INFLUENCE OF OXYGEN DEFECTS ON ELECTRIC AND THERMOELECTRIC PROPERTIES OF SODIUM AND POTASSIUM NIOBATE CRYSTALS

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The influence of oxygen defects on temperature dependences of electric conductivity, electric permeability and the thermoelectric force coefficient is presented for monocrystals of $KNbO_3$ and $NaNbO_3$. It was stated that oxygen defects caused a strong increase in electric permeability besides the strong increase in electric conductivity and a decrease in activation energy of current carriers. In the case of reduced $KNbO_3$ monocrystals the strong changes of value and even the sign of the thermoelectric force were also found.

1. Introduction

The monocrystals or ceramics of the ABO_3 type compounds are obtained frequently in the technological process in the less or more reduced state — ABO_{3-x}. The degree of oxygen reduction (x) can be raised also purposely by the process of heating the samples in a vacuum or under an inert gas atmosphere. The review of works and the information concerning the oxygen reduction in $BaTiO_3$ are in [1].

It is known from numerous works that the crystals of reduced compounds ABO_{3-x} show many properties typical for semiconductors [2, 3]. During investigations of a model ferroelectric crystal — $BaTiO_3$, considerable progress has been made in explaining many complicated problems in the correlation between electric conductivity and the properties characterizing the ferroelectric state. Progress also has been achieved in the explanation of the special nature of oxygen defects. The information concerning this problem are in review articles [4, 5] and in some monographs [1, 3, 6, 7].

It is of interest to explain the following problem: can the experimental information and theoretical interpretations obtained for barium titanate be related to the many other ferroelectric and antiferroelectric crystals having a perovskite-type structure.

In this paper, the extremely strong influence of oxygen defects on electric conductivity, electric permeability and the thermoelectric properties is shown for monocrystals $KNbO_3$

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and $NaNbO_3$. In these crystals the ferroelectric or antiferroelectric state occur at considerably higher temperatures with respect to the $BaTiO_3$. This permits us to obtain the thermodynamical equilibrium of defects in a reasonable time and then to produce the conditions necessary to obtain reproducible results.

2. Technique and results of experiments

The characteristics presented below were obtained for monocrystals grown from a solution of melted salts: K_2CO_3—Nb_2O_5 for $KNbO_3$ and Na_2CO_3—Nb_2O_5—NaF for $NaNbO_3$, using the technology proposed by Wood [8]. As an effect of slow cooling of the solution, the crystals having the form of plates, rectangular prisms or needles with linear sizes from ten to twenty mm were obtained. In most cases, for $NaNbO_3$, the crystals were transparent and yellow. For $KNbO_3$, completely transparent and colourless crystals of the minimal reduced compounds were obtained near the surface of the solution with good conditions for free air access. Most often, the semitransparent, dark-blue and even nontransparent, nearly black crystals were obtained from the deeper layers of the solution. In this case, the deficiency of oxygen determined the process of crystal growth of the reduced $KNbO_{3-x}$ compound, with the degree of reduction dependent on the partial pressure of oxygen in the surroundings of the crystal grown. Afterocoling down to considerably lower temperatures, the crystals reduced during crystal growing occur in the metastable state —

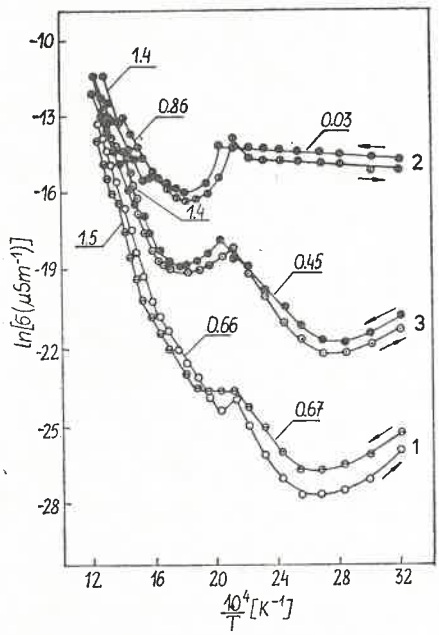

Fig. 1. Temperature dependence of electric conductivity for $KNbO_3$ single crystals. Curves *1* — full transparent, nonreduced crystal, curves *2* — crystal strongly reduced, nontransparent, curves *3* — crystal partly reduced. Numerical data are in eV

the freezing of oxygen defectation. The selection of crystals from the deeper regions of the volume of the platinum crucible permits one to obtain crystals with an increasing degree of reduction, up to the maximum value for crystals from the bottom of the crucible, where access to oxygen was minimal.

Figure 1 shows the temperature dependence of electric conductivity for $KNbO_3$ monocrystals with three different states of oxygen reduction. For all these states, the crystals show a singularity in $\sigma(T)$ at phase transition points: between rhomboedrical and tetragonal phases ($T \cong 225$°C) and between tetragonal and cubic phases ($T \cong 435$°C). The value of electric conductivity rises with an increasing degree of reduction, particularly, for low--temperature phases. Moreover, for the reduced crystals, the strong decrease in activation energy of carriers is observed for these phases. The values of the activation energy of carriers are given in Fig. 1 beside the individual straight-line sections. At temperatures lower than about 150°C the transition to the region with positive temperature coefficient of resistivity is observed. Similar dependences $\sigma(T)$ for $KNbO_3$ crystals have been observed previously [9, 10].

In the case of $NaNbO_3$ monocrystals, a different degree of oxygen reduction was obtained by vacuum heating at different temperatures. Fig. 2 shows the temperature dependences of electric conductivity for the $NaNbO_3$ crystals reduced by heating in an atmosphere of air under a pressure of about 0.1 pascal for 2 hours at temperatures of

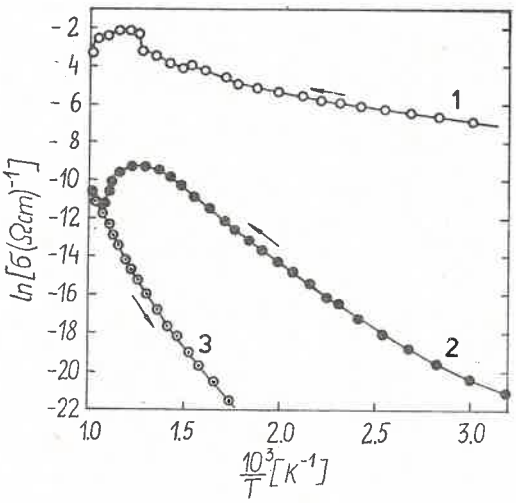

Fig. 2. Temperature dependence of electric conductivity for the $NaNbO_3$ single crystal: reduced by heating in a vacuum (curve *1*, *2*) and oxidized by heating in an air atmosphere at normal pressure (curve *3*)

800°C and 600°C (curves *1* and *2*, respectively). After cooling down in a vacuum the crystals are still reduced in spite of the air access at room temperature. During the following process of heating a strongly increased electric conductivity and decrease in activation energy of carriers are observed. The activation energy changes within the limits of 1.0–1.6 eV and 0.1–0.7 eV for the conditions shown in Fig. 2 for unreduced and reduced crystals, respec-

tively. The "impurity" levels determined using photoelectric methods for $NaNbO_3$ [11, 12] are within these limits. When approaching the range of temperature where the crystal was previously reduced the conductivity decreases to the value characteristic for the unreduced crystal. Then the temperature dependences of conductivity are identical with the dependences obtained for the unreduced sample for each following cooling process (Fig. 2, curve *3*). Therefore, the observed reversibility of the processes of reduction and oxidization of $NaNbO_3$ crystals makes possible the manifold repetition of investigations for the same crystal and the obtainment of the different and controlled degree of oxygen defectation. Other experiments concerning the investigations of changes in the conductivity in $NaNbO_3$ as an effect of reduction and oxidization are shown in [13, 14].

The electric conductivity of the crystals investigated depends not only on the degree of oxygen nonstoichiometry but also on the polarization of oxygen defects. The changes of conductivity caused by the reduction and polarization of oxygen defects were observed between others during investigations of current-voltage characteristics. The *I-V* characteristics were investigated for 4 different states of the $NaNbO_3$ monocrystal:

— an unreduced and nonpolarized crystal and the crystal previously polarized by an electric field of 0.15 kV/cm for 1 hour at a temperature of 450°C, then cooled down to 150°C in the presence of the field in order to freeze the state of polarization,

— the crystal was reduced at a temperature of 700°C for 2 hours under an air pressure of the order of 0.1 pascal, nonpolarized and polarized in a field of 0.075 kV/cm (the other conditions were as above).

For all the states mentioned above the crystal shows different values of conductivity. The temperature dependences of conductivity, determined from the Ohm's parts of the

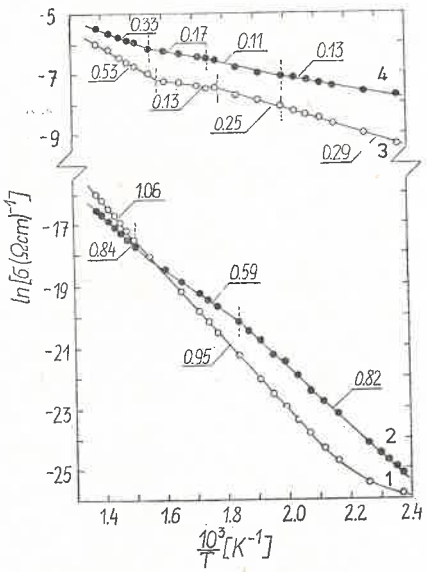

Fig. 3. Conductivity versus temperature for $NaNbO_3$ in 4 different states of crystal: nonreduced (curve *1* and *2*), reduced (curve *3*, *4*), unpolarized (curve *1*, *3*) and polarized (curve *2*, *4*). Numerical data are in eV

current-voltage characteristics, are presented in Fig. 3. The increase in conductivity caused by oxygen reduction is most distinct (Fig. 2). For the degree of reduction obtained for the above conditions, the gain in conductivity is 5–7 orders of magnitude. Moreover, the increases of conductivity caused by a previous polarization are shown in Fig. 3. The values of the activation energy of the carriers, determined from the slopes of the straight-line sections in the plot $\ln \sigma = f\left(\frac{1}{T}\right)$, are given beside these sections.

The investigations of *I-V* characteristics provide evidence that oxygen reduction and the polarization of ionic defects alike cause the strong changes of the voltage range where Ohm's law is valid. Fig. 4 shows the temperature dependence of voltage limiting the range

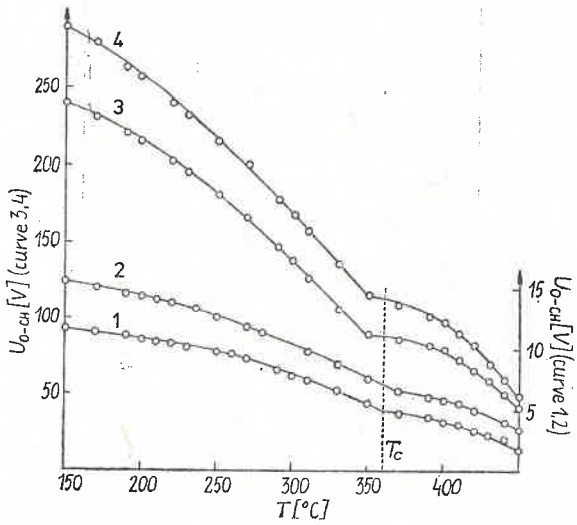

Fig. 4. Temperature dependence of voltage limiting Ohm's part of *I–V* characteristics for 4 states of the $NaNbO_3$ crystal (see text)

of validity of Ohm's law for the 4 states of $NaNbO_3$ crystals mentioned above. For a greater part of the investigated temperature range of 150–450°C, the voltages, $U_{\Omega-Ch}$, correspond to the points of transition of the straight-lines corresponding to Ohm's law and Child's law (for the solid state). The theory of current limiting by space charge [15] permits one to determine the concentration band of a neutral crystal using the values of $U_{\Omega-Ch}$ and, additionally, the values of dielectric permeability.

The reduced crystals show an effect of a strong rise in electric permeability, ε, determined in a measuring field with frequency of 1 MHz. Figure 5 shows the temperature dependence of ε for the processes of heating and cooling for the $KNbO_3$ crystal unreduced and highly reduced during the technological process (curves *1*, *2* and *3*, *4*, respectively). For the highly reduced crystals of $KNbO_{3-x}$ the values of ε are nearly 2 orders of magnitude greater with respect to the unreduced $KNbO_3$ crystal.

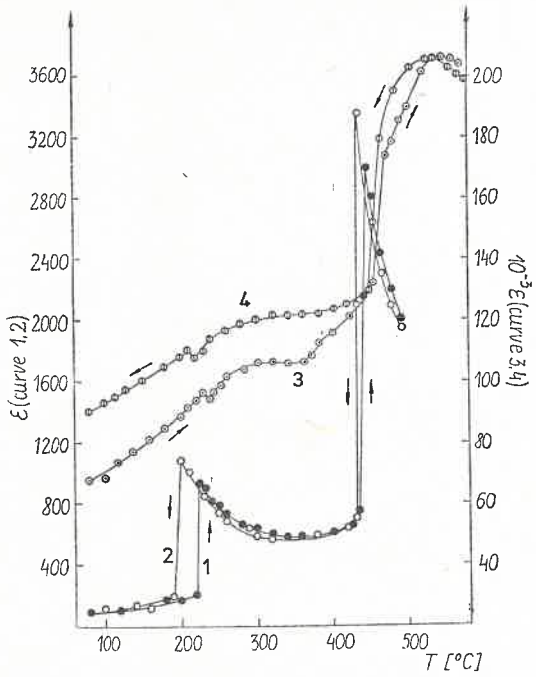

Fig. 5. Temperature dependence of electric permeability in heating and cooling processes for the $KNbO_3$ nonreduced crystal and strongly reduced in the technological process (curves *1,2* and *3,4* respectively)

Similar characteristics, $\varepsilon(T)$, for unreduced (curve *1*) and reduced (curve *2*) $NaNbO_3$ crystals are shown in Fig. 6. In this case, the relatively small degree of reduction caused by heating the crystal in a vacuum (temperature $\sim$600°C, air pressure $\sim$0.1 pascals, time of reduction $\sim$1h) caused the rise in the maximum value of ε by 1 order of magnitude "only". Curve *3* (Fig. 6) was obtained for the same crystal, additionally oxidized by heating at a temperature of 800°C in the air atmosphere. A comparison of curves *1–3* (Fig. 6) indicates, that the observed changes of value and temperature dependence of ε are indeed due to oxygen defects.

The considerable rise in the value of ε for reduced samples can be caused also by a previous polarization in a d.c. field. Fig. 7 shows, e.g., the changes of $\Delta\varepsilon$ in time, based on time changes of the current of depolarization. These data were obtained for the highly reduced (in the growing process) $KNbO_{3-x}$ crystals polarized in the field with an intensity of 300 V/cm, at a temperature of 360°C. The subsequent observations of time changes of $\Delta\varepsilon$ and j_d were made at the same temperature. The values of $\Delta\varepsilon$ and j_d were measured at following time intervals when the sample had been connected commutatively to the measuring circuits for both quantities, respectively.

In spite of the data presented in Figs 1–3 the effects of the strong increase in conductivity in reduced crystals of $KNbO_{3-x}$ and $NaNbO_{3-x}$, the changes of value and sometimes the change of the sign of thermoelectric force coefficient occur. Figure 8 shows the exemplary temperature dependence of the thermoelectric force coefficient for $KNbO_3$ crystals unredu-

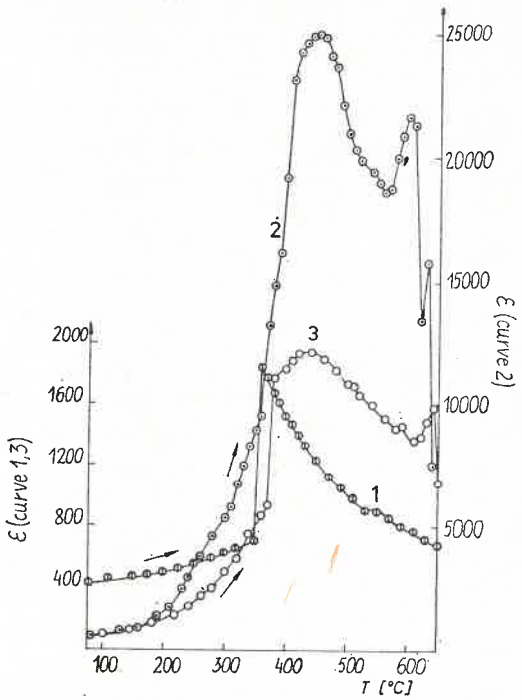

Fig. 6. Temperature dependence of electric permeability for $NaNbO_3$ in the nonreduced state — curve *1*, reduced — curve *2* and oxidized by heating in air after the reduction process — curve *3*

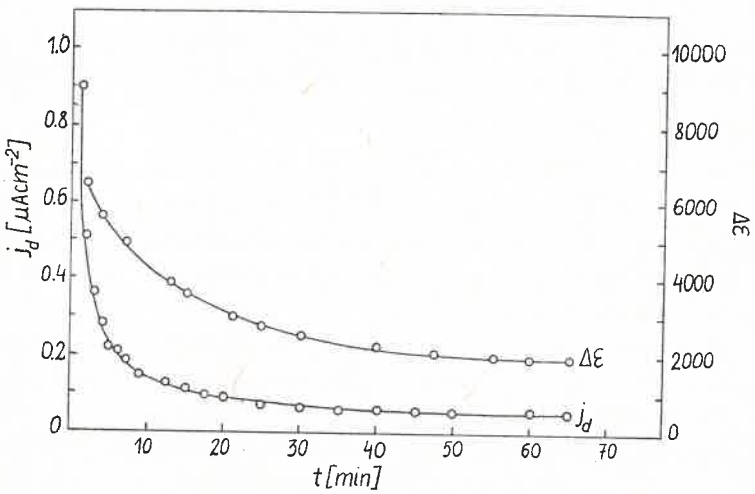

Fig. 7. Time dependences of electric permeability, $\Delta\varepsilon$, and depolarizing current, j_d, for a strongly reduced $KNbO_3$ crystal

ced (curve *1*) and reduced (curve *2*). The crystals with a full degree of oxidization indicate the p-type conductivity at higher temperatures where the measurements of the thermoelectric force were carried out. In the $KNbO_{3-x}$ crystals, with a strong degree of reduction, the sign of the thermoelectric force changes and then the n-type conductivity appears. The dependence of the thermoelectric force coefficient vs the logarithm of electric conductivity

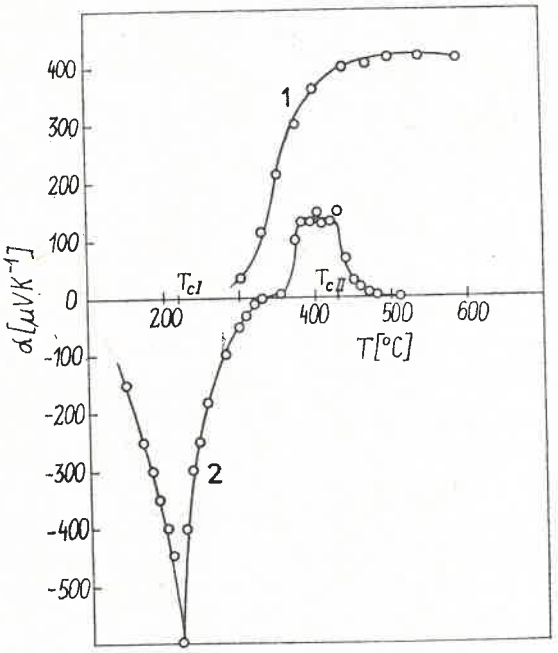

Fig. 8. Seebeck coefficient as a function of temperature for a nonreduced (curve *1*) and reduced (curve *2*) $KNbO_3$ crystal

is linear for $KNbO_{3-x}$ monocrystals with a different degree of reduction. It was shown previously for $BaTiO_3$ [1] and $KNbO_3$ [16], that this was the property of the hopping polaron mechanism of conductivity.

3. Discussion

All fundamental effects, known from $BaTiO_3$, consisting in the changes of electric properties under the action of oxygen reduction were observed for $NaNbO_3$ and $KNbO_3$ crystals which were investigated:

— a strong increase in electric conductivity up to 7 orders of magnitude,

— a decrease in activation energy of current carriers down to values of the order of 10^{-1}–10^{-2} eV,

— a change in the value of the thermoelectric force coefficient,

— a strong changes in the value and temperature dependence of electric permeability.

These effects were observed for a model crystal of $BaTiO_{3-x}$ and also for other compounds of the ABO_{3-x} type [1–7].

The majority of authors consider that the role of oxygen vacancies consists in its ability to bind one or two electrons creating F_1 or F_2 centres and in the change of valencies of the central ions in the oxygen octahedra: $Ti^{4+} \rightarrow Ti^{3+}$. Empty vacancies and monoelectron states can be considered as the deep and shallow trap states or acceptor states. The F_2 states, which are able to give one electron to the conductivity band, can be treated as donors. Therefore, the reduced crystals of compounds ABO_{3-x} can show properties of the p-type or n-type semiconductor depending on the conditions. It was stated for $BaTiO_3$ that the type of conductivity observed depended not only on a total concentration of oxygen vacancies but also on the concentration ratio of F_1 and F_2 centres and the presence of other impurity defects in the lattice.

The effects presented consisting of changes in electric properties which depend on the reduction of $KNbO_3$ and $NaNbO_3$ crystals can be explained on the basis of the considerations presented. An essential role is played not only by the presence of oxygen defects but also by their polarization produced by the polarizing field applied or by the measuring field. The effective polarization during the action of the field is composed of inertialess induced polarization, the inertial polarization of the space charge and the spontaneous polarization (for the ferroelectric state). The effective polarization determines the processes of charge exchange with the electrodes. It also determines the effective current in the sample circuit. The injected electrons can cause the transition of empty oxygen vacancies and F_1 states localized inside the near-electrode layer to F_2 states. At sufficiently high temperatures the thermal generation of electrons from F_2 centres and the subsequent transition to the F_1 state can take place. Consequently, some coupling takes place. The polarization of the ion space charge stimulates the process of injection of carriers from the electrodes, the injected charges screen this polarization thus producing its unusual stability and behaviour which is similar to the electret effect.

The observed rises in electric permeability, $\Delta\varepsilon$, can be explained partly by an influence of plasma oscillations of the electron gas with the concentration increased in the reduced samples [17] and by changes in the electric moment connected with long-term polarization of the ion space charge which is connected with the displacement of ion lattice defects at macroscopic distances. The gradual decay of some part of $\Delta\varepsilon$ as progressive depolarization of the crystal is strong evidence of the participation of the last mechanism (Fig. 7).

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