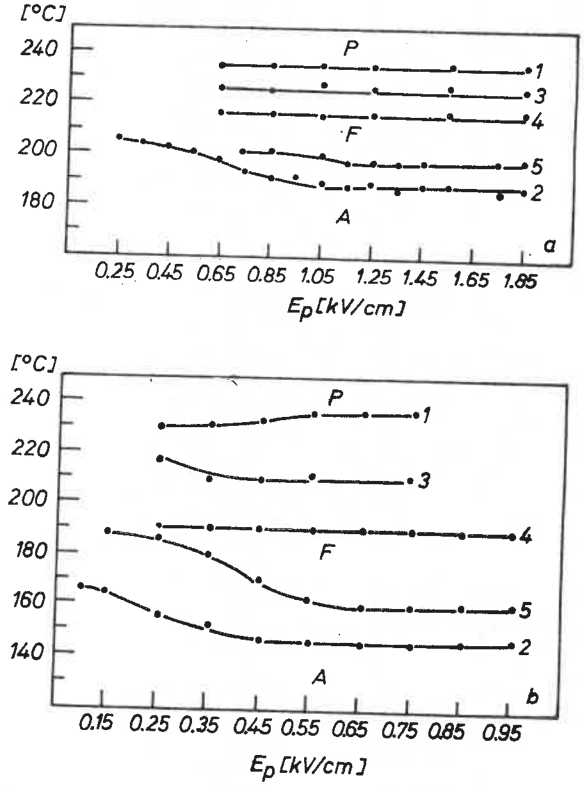

Fig. 5. Temperature dependence of phase transitions and observed singularities of d_{31} (T) on polarization field intensity for ceramics: a. $PbZr_{0.99}Ti_{0.01}O_3$, b. $PbZr_{0.98}Ti_{0.02}O_3$

A characteristic feature is the stabilizing of phase transition temperatures and temperatures at which anomalies occur under a continuously increasing polarization field. Similar dependences are observed in the case of the remaining solutions. During pyroelectric and piezoelectric investigations of a monocrystal, no similar dependence was observed.

The observed dependences of the phase transition points and other singularities of d_{31} (T) as functions of the polarization field where utilized in the preparation of the plot depicted in Fig. 6. This shows the dependence of the observed characteristic temperatures on the percentage of titanium in $PbZr_xTi_{1-x}O_3$ solutions. It is worth noting, that curves 4 and 5 on Fig. 6 correspond to the temperatures $T_{A\to F}$ and $T_{F\to A}$ observed in derivatographic investigations [11] and clearly visible on the ε (T) plots for non-polarized samples (Fig. 1).

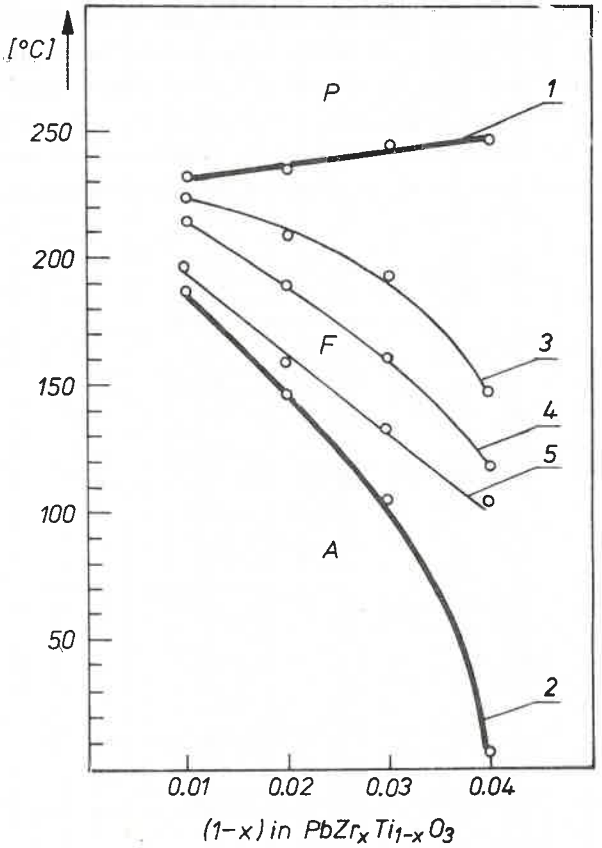

Fig. 6. Phase diagram for $PbZr_xTi_{1-x}O_3$ compounds for $x > 0.95$ obtained from piezoelectric module d_{31} temperature variation measurements

3. *Discussion*

The derivatographic and neutronographic investigations of $PbZr_xTi_{1-x}O_3$ solid solutions conducted in paper [9] also showed the existence of additional phase transitions in the ferroelectric state region. From the similarity between the diagrams obtained from neutronographic investigations, performed on the powders of the above mentioned materials [9], and from piezoelectric investigations (Fig. 6) one can conclude that the observed $d_{31}(T)$ singularities are related to the additional phase transitions occurring in the ferroelectric range and are not due to the pre-polarization necessary for the observation of piezoelectric effects in a ceramic. It must be emphasized that the observed complex phase composition appears both during heating and cooling.

It is possible, that the source of the observed complex phase composition is the occurrence of regions of clearly higher or lower Ti content in the investigated materials which, because of the strong dependence of $T_{F\rightleftarrows A}$ on the Ti content in these solutions [11], interact differently on the antiferroelectric $PbZrO_3$ matrix at different temperatures. This fact could be related to, for example, a fluctuation in the composition in the crystal or to the occurrence of crystallites with varying composition in the ceramic. The composition analysis of the investigated monocrystal, conducted on an X-ray microanalyzer did, in fact, show the existence of regions with titanium content differing from the average value by $\pm 0.5\%$.

However, the fact that the phase transition temperatures obtained for $PbZr_xTi_{1-x}O_3$ ceramics with $x > 0.95$ lie on "regular" curves (Fig. 6) and agree with the temperatures obtained from neutronographic studies [9]. Also, the singularities shown by ceramics are also observed in a monocrystalline sample (e.g. Fig. 4a). Perhaps one should incline oneself to the theory of Morozov et al. [9], according to which Ti ions form ferroelectric clusters in the $PbZrO_3$ matrix which are responsible both for the transition mechanism between the A and F states, and for the complex phase composition.

In addition to this, the fact that the defecting of Pb and O sublattices (oxygen and lead vacancies) can enhance the forming of ferroelectric phase incipient crystals in pure $PbZrO_3$, has been shown in paper [12]. In view of the easy sublimation of lead oxide during the production of $PbZr_xTi_{1-x}O_3$ solid solutions, one can expect similar defecting in these materials. Therefore, the existence of clusters can be related both to Ti ions as well as to the defecting of the investigated materials.

The authors of papers [13, 14] also refer to a cluster mechanism of the occurrence of a ferroelectric state in $PbZr_xTi_{1-x}O_3$ solid solutions with $x > 0.95$.

Therefore, on the basis of the investigations of the dielectric and piezoelectric properties one can arrive at the following conclusions:

1. In $PbZr_xTi_{1-x}O_3$ solid solutions, the ferroelectric state occurs in the entire region of $x > 0.95$.

2. The above materials exhibit a complex phase composition.

3. The results obtained indicate a cluster mechanism for the forming of the F phase in $PbZr_xZi_{1-x}O_3$ compounds with $x > 0.95$.

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