ELECTRICAL CONDUCTIVITY AND SEEBECK'S COEFFICIENT IN $Pb(Zr_xTi_{1-x})O_3$ SOLID SOLUTION NEAR THE MORPHOTROPIC PHASE BOUNDARY $0.46 \leqslant x \leqslant 0.60$

By Z. Wróbel

Institute of Engineering Techniques, Silesian University, Katowice*

(Received January 26, 1978; revised version received July 6, 1978)

Temperature dependence of the electric permeability (ε), electric conductivity (σ) and Seebeck's coefficient (α) near the morphotropic phase boundary at $x = 0.53$ which separates a tetragonal Ti-rich phase from a rhombohedral Zr-rich phase, of $Pb(Zr_xTi_{1-x})O_3$ solid solutions has been investigated. The obtained results have been used to find and determine the type of conductivity and to find the activation energy of the charge carriers. On the basis of Seebeck's coefficient and electric conductivity, the mobility and concentration of majority current carriers were calculated.

1. Introduction

Solid solutions of lead zirconate-titanate $Pb(Zr_xTi_{1-x})O_3$ have attracted much attention from both the physical and technical points of view, and many studies have been reported on them [1÷12]. The greatest advantage of these solid solutions is the possibility of making use of them in the form of ceramics. The process of monocrystals cultivation is still known well enough to be used on a large technical scale [2÷4].

The morphotropic rhombohedral-tetragonal phase boundary, which occurs in solid solutions $Pb(Zr_xTi_{1-x})O_3$, has very interesting properties. Most studies have been concentrated so far on the piezoelectric, dielectric properties [5÷9] of $Pb(Zr_xTi_{1-x})O_3$ solid solutions situated close to the morphotropic phase boundary at $x \approx 0.53$, which separates a tetragonal Ti-rich phase from a rhombohedral Zr-rich phase. Little attention has been paid so far to the electric conductivity and other transport phenomena in these materials [10÷12].

Electric conductivity of the solid solutions $Pb(Zr_xTi_{1-x})O_3$ was treated as a second rate question while research efforts were mainly concentrated on ceramics with the optimum of piezoelectric characteristics.

* Address: Instytut Problemów Techniki, Uniwersytet Śląski, Żeromskiego 3, 41-200 Sosnowiec, Poland.

The aim of this paper was to examine the temperature dependence of electric conductivity, Seebeck's coefficient and electric permeability for the solid solutions $Pb(Zr_xTi_{1-x})O_3$ near the morphotropic phase boundary $0.46 \leqslant x \leqslant 0.60$.

2. *Sample preparation*

Lead zirconate titanate ceramics have been prepared according to the conventional technology. Ceramics of $Pb(Zr_xTi_{1-x})O_3$ have been prepared by mixing the previously obtained ceramics of $PbZrO_3$ and $PbTiO_3$ in a suitable molar percentage. The sintering temperatures of seperated compositions of $Pb(Zr_xTi_{1-x})O_3$ have been fitted experimentally, that all obtained samples had similar mechanical properties, porosity and size of crystallites. The processes were as follows: first, the temperatures of the sintering process varied from 1150°C to 1180°C and the time of the sintering process was four hours, second, the temperatures varied from 1200°C to 1250°C and time of the sintering process was also four hours.

In order to decrease the losses of lead, the sintering of samples was performed in a platinum crucible which has been coated by a thick-wall fire-clay crucible, and some quantity of PbO was placed inside, near the sample.

The density of the obtained ceramics was 96–98% of the theoretical value. The PbO content in those sintered samples was less than 1%. All samples showed the same microstructure, their size was about 5 μm. The thickness of the samples was 2 mm, and the surface area 50 mm^2. The platinum electrodes have been produced by coating sample with platinum paste and then by sintering the sample at 700°C.

3. *Experimental results*

a. Electric conductivity

Analysing the literature data concerned with the electric conductivity of polycrystallic samples, a wide range of results has been noticed. This fact can be explained either by varying ceramic technologies or by varying experimental conditions. Besides the above mentioned factors, the conductivity of a given materials depends on the electric voltage of the measuring field [10, 13].

Electric conductivity of solid solutions $Pb(Zr_xTi_{1-x})O_3$ was examined in the cooling process (rate of cooling was 40 K/hour), by applying to the sample a constant measuring field (of the range $E = 10$ V/cm) and by measuring the current flowing through the sample. The dependence of the electric conductivity on temperature for the solid solution $Pb(Zr_{0.52}\,Ti_{0.48})O_3$ was indicated in Fig. 1 in the form of $\ln \sigma = f(1/T)$.

On the basis of the rectilinear parts of the relationship $\ln \sigma = f(1/T)$, the energy of activation was calculated below and above the points of phase transition where the change in slope is observed. For the individual proportional composition of the solid solutions of $Pb(Zr_xTi_{1-x})O_3$, values of activation energy are limited within the range: above the Curie temperature $W_1 = 0.8 \div 0.9$ [eV], and below — $W_2 = 1.0 \div 1.1$ [eV]. The values

of the activation energy for the particular solid solutions within the whole range of the examined temperatures are smaller than the forbidden band of pure components established to be of about 3 eV [14]. Thus, it could be concluded that the electric conductivity of $Pb(Zr_xTi_{1-x})O_3$ solid solutions has a donor or an acceptor character for the temperatures within the tested range.

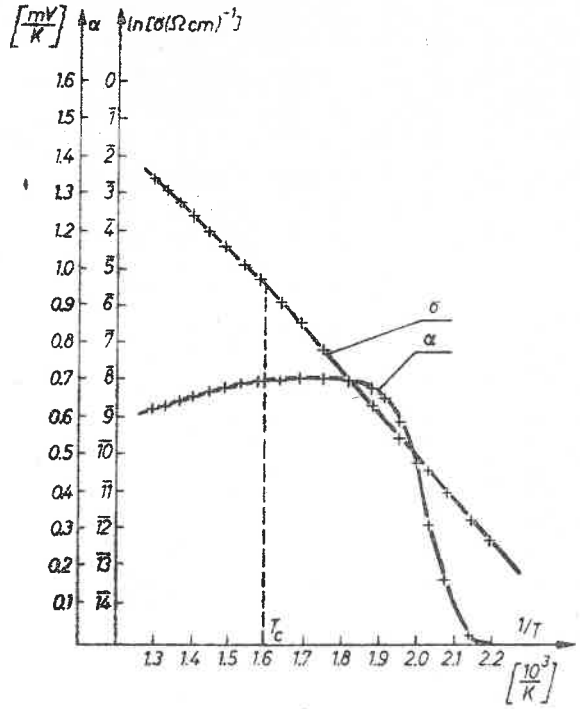

Fig. 1. The dependence $\ln \sigma = f(1/T)$ and $\alpha = f(1/T)$ for the solid solutions $Pb(Zr_{0.52}Ti_{0.48})O_3$

b. Seebeck's effect

Seebeck's coefficient has been studied in order to define the type of electric conductivity. The example of the relationship $\alpha = f(1/T)$ for one of the tested samples of solid solutions of $Pb(Zr_{0.52}Ti_{0.48})O_3$ is presented in Fig. 1.

Examining the sign of the thermoelectric power in the cooler junction, the conductivity of the *p*-type at high temperature $T > 300°C$, and the tendency of majority carriers to change sign at lower temperature, $T < 200°C$, were found in all materials. The obtained values of Seebeck's coefficient can be compared with the literature data [10, 11] (α = 500 μV/deg) determined for some solid solutions of $Pb(Zr_xTi_{1-x})O_3$.

c. Electric permeability

In order to establish the phase transition point in relation to the proportional composition of $Pb(Zr_xTi_{1-x})O_3$ solid solutions, the temperature dependence of the electric permeability has been investigated for individual samples. The electric permeability was

tested by a measurement of field frequency equal to 1 MHz and amplitude of above 1V. The dependence of the maximum electric permeability on proportional composition of the solid solutions of $Pb(Zr_xTi_{1-x})O_3$ is presented in Fig. 2.

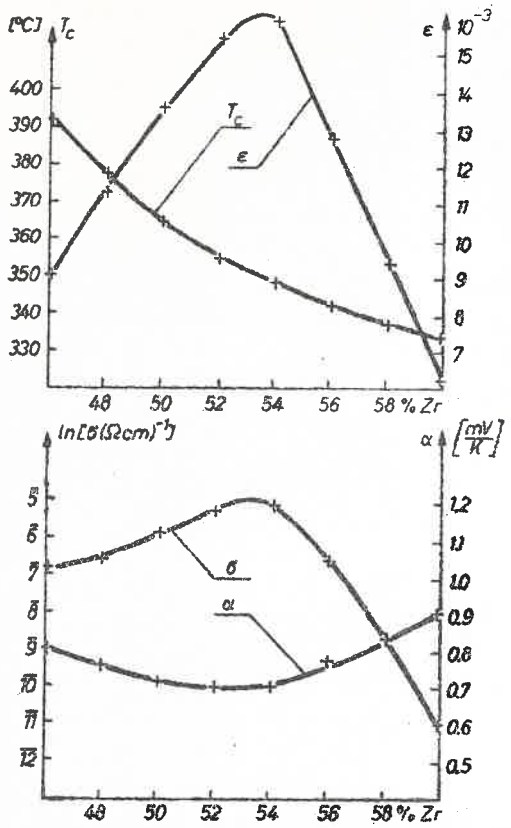

Fig. 2. Curie temperature (T_c) and electric permeability (ε), electrical conductivity (σ) and Seebeck's coefficient (α) at the Curie point as functions of the compositions of $Pb(Zr_xTi_{1-x})O_3$ solid solutions

4. Discussion of results

Analysing the phase diagram of $Pb(Zr_xTi_{1-x})O_3$ solid solutions it could be expected that close to the morphotropic phase boundary, dividing the phases of rhombohedral and tetragonal symmetry, local extremum in the graphs of the relationship of the examined values (ε, σ, α) could be found, similar to characteristic parameters for electromechanic properties of these materials [1–8].

In Fig. 2 the dependence of the values of the Curie temperature T_c and electric permeability (ε), electric conductivity (σ) and Seebeck's coefficient (α) at Curie's point on the percentage composition of $Pb(Zr_xTi_{1-x})O_3$ solid solution is shown. In all the diagrams, the "deviations" of the examined values for the solution close to the morphotropic phase

boundary can be observed. Two ways of explaining of the dielectric and the piezoelectric constants are known. They are as follows:

— in order to explain the maximum value of the dielectric constant, the Devonshire theory is used [15, 16]. Assuming that the coefficients vary ad hoc with the concentration x it is possible to show that the dielectric constant perpendicular to the direction of polarization increases in the two phases as the concentration x reaches the critical value. The maximum of the piezoelectric activity is merely a consequence of the maximum of the dielectric constant,

— in order to explain that the polarization has a maximum, and the coercive field has a minimum, Isupov suggests [16] that there is a mixture of phases i.e. in the tetragonal phase (near the morphotropic boundary) there are islands with rhombohedral structure and vice versa.

The ferroelectric-semiconductor ceramics exhibit a certain correlation between their ferroelectric and semiconductor properties according to the results of Fridkin [17]. The thermodynamic potential ϕ can be generalized in the following form

$$\phi = \phi_1 + \phi_2, \tag{1}$$

$$\phi_1 = A(P_x^2 + P_y^2 + P_z^2) + B(P_x^4 + P_y^4 + P_z^4) + C(P_y^2 P_x^2 + P_y^2 P_z^2 + P_z^2 P_x^2), \tag{2}$$

$$\phi_2 = \sum_i N_i E_i, \tag{3}$$

where ϕ_1 is thermodynamic potential characterizing ferroelectric properties, ϕ_2 — thermodynamic potential characterizing semiconductor properties, A, B, C — expansion coefficients, P — polarization, N_i — concentration of the charge carriers, E_i — energy of carrier current activation.

It has been assumed that A, N and E are functions of concentration x and temperature T, but B and C are only functions of x ($B > 0$ and $C > 0$). It is known [18] that from the expression (2), there are only two possibilities: if $2B > C$ the stable phase has the tetragonal structure. This means that the critical concentration x_0 is given by $2B(x_0) \approx C(x_0)$. The critical concentration x_0 for a solid solution $Pb(Zr_xTi_{1-x})O_3$ is $x_0 \approx 0.53$. The second term of equation (1) expresses the effect of semiconductor properties, such as the concentration of free carriers and the charge carriers activation energy, on the ferroelectric properties of the material.

As it has been shown in the paper written by Fridkin [17], the dislocation of the Curie point, as well as the changes of spontaneous polarization, temperature hysteresis and dielectric and piezoelectric properties of a material can be observed for $N \neq 0$. The concentration of free current charge carriers and the activation energy depend on the tetragonal and rhombohedral structure, of crystallites existed in tested $Pb(Zr_xTi_{1-x})O_3$ solid solutions.

As it has been shown in the reports [15, 16], both crystallites of tetragonal structure (inside) with rhombohedral coating (outside) and the crystallites of rhombohedral structure with tetragonal coating exist. The existence of the metastable, tetragonal-rhombohedral phase of crystallites, with different percentage composition, affects the electrical properties

(σ, α, p, μ) of $Pb(Zr_xTi_{1-x})O_3$ solid solutions, as it was shown in Figs 2, 3. The previously suggested mechanism of electrical conductivity in the solid solution $Pb(Zr_xTi_{1-x})O_3$ is based on the concept of the determining role of oxygen vacancies and taking into account the lead vacancies [10, 19÷21]. The oxygen vacancies are able to set up F_2 (2 electrons), F_1 (1 electron) and V (without electrons) centers. The F_2 center, which is weaker than the oxygen ion holding the electrons, plays the part of donor, and the V center, which is able to trap one electron, plays the role of an acceptor. The ratio between the total number

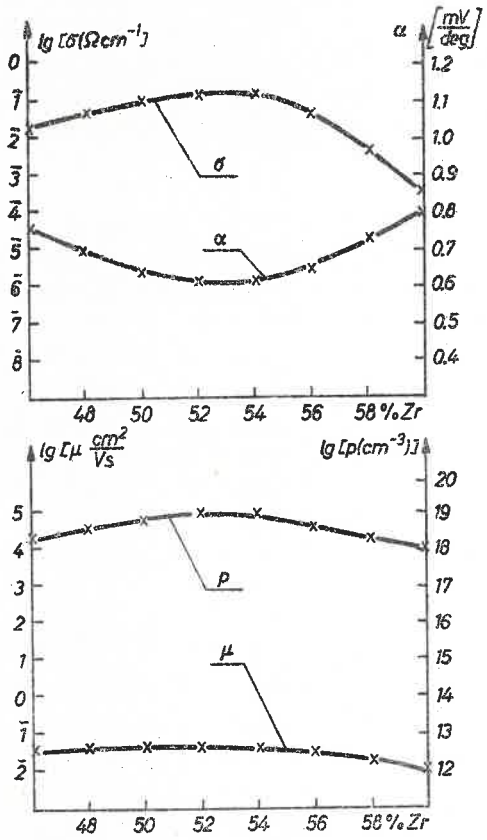

Fig. 3. Electrical conductivity (σ), Seebeck's coefficient (α), mobility (μ), and density (p) of the majority charge carriers at $T = 500°C$ as functions of compositions of $Pb(Zr_xTi_{1-x})O_3$ solid solutions

of the remaining oxygen vacancies and the number which captured the electrons of the structural defects determines the number of donors and acceptors and as a result the conductivity type n or p.

In $Pb(Zr_xTi_{1-x})O_3$ experiments have shown that the conductivity is p-type. This is presumable due to "superoxidation", that is an excess of cation over oxygen vacancies. These Pb-position vacancies attract electrons to complete the electron shells of the surrounding oxygens, they act as acceptors causing the presence of holes (electron defects)

in the lattice according to

$$V_{Pb} \rightarrow V_{Pb}^{2-} + 2h. \tag{4}$$

A knowledge of Seebeck's coefficient (α) and electric conductivity (σ) enables us to determine the mobility (μ) and density (p), of the majority charge carriers [22÷24] using the formula

$$\alpha = \frac{k}{e}\left(\ln \frac{N_{eff}}{p} + a\right) \tag{5}$$

$$\sigma = ep\,\mu, \tag{6}$$

where k is Boltzmann's constant, e — elementary charge, N_{eff} — effective state density, a — transport coefficient of the carriers.

For the temperature ranging from 400°C to 500°C, the plotted dependence $\alpha = f(\ln \sigma)$ is a straight line with a slope of $\sim k/e$. According to the theory it shows that the effective state density equals ca 10^{22}. Values of electric conductivity (σ), Seebeck's coefficient (α) and mobility (μ), density (p) of the majority charge carriers in temperature $T = 500$°C for $a = 0$ as a function of percentage composition of $Pb(Zr_xTi_{1-x})O_3$ solid solutions are shown in Fig. 3. The choice of that temperature has been dictated in relation to the theory of transport phenomena which does not take the specific properties of ferroelectrics into account (at $T = 500$°C all solid solutions of $Pb(Zr_xTi_{1-x})O_3$ are present in the paraelectric phase). Comparing the values of the mobility and density of charge carriers, resulted from the studies of Seebeck's coefficient and electric conductivity, with the μ values obtained in the measurement of Hall's effect for solid solutions of $Pb(Zr_xTi_{1-x})O_3$ and for affined perovskite materials [23, 24], we can assess those values as true and correct, at least as far as order of magnitude is concerned.

5. *Conclusions*

The electric permeability (ε), electric conductivity (σ), Seebeck's coefficient (α) as well as mobility (μ) and density (p) of the majority charge carriers exhibits local extremum $x = x_0$ near the "tetragonal-rhombohedral" phase boundary. In solid solutions of $Pb(Zr_xTi_{1-x})O_3$ near the morphotropic phase boundary in which in addition to oxygen vacancies there are vacancies of Pb, V-center predominates and the conductivity is of p-type at high temperature $T > 300$°C, and tendency to change of the sign of majority carriers at lower temperature $T < 200$°C, have been found in all materials.

Near the morphotropic phase boundary, the coexistence of the tetragonal and rhombohedral phases has been found. The research carried out by the authors [15, 16] indicates that in the solid solution with the composition close to the morphotropic phase boundary, both crystallites of tetragonal structure with rhombohedral coating and crystallites of rhombohedral structure with tetragonal coating could exist. The authors of the papers [15, 16] assumed that these particular crystalline properties also explained the deviations in electromechanical properties.

The concentration of charge carriers and energy of carriers current activation depend on the crystallic structure ceramics. In the near morphotropic phase boundary the mixture of phase is observed, i.e. in the tetragonal Ti-rich phase there are islands with rhombohedral structure and vice-versa. The observed anomalies of electric properties (σ, α, p, μ) are probably induced by a fluctuating metastable tetragonal-rhombohedral phase.

REFERENCES

[1] B. Jaffe, W. Cook, H. Jaffe, *Piezoelectric Ceramics*, London 1971.
[2] M. L. Sholokhovich, E. G. Fesenko, *Izv. Akad. Nauk SSSR* **24**, 1242 (1960).
[3] S. Fushimi, T. Ikeda, *Jap. J. Appl. Phys.* **3**, 171 (1964).
[4] K. Tsuzuki, K. Sakata, G. Ohara, M. Wada, *Jap. J. Appl. Phys.* **12**, 1500 (1973).
[5] G. Shirane, A. Takeda, *J. Phys. Soc. Jap.* **7**, 5 (1952).
[6] B. Jaffe, R. S. Roth, S. Marzullo, *J. Appl. Phys.* **25**, 803 (1954).
[7] D. A. Berlincourt, C. Cmolik, H. Jaffe, *Proc. Inst. Radio. Engrs* **48**, 220 (1960).
[8] K. Carl, K. H. Härdtl, *Ber. Dtsch. Keram. Ges.* **47**, 687 (1970).
[9] N. Uchida, T. Ikeda, *Jap. J. Appl. Phys.* **4**, 876 (1965).
[10] V. M. Gurevich, *Elektroprovodnost Segnetoelektrikov*, Moskva 1969.
[11] R. Gerson, H. J. Jaffe, *J. Phys. Chem. Solids* **24**, 979 (1963).
[12] Z. Wróbel, J. Hańderek, *Acta Phys. Pol.* **A45**, 779 (1974).
[13] Z. Wróbel, J. Dudek, *Acta Phys. Pol.* **A46**, 83 (1974).
[14] A. T. Yatsenko, *Izv. Akad. Nauk SSSR* **24**, 1308 (1960).
[15] K. Carl, K. M. Härdtl, *Phys. Status Solidi* **8**, 87 (1971).
[16] V. A. Isupov, *Fiz. Tver. Tela* **12**, 1380 (1970).
[17] V. M. Fridkin, *Segnetoelektriki-poluprovodniki*, Moskva 1976.
[18] H. Thomas, K. A. Muller, *Phys. Rev. Lett.* **21**, 1256 (1968).
[19] O. I. Prokopalo, *Izv. Akad. Nauk SSSR* **35**, 1956 (1971).
[20] S. Ikodami, J. Ueda, *J. Phys. Soc. Jap.* **19**, 159 (1964).
[21] O. I. Prokopalo, A. S. Bogatin, V. A. Servouli, *Ferroelectrics* **5**, 99 (1973).
[22] J. G. Austin, N. F. Mott, *Adv. Phys.* **18**, 41 (1969).
[23] P. Gersthsen, R. Groth, K. H. Härdtl, *Phys. Status Solidi* (a) **11**, 303 (1965).
[24] G. Gazda, W. Plesiewicz, *Acta Phys. Pol.* **33**, 455 (1968).