

THERMOELECTRIC EFFECT IN SEMICONDUCTIVE PbZrO_3

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The thermoelectric effect in the Pt— PbZrO_3 —Pt system was investigated in the 340 to 600°C range. Obtained results were used for determining the temperature changes of electric conductivity and the activation energy of current carriers. The conductivity was found to be of the *p*-type.

1. Introduction

Almost all ferroelectrics were initially treated as dielectrics. Subsequent research showed that many of them also possess properties typical of semiconductors. These are due both the electric conductivity, higher than the limit conventionally separating insulators from semiconductors, and to the magnitude of activation energy, photosensitivity, and so on. The value of activation energy for lead zirconate was found to depend on the type of the electrode material used. For platinum electrodes it amounts to 2.52 eV below the Curie point and 1.36 eV above it [1].

The authors of this paper, continuing their studies on the semiconductive properties of PbZrO_3 , made use of the thermoelectric effect to this aim. This effect, extensively investigated in typical semiconductors, makes it possible to determine the type of the conductivity, while knowledge of the Seebeck coefficient enables a determination of the width of the forbidden band, mobility and concentration of current carriers to be made.

The studies of Pigoń and Chojnacki [2, 3] were among the first on the thermoelectric effect in ferroelectric substances. The authors of these studies investigated the temperature-dependence of the Seebeck coefficient in polycrystalline samples of alkali-earth metal titanates (BaTiO_3 , MgTiO_3 , SrTiO_3 and CaTiO_3), determined the type of conductivity and calculated the mobility of carriers in BaTiO_3 . In the successive work on BaTiO_3 an attempt was made to explain the anomalies in thermal E. M. F., and the influence of La, Ce, Tb and Mg impurities on their character was looked into [4–9]. The Seebeck effect was also studied in other ferroelectric materials, such as PbTiO_3 [10, 11] and in $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ solid solutions [12]. Lead zirconate exhibits certain similarities to the mate-

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rials mentioned above. It possesses perovskite-type structure with a phase transition at approx. 230°C , below which there are antiferroelectric and ferroelectric phases [13–16].

No attempts have hitherto been made as regards the thermoelectric effect in PbZrO_3 . The authors of this paper, undertaking this work, have hopes that the found results will at least partially fill the existing gap and enable a better understanding of the properties of semiconductive lead zirconate to be achieved, as this substance is interesting from both the viewpoint of science itself and practical application.

2. Experimental technique and results

Polycrystalline samples of PbZrO_3 were obtained by the commonly known method of synthesizing components mixed together in appropriate stoichiometric ratio. The reactants were analytically pure PbO and ZrO_2 . The ceramic samples obtained in this way in the form of discs of an area of approx. 1.4 cm^2 were ground down to a thickness of 0.1 cm , after which platinum electrodes were deposited by the thermal technique at a temperature of about 800°C . Electric permittivity measurements enabled the Curie point to be established; it was found to be $T_{\text{CI}} = 231^{\circ}\text{C}$ in the heating process and $T_{\text{CII}} = 227^{\circ}\text{C}$ in the cooling process.

Thermal electromotive force measurements were carried out by a compensational method, employing a compensator making possible measurements with an accuracy of up to 0.001 mV . Elements of the Pt–PtRh thermocouples in direct contact with the sample surfaces were utilized as electric leads. A diagram of the circuit for thermal E. M. F. measurements is shown in Fig. 1. The sample, together with the adhering thermocouples,

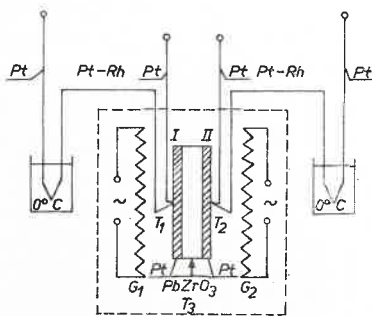


Fig. 1. Diagram of circuit for measuring thermal E.M.F. and thermodiffusion currents

was placed between two corrective heaters G_1 and G_2 , the task of which was to generate or liquidate, as need be, the temperature gradient between its surfaces I and II. The whole was inserted into an appropriate heating device permitting a considerable temperature (up to about 600°C) to be reached.

To find the thermal electromotive force, a temperature gradient $\Delta T = T_1 - T_2$ was generated and, changing its value (from 0° to 20°C) and direction (first in the direction I, then in direction 2, as shown in Fig. 2), the value of thermal E. M. F. was measured each

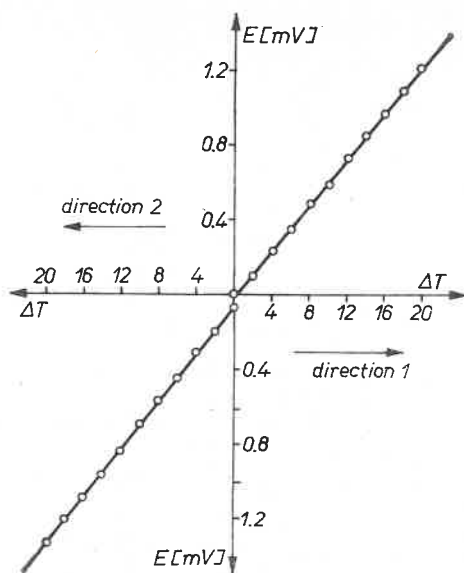


Fig. 2. Thermal E.M.F. = $f(\Delta T)$ dependence for $T_{av} = 480^\circ\text{C}$

time. Then the value of the Seebeck coefficient was determined, relating it to the mean temperature,

$$\alpha = \left(\frac{\Delta E}{T_1 - T_2} \right) T_{av} \quad \text{where} \quad T_{av} = \frac{T_1 + T_2}{2} \quad (1)$$

One of the thermal E. M. F. = $f(\Delta T)$ curves obtained in this way for $T_{av} = 480^\circ\text{C}$ is presented in Fig. 2. As is seen, there is a strict proportionality between the thermal E. M. F. and temperature gradient, while the very slight parallel shift of the straight lines is presumably due to a possible polarizing of the sample under the effect of the potential difference generated during measurement in the direction 1. In order to achieve reproducible results the applied measuring technique had to be such that the history of the sample would be taken into account and, especially, the traces of previous polarization had to be removed.

Proceeding in the manner described; the Seebeck coefficient was measured within a range of mean temperatures from 340 to 600°C . Results of these measurements are presented in Fig. 3. It was ascertained beyond any doubt that within the examined range of temperatures PbZrO_3 is a p -type semiconductor, what follows directly from the sign of the thermal electromotive force. In the 400 to 460°C range the magnitude of the Seebeck coefficient is almost independent of temperature and equals about $62 \mu\text{V}/\text{deg}$. Above this temperature there is observed a slow rise in α (about 10% per 100°C), whereas below it there is a sharp drop, suggesting that conductivity tends to change its type. Measurements at temperatures below 340°C proved to be infeasible because the applied measuring technique could not overcome the problem of strongly increasing sample resistance.

The thermoelectric effect was utilized additionally in this work to determine the value

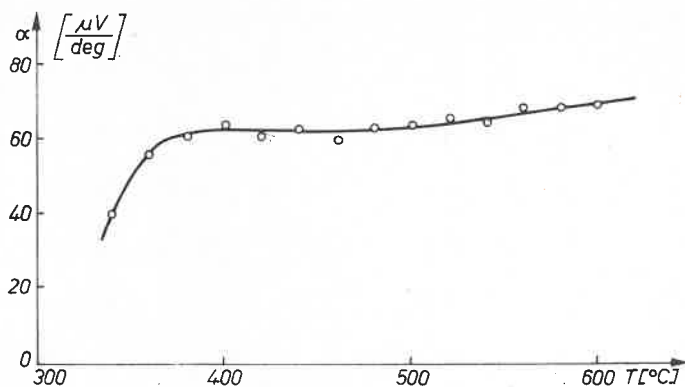


Fig. 3. Temperature-dependence of the Seebeck coefficient

of electric conductivity within the examined range of temperatures. To this aim investigations were also made on the thermodiffusion current as a function of external resistance R of the circuit into which the sample was included. Figure 4 presents an example of such a dependence at two different temperatures, namely, $T = 460^\circ\text{C}$ (curve 1) and $T = 560^\circ\text{C}$ (curve 2). Attention should be turned to the fact that the thermodiffusion current reaches a value almost independent of resistance in a much broader range of small R values at 460°C than at 560°C .

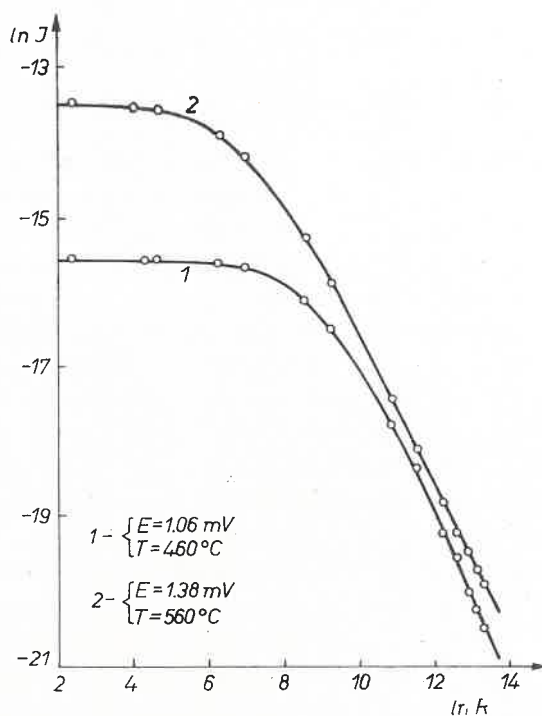


Fig. 4. Changes in thermodiffusion current as a function of external resistance R .

When analyzing the above relation, $I = f(R)$, the semiconductive lead zirconate may be represented by means of the equivalent circuit shown in Fig. 5. Sample resistance is represented here by the series resistance r_1 . During experiments it was found that the resistances r_1 and r_2 in this circuit are a function of temperature, and the resistance r_2 in parallel plays the role of leakage resistance. Measuring the thermal E. M. F. (for $\Delta T = \pm 20^\circ\text{C}$)

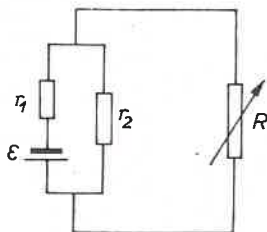


Fig. 5. Equivalent circuit for semiconductive PbZrO_3 together with external resistance R

and magnitude of the thermodiffusion current at two different external resistances yields with the use of the presented equivalent circuit a determination of the resistances r_1 and r_2 on the basis of the formulae

$$r_1 = \frac{E(J_2 R_2 - J_1 R_1)}{J_1(J_2 R_2 - J_2 R_1)} \quad (2)$$

and

$$r_2 = \frac{E(J_2 R_2 - J_1 R_1)}{E(J_1 - J_2) + J_1 J_2 (R_1 - R_2)}. \quad (3)$$

The value of resistance r_1 was assumed to be a measure of electric conductivity. As investigations have shown, the value of r_2 is some 15 times larger than the value of r_1 in almost the whole of the examined temperature range. The $\ln \sigma = f\left(\frac{1}{T}\right)$ curve for the examined 340 to 600°C range is shown in Fig. 6. The presence of straight line segments in this plot implies that electric conductivity in the $\text{Pt}-\text{PbZrO}_3-\text{Pt}$ system can be expressed in the form of the formula

$$\sigma(T) = \sigma_0 e^{-\varphi/kT}. \quad (4)$$

It is easily seen that in the range of temperatures from 455 to 465°C there occurs a distinct change in activation energy. Below this range the determined value of φ equals 1.31 eV, whereas above it, 1.03 eV.

In addition, the dependence of electric conductivity on the state of sample polarization was looked into. As has already been mentioned, semiconductive PbZrO_3 is relatively easy to polarize. Despite the use of small fields ($U \cong 2$ mV), this effect has proved to be of some significance in the determination of conductivity. The results presented in Fig. 6 are mean values determined from data obtained for ΔT 's of the same magnitude but opposite sign.

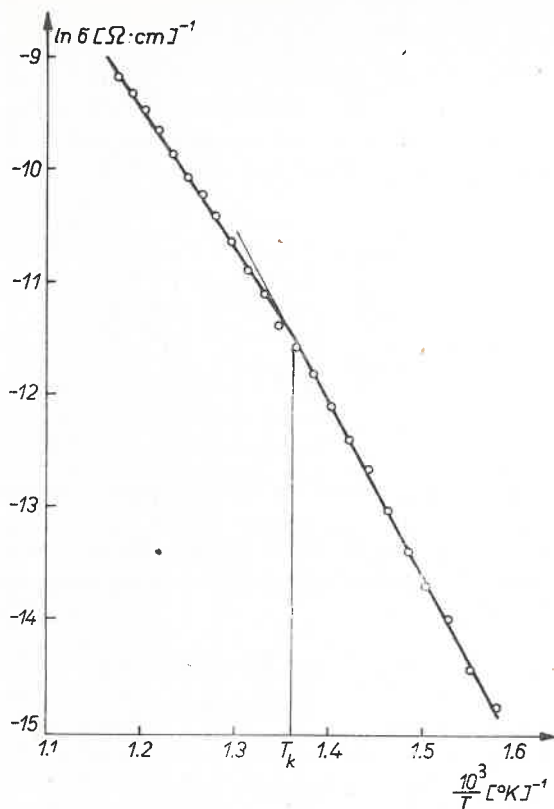


Fig. 6. Graphical representation of $\ln \sigma = f\left(\frac{1}{T}\right)$ dependence

3. Discussion of results

More and more facts speak in favour of the hypothesis stating that in the phenomena under study, besides the carriers originating from the impurity levels, an important role is played by carriers introduced into the ferroelectric substance from the electrodes in the process of thermopolar emission. Indeed, it may be precisely this process which brings about the change in type of conductivity appearing somewhere between 100 and 200°C in almost all hitherto examined ferroelectric materials of perovskite structure. As is known, this is the temperature at which strong thermoemission just begins to appear, and it is particularly dependent on the existing electric fields. The pronounced drop in Seebeck coefficient at temperatures below 340°C (Fig. 3) suggests there is a similar change in PbZrO_3 , also. Unfortunately, using the described measuring technique, we were unable to experimentally investigate the type of conductivity in the range of lower temperatures. Obviously, studies must be continued by another measuring technique. In the examined temperature range, 340 to 600°C, PbZrO_3 is a *p*-type conductor. This fact may be explained as in the case of BaTiO_3 [3] by the considerable difference in mobilities of electrons and holes in this range.

The method of determining electric conductivity from data obtained by measuring the Seebeck coefficient is applicable especially in the range of higher temperatures. By applying small measuring fields the field influence on state of sample polarization and indirectly on the conduction process was minimized. This method also makes it possible to control the temperature gradient generated by the flow of conduction current (the Peltier effect). An important fact is that the reproducibility of results is quite good.

The decrease in activation energy in the range of temperatures above 455–465°C may be due to a change in conditions of carrier diffusion in the polycrystalline material. For it is well known that electric conductivity determined for a polycrystalline substance may be referred to volume phase with any certainty at sufficiently low temperatures. At high temperatures the presence of electronic gas in the pores between crystallites sufficiently changes its character [17] and, at the same time, the considerable thermal radiation also makes it possible to relate the generated temperature gradients to the volume phase [18]. It should also be mentioned that the obtained value of activation energy in the range of temperatures below 455°C is almost identical with that obtained by the author of Ref. [1] for temperatures higher than the Curie point ($\varphi = 1.36$ eV). The temperature at which the change in activation energy occurs (455–465°C) is in the $\alpha(T)$ curve (Fig. 3) that point above which a slow rise in Seebeck coefficient is observed. A detailed explanation of the observed effect of activation energy change in the region of the same phase in PbZrO_3 requires further inquiries.

Research on the thermoelectric phenomenon in ferroelectric ceramic materials bear some importance owing to numerous attempts now being made to utilize this effect for directly converting thermal energy into electricity [19].

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