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Study of intrinsic point defects in oxides of the perovskite family: II. Experiment

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Abstract. The electrical conductivity of $ATiO_3$ and $A^{1+}B^{5+}O_3$ perovskite-type oxides converted by vacuum annealing into states with weak and strong compensation between donors and acceptors has been measured. It was shown that the reduced samples had both shallow and comparatively deep levels which were attributed to the neutral and singly-charged oxygen vacancy, respectively. The experimentally determined activation energies are consistent with the results of the theoretical computation reported in Part I.

1. Introduction

The theoretical treatment carried out in the first part of the present work [1] showed that, in oxides of the perovskite family (OPFs), the lowest energy level of the neutral oxygen vacancy, V_O , is very shallow; it is several hundredths of an electronvolt. The singly-charged vacancy has a deeper level; its energy is several tenths of an electronvolt. Activation energies of the order of hundredths of an electronvolt, that can be attributed to shallow levels of the neutral V_O , were observed in several heavily reduced perovskites [2–7]. However, experimental data concerning the activation energy of the singly-charged V_O are contradictory. The range of the observed values is spread over the interval from 0.3 to 1.7 eV, even for the most studied OPFs [2–4]. This discrepancy is most likely to be a consequence of the fact that, in OPFs, the V_O concentration and, hence, the degree of the compensation of the donor and acceptor centres (as well as the donor/acceptor concentration ratio) may vary significantly in the course of the experiment, especially in the high temperature region (above 500–600 °C). Note that the major role of oxygen in the reaction between the gaseous phase and the solid is supported by the partial vapour pressure values obtained in [9–18]. For $ATiO_3$ perovskites ($A = Ba, Sr, Ca$), at temperatures below approximately 1200 K, the equilibrium vapour pressures of the A-cations and Ti appear to be much lower than the oxygen pressure.

One of the ways of getting reproducible experimental curves is to keep the concentration of point defects constant. To achieve this we proposed a special sample treatment and a special measuring procedure. To use our mode one needs to apply the usual equipment for electric measurements. The main idea for the approach is that a sample that is reduced at a high temperature cannot be oxidized in vacuum at lower temperatures because of the absence of the desired oxygen in a vacuum. Further reduction of the sample cannot occur as well because decreasing the temperature can only lead to a decrease of the equilibrium concentration of V_O but not to an increase.

At definite pressure and annealing temperature, T_a , there exists a definite equilibrium concentration of V_O . We emphasize that this concentration can be thought to be in equilibrium if T_a is high enough to allow the diffusion processes to end in a few hours during which one makes the thermal treatments of the sample. When further decreasing the temperature in vacuum the concentration of V_O cannot change because of the above-mentioned circumstances and, because of this, it remains constant. Hence one may reduce a sample at a high temperature and, further, measure the conductivity at lower temperatures in vacuum. In this case the concentration of the main point defects, V_O , would be a constant and the experimental curves should be reproducible. We will show here how it is possible to evaluate the energies of the trap levels connected with V_O .

It should be noted that in our procedure much attention has been concentrated on the measurement time of each of the points of the temperature–conductivity plot. Indeed measuring the points is accompanied by some restoration processes. These processes are of two types. The first is connected with the relaxation of the electron subsystem and local lattice distortion near point defects (e.g., V_O). The second can stem from changing the concentration of the point defects. It is obvious that the first process is much faster in comparison with the second. Indeed, at 900 K, SrTiO₃ and BaTiO₃ ceramics require $(1-3) \times 10^5$ s for full equilibration [11] whereas, at the same temperature, the period of time for the conductivity measurement does not exceed 10^2 s after an equilibrium V_O concentration has been achieved at this or a higher temperature. The former figure is the result of a careful experimental investigation of oxygen diffusion in the perovskite-type lattice. The latter figure is the result of our experience. It is based on the evidence that, after the above-mentioned period of time, conductivity does not change within the experimental error (usually 3–4%). As the temperature lowers the difference between the measuring and defect equilibrium restoration times increases dramatically. While, for example, at 600 K, the former does not exceed 10^3 s, the latter (estimated using the oxygen diffusion coefficient value obtained by the extrapolation of data from [10] to $T = 600$ K) is of the order of 10^{11} s. This estimation is consistent with the conclusion of [9] that, in the temperature range below approximately 600 K, the changes of charge carrier concentrations in titanates are only the result of changes in the degree of the ionization of defects but not the result of changes in the total concentrations of the defects.

If full equilibration was achieved at each of the measuring points then the slope of the logarithm of conductivity against reverse temperature would correspond to the sum of the electron trapping energy, W_t , formation energy of V_O , W_f , and the activation energy of mobility, W_μ . It will be shown later, that in the OPFs studied, W_μ can be neglected as compared to W_t . As in the course of the experiment the concentration of V_O does not change, the energy of the formation of V_O should not be taken into account. If one took it into account then the total activation energy of carriers in the conduction band would be of the order of a few electronvolts (the known values of W_f are almost the same for all the perovskites under consideration, namely 5.4–6.0 eV for SrTiO₃ [16, 17], BaTiO₃ [9, 18] and KTaO₃ [19]). In fact we observed only small activation energies of the order of a few tenths of an electronvolt. This indirectly supports our assumption that the time required for the restoration of the equilibrium concentration of V_O is much longer than the measuring time under the experimental conditions used. However, we should emphasize that the measuring time is longer than the electron and local lattice relaxation time. Additional support for this assumption gives evidence of the depletion of the donor's levels in our experiment. It is obvious that if the concentration of the point defects was not a constant then the depletion region would not be seen.

It should be mentioned that, for the present investigation, only the donor/acceptor compensation ratio but not the absolute values of either the donor or acceptor concentration

are of importance. So the initial defect structure of a specimen as well as the non-controllable impurity concentration are of minor significance. We used polycrystalline samples of OPFs because they were much easier to prepare and the kinetics of defect equilibrium restoration in ceramics is usually faster than in a single crystal [11].

A few words should be said regarding the use of expressions for the conductivity treatment having kT and $2kT$ in the Boltzmann distribution function. It is well known [8] that, in semiconductors having both the donor and acceptor states, the following relations between the donor and acceptor concentrations can be realized:

1. $2N_d < N_a$
2. $0 < (2N_d - N_a) < N_d$
 - 2.1. $0 < (2N_d - N_a) \ll N_d$
 - 2.2. $0 < (2N_d - N_a) \approx N_d$
3. $N_d < (2N_d - N_a)$

where, in our case, N_d is the V_O concentration while N_a is the concentration of singly-charged (for the sake of definiteness) acceptors.

In the first case electric conductivity is p-type, while in the second and third cases it is n-type. In the second case, the first (deep) V_O level is partially occupied while the second (shallow) level is empty. In the third case the latter is already partially occupied. It should be noted that there are two extremely different situations in the second case (2.1 and 2.2). The first one corresponds to the strong compensation of donors and acceptors while the second situation deals with the weak compensation.

It is well known that, when the strong compensation occurs, the electron concentration in the conduction bands is given by the following expression

$$n \sim \exp\left(-\frac{W_1}{kT}\right) \quad (1)$$

where W_1 is the thermal ionization potential of a point defect. The other dependence is valid when the compensation is weak

$$n \sim \exp\left(-\frac{W_1}{2kT}\right). \quad (2)$$

Thereby, while going from the case 2.1 to 2.2, the effective ionization potential decreases twice. In the following it will be shown that all these dependences can be observed experimentally in OPFs if one uses the special treatment procedure.

In the present work we study the temperature dependence of the electric conductivity σ , in several OPFs including the classic objects of theoretical calculations such as SrTiO_3 and KTaO_3 . The polycrystalline samples were converted into states with strong and weak degrees of the donor/acceptor compensation ratio by means of the reduction and oxidation treatment. In either of these states the activation energy of the donor level corresponding to the singly-charged V_O was determined from the temperature dependence of σ with high degree of reliability.

The structure of the paper is as follows. The second section is devoted to a characterization of the samples and experimental methods in use. The results of the experiments are represented in section 3. This section is divided into three subsections: experiments on titanates, a theoretical treatment of the data for titanates and experiments on $A^{1+}B^{5+}O_3$. Then we discuss the results obtained in the light of the model proposed in Part I [1].

2. Preparation and characterization of the samples

The ceramic ABO_3 samples were prepared by using high-purity materials. The calculated quantities of the A -element carbonate and the B -element oxide were mixed thoroughly in an agate mortar in the presence of ethyl alcohol. Then the synthesis was carried out at 1100 to 1200 °C for titanates and at 750 to 850 °C for $A^{1+}B^{5+}O_3$ compounds. The synthesis was performed in two 4 h long stages. After each stage the product of the reaction was crushed and mixed in an agate mortar as described above.

The ceramic samples were pressed in the form of disks of 5 to 15 mm in diameter at 100 MPa. The sintering was carried out at 1300–1400 °C. Pellets were placed on a Pt foil. The obtained ceramics had a density of about 93–95% of the theoretical density. The x-ray analysis revealed the absence of non-perovskite phases.

Rectangular plates (typically 4 mm × 4 mm × 1 mm) were cut from the pellets for the electric conductivity measurements. Electrodes were applied to the large edges by firing the Pt paste or by rubbing the In–Ga alloy.

The thermo-emf measurements were carried out in air at temperatures above 400–500 °C when the sample's resistance became low enough. Thermo emf was measured by an electrometer at a temperature difference between the opposite edges of 20–30 °C. To eliminate the effect of thermostimulated current, prior to measurements, the samples were heated up to the maximum temperature of the measurements and the emf was measured in the course of the consequent cooling. The temperature at each measuring point was stabilized within ± 0.5 °C accuracy and the thermo-emf signal was detected repeatedly three to five times at different signs of the temperature gradient until stable steady-state values were obtained.

The results of thermo-emf measurements (figure 1) show that, for the $ATiO_3$ samples above 500 °C, the Seebeck coefficient α is positive and approximately linearly decreases with temperature. In $A^{1+}B^{5+}O_3$ compounds, α is substantially smaller than in titanates and the $\alpha(T)$ dependence is more complex. In the high-temperature region, all the $A^{1+}B^{5+}O_3$

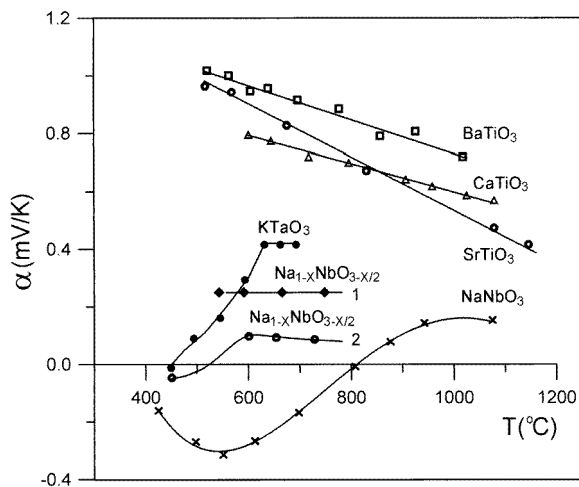


Figure 1. The temperature dependences of Seebeck coefficient α , for the investigated OPFs. 1. NaNbO_3 reduced in vacuum at 1000 °C for 2 h and then oxidized in air at 800 °C for 2 h. 2. $\text{Na}_{0.95}\text{NbO}_{2.75}$ ceramic obtained by the sintering of non-stoichiometric mixture of components.

samples had p-type conductivity. The decreasing temperature led to a change of the type of conductivity, from p to n.

Relatively low values of α in $A^{1+}B^{5+}O_3$ compounds, as compared to ones in the $ATiO_3$ oxides, are likely to be caused by a higher degree of the donor/acceptor compensation in $A^{1+}B^{5+}O_3$. One of the reasons for such an explanation may be the easier formation of V_A in $A^{1+}B^{5+}O_3$. We will return to this question at the end of this section in connection with the effect of the reduction temperature on the conductivity of OPFs.

Our results of thermo-emf measurements are consistent with numerous data from the literature (see, e.g., [2, 12–14, 20]). All the references reported that nominally pure OPFs contain an excess of acceptors with respect to donors. The origin of these acceptor states is a topic for discussion [2, 20]. Nevertheless it is common to change the degree of the donor/acceptor compensation by changing the oxygen vacancy concentration. To do this we used the annealing in vacuum with a residual pressure of about 10^{-1} Pa.

The samples were placed in a horizontal vacuum ceramic tube. This tube was heated in a furnace to the annealing temperature, T_a , at a rate of 500°C h^{-1} . The annealing time was 2–4 h for $A^{1+}B^{5+}O_3$ and 1–2 h for $ATiO_3$. The increase of this time did not significantly change the σ values at room temperature. In order to fix the defect structure formed as a result of annealing, the samples were quenched by pulling the ceramic capsule with the specimens, connected by a piece of steel, out of the hot zone of the furnace with the help of a magnet. After cooling the samples were provided with electrodes by rubbing with In–Ga alloy and σ values were measured at room temperature. For the sake of reproducibility the investigation of the $\sigma(T_a)$ dependence for each oxide was performed by using samples cut from the same pellet.

The results obtained are shown in figure 2. It can be seen that, for titanates, conductivity increases with T_a although, for $BaTiO_3$, the $\sigma(T_a)$ dependence has a tendency to saturate. The rapidly increasing portions of the $\sigma(T_a)$ curves for $SrTiO_3$ and $CaTiO_3$ are shifted to

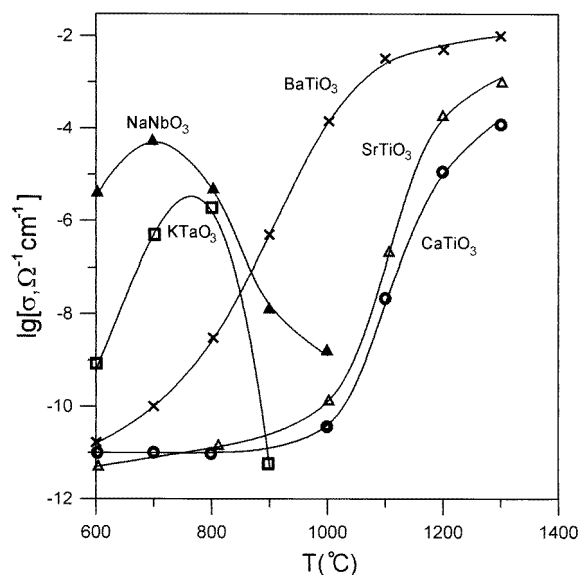


Figure 2. The electric conductivity measured at room temperature as a function of the vacuum annealing temperature.

high temperatures, as compared to BaTiO₃, hence the saturation portions are not observed within the investigated temperature interval.

For $A^{1+}B^{5+}O_3$ oxides the character of the $\sigma(T_a)$ dependence is extremely different from that for titanates. At low annealing temperatures σ increases with T_a , after that it reaches the maximum at $T_a \approx 800^\circ\text{C}$ and then decreases. The decrease of σ above 800°C is likely to be caused by the formation of not only V_O but also V_A . The latter form acceptor levels in the band gap. This assumption is consistent with the data of chemical, thermogravimetric and x-ray analysis showing that, during vacuum annealing, KNbO₃ and NaNbO₃ lose only oxygen in the region $400\text{--}800^\circ\text{C}$, while above 800°C intensive evaporation of alkali metal oxide takes place [21–23]. As a result a defect solid solution of the $[A_{1-x}(V_A)_x]Nb[O_{3-x/2}(V_O)_{x/2}]$ type is formed. In the case of NaNbO₃ this solid solution has the perovskite structure up to $x \approx 0.1$. This explanation is consistent with changes in the colour of $A^{1+}B^{5+}O_3$ specimens which resulted from vacuum annealing. The sintered in air ceramics of ATiO₃ and $A^{1+}B^{5+}O_3$ are light-yellow in colour. As the vacuum annealing temperature is increased the colour of the titanates changes to grey, dark-grey and finally to black. The colour of $A^{1+}B^{5+}O_3$ specimens changed with T_a in a similar way up to $T_a \approx 800^\circ\text{C}$. Above this temperature the colour of the specimens became less dark and a yellowish tint appeared. The intensity of this tint increased with T_a . After annealing in vacuum at $T_a = 1100^\circ\text{C}$ the NaNbO₃ ceramics had a yellowish-brown colour.

Figure 1 shows the thermo-emf of NaNbO₃ annealed in vacuum at 1000°C for 2 h and then oxidized in air at 800°C for 2 h (curve 7). This sample has the stable p-type conductivity in the temperature region below 700°C where air-sintered nominally stoichiometric ceramics have n-type conductivity. Moreover the Seebeck coefficient of the specimen annealed in vacuum proved to be substantially larger as compared to the non-annealed one. This result shows that the effective acceptor concentration increases after vacuum annealing at $T_a \geq 800^\circ\text{C}$, that is in accordance with the proposed scheme of the defect formation.

The above explanation is also consistent with the thermo-emf data for the non-stoichiometric NaNbO₃ ceramics in which the Na₂O deficiency was achieved by using the non-stoichiometric mixture of Na₂CO₃ and Nb₂O₅ taken in the molar ratio $\text{Na}_2\text{O}/\text{Nb}_2\text{O}_5 = 0.95$ [22]. In this specimen the transition from the n- to p-type of conductivity took place at significantly lower temperature than in nominally stoichiometric NaNbO₃ ceramics (figure 1, curve 8).

The decrease of the $A^{1+}B^{5+}O_3$ conductivity caused by the vacuum treatment at high T_a may be compensated by appropriate donor doping. Figure 3 shows the effect of vacuum annealing on the conductivity of Ca-doped NaNbO₃ ceramics. Though the increase of T_a leads to the decrease of the σ values both in the doped and undoped ceramics, σ increases dramatically with Ca content. This fact supports the assumption that Na₂O evaporation increases the acceptor's concentration.

3. Investigation of the temperature dependence of the electrical conductivity

3.1. Titanates

The conductivity of the samples with fired platinum electrodes was measured in a weak electric field ($E \leq 10 \text{ V cm}^{-1}$) with the help of an electrometer. At every measuring point the linearity of the volt-ampere characteristic and fulfilment of the Ohm law was checked. To avoid the influence of the thermostimulated current on the result, prior to measurements, the samples were heated up to the maximum temperature of our study and the temperature

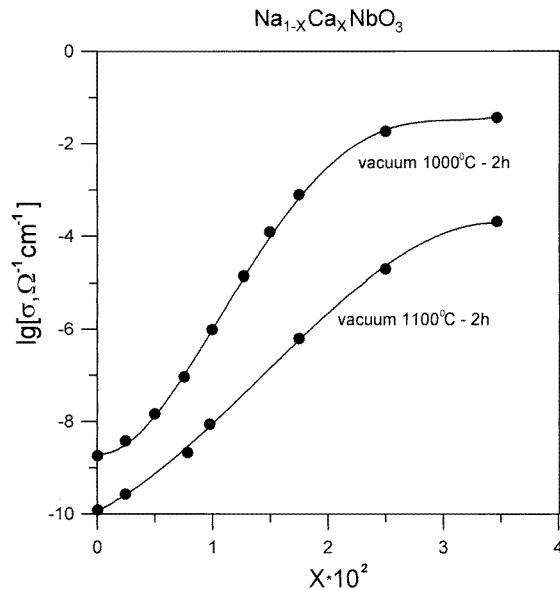


Figure 3. The effect of vacuum annealing for 2 h at 1000 and 1100 °C on the electric conductivity of $\text{Na}_{1-x}\text{Ca}_x\text{NbO}_3$ measured at room temperature.

dependence of σ was measured in the course of cooling. At every measuring point the temperature was stabilized within $\pm 0.5^\circ\text{C}$ accuracy and steady-state values of the current were used for the calculation of σ .

After measuring the $\sigma(T)$ in air the samples were placed into a vacuum measuring furnace. The initial heating was usually performed up to 750°C in vacuum with the residual pressure 10^{-1} Pa. The samples were annealed at this temperature for 1 h, then the temperature dependences of σ were measured in vacuum in the course of cooling and subsequent heating. The curves obtained during cooling and further heating were found to be identical, that is the $\log \sigma = f(1/T)$ dependences were reproducible. This fact indicates that the 'frozen' non-equilibrium concentration of oxygen vacancies does not change during measurements, i.e. the condition of constant composition is fulfilled. New stable defect states of the specimens (with higher V_O contents) were achieved by increasing the annealing temperature by 50 K steps. After each of the steps the $\sigma(T)$ dependence was measured again under cooling and subsequent heating. As a result for each sample a set of $\log \sigma = f(1/T)$ curves was obtained with different degrees of the donor/acceptor compensation (figures 4–6).

It should be mentioned that, within the described method, the reproducibility of $\log \sigma = f(1/T)$ curves was observed only at temperatures below approximately $900\text{--}930^\circ\text{C}$ (full curves in figures 4–6). At higher temperatures the equilibrium between the sample and ambient is likely to be achieved very quickly and one cannot obtain a non-varying 'frozen' concentration of oxygen vacancies during measurements, i.e. to fulfil the condition of constant composition. Indeed, using the oxygen diffusion coefficient data from [10] gives a value of about 10^2 s for the equilibrium restoration time of the V_O concentration at $T = 1200$ K which is of the same order as the conductivity measuring time.

The preliminary investigation showed that the increase of the degree of the vacuum reduction causes a shift of the high-temperature linear portion of the $\log \sigma = f(1/T)$

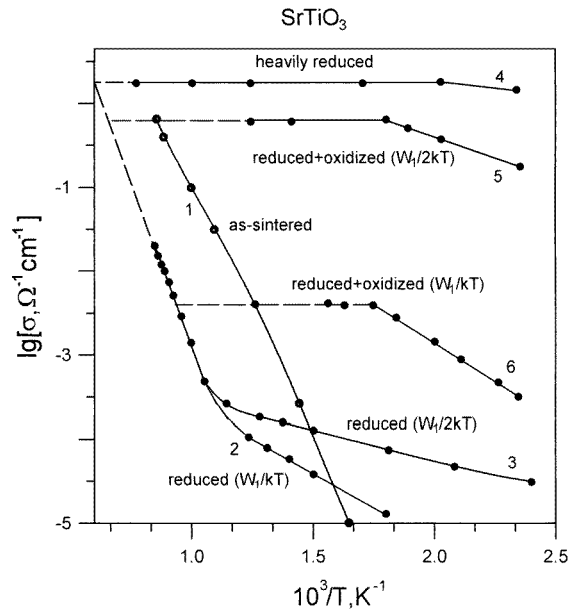


Figure 4. $\log \sigma = f(1/T)$ dependences for SrTiO_3 measured in air (1, 5, 6) and in vacuum (2–4). 1. As-sintered sample. 2. After vacuum annealing at 750°C for 1 h (strong degree of donor/acceptor compensation $\sigma \sim e^{-w_1/kT}$). 3. After subsequent vacuum annealing at 800°C for 1 h (weak degree of donor/acceptor compensation $\sigma \sim e^{-w_1/2kT}$). 4. After subsequent vacuum annealing at 1300°C for 3 h (heavily reduced sample). 5. After oxidizing the heavily reduced sample by heating it in air up to 900°C (weak degree of donor/acceptor compensation $\sigma \sim e^{-w_1/2kT}$). 6. After subsequent oxidation of the same sample by heating it in air up to 700°C (strong degree of donor/acceptor compensation $\sigma \sim e^{-w_1/kT}$).

dependence to lower σ values as compared with the similar dependence measured in air for as-sintered samples (curves 1 and 2 in figures 4–6). This shift is accompanied by the increase of the slope of the high-temperature portion of the $\log \sigma = f(1/T)$ dependence. At higher degrees of reduction both the σ value and the slope of the high-temperature portion did not change significantly (curves 2–4 in figures 4–6).

The values of σ and the slope of the high-temperature portion of the $\log \sigma = f(1/T)$ curves measured in vacuum agree well with the $\log \sigma_m = f(1/T)$ dependences obtained for BaTiO_3 and SrTiO_3 in [12–14], where σ_m is the minimum value of the equilibrium conductivity taken from conductivity–partial oxygen pressure dependence. Thus σ_m is the σ value corresponding to the case of the strong donor/acceptor compensation. These results are consistent with the theoretical predictions [8] that the temperature of the transition from extrinsic to intrinsic conductivity decreases with the increase of the donor/acceptor compensation degree. Thus the high-temperature portions of the $\log \sigma = f(1/T)$ dependences measured in vacuum are likely to correspond to the intrinsic conductivity and their slopes correspond to one half of the band gap (E_g) value. The E_g values for titanates, shown in table 1, determined from the data shown in figures 4–6, agree well with the values obtained from experiments on optical absorption, photoconductivity [2] and from the $\log \sigma_m = f(1/T)$ dependences [12–14].

It is of interest to note that the results obtained show that the state with high degree of the donor/acceptor compensation is stable enough, though according to theoretical calculations [24] the condition of the strong compensation is very rigid.

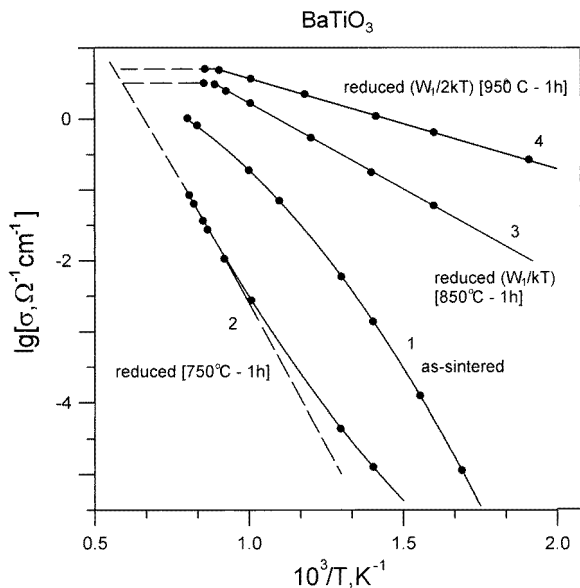


Figure 5. $\log \sigma = f(1/T)$ dependences for BaTiO_3 measured in air (1) and in vacuum (2–4). 1. As-sintered sample. 2. After vacuum annealing at 750°C for 1 h. 3. After subsequent vacuum annealing at 850°C for 1 h (strong degree of donor/acceptor compensation $\sigma \sim e^{-w_1/kT}$). 4. After subsequent vacuum annealing at 950°C for 1 h (weak degree of donor/acceptor compensation $\sigma \sim e^{-w_1/2kT}$).

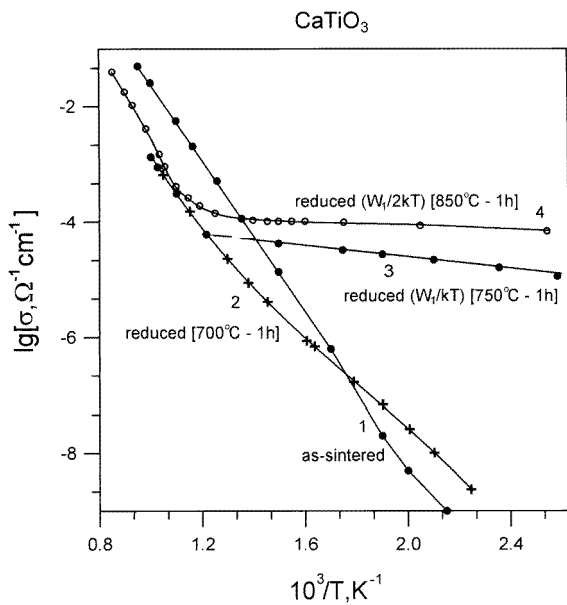


Figure 6. $\log \sigma = f(1/T)$ dependences for CaTiO_3 measured in air (1) and in vacuum (2–4). 1. As-sintered sample. 2. After vacuum annealing at 700°C for 1 h. 3. After subsequent vacuum annealing at 750°C for 1 h (strong degree of donor/acceptor compensation $\sigma \sim e^{-w_1/kT}$). 4. After subsequent vacuum annealing at 850°C for 1 h (weak degree of donor/acceptor compensation $\sigma \sim e^{-w_1/2kT}$).

Table 1. Experimental band gap E_g values, experimental (ΔW_e) and calculated in [1] (ΔW_c) values of a singly-charged oxygen vacancy level activation energy and values of polaron energy ΔE_p (from [33]) for the investigated OPFs.

OPFs	E_g (eV)	ΔW_e (eV)	ΔW_c (eV)	ΔE_p (eV)
BaTiO ₃	3.2–3.3	0.5–0.6	0.15	0.35
SrTiO ₃	3.3–3.4	0.3–0.4	0.14	0.15
CaTiO ₃	3.1–3.2	0.1–0.2	0.14	
NaNbO ₃		0.5–0.6	0.11	0.4
KTaO ₃		0.1–0.2	0.10	

The change of the donor/acceptor compensation degree due to vacuum treatment of the titanate ceramics (the transition from the strong to weak compensation) is confirmed by the change of the slope of the low-temperature portion of the $\log \sigma = f(1/T)$ dependences by a factor of two (figures 4–6).

For SrTiO₃ the effect of oxidation on the slope of the $\log \sigma = f(1/T)$ dependence was also studied. The temperature dependences of σ were measured in air at relatively moderate temperatures where oxidation was not observed. Special attention was paid to the elucidation of the formation of barrier layers near the electrode surface of the specimen. In some cases the linearity of the volt–ampere characteristic after oxidation was restored by applying a short pulse of high voltage (300–600 V). The results obtained are shown in figure 4. Curve 4 represents the temperature dependence of σ for a heavily reduced specimen (the initial state). Curve 5 was measured after oxidation of the specimen by heating it in air up to 900 °C and curve 6 was produced after subsequent heating in air up to 700 °C. As a result of oxidation the slope of the low-temperature portion of the $\log \sigma = f(1/T)$ dependence increased by a factor of two (figure 4, curves 5 and 6). The activation energy calculated from the slope of either dependences 3 and 5 by using formula (2) or dependences 2 and 6 by using expression (1) is practically the same (0.3–0.4 eV) and agrees well with the calculated value $W = 0.2–0.4$ eV (see [1]).

3.2. Theoretical treatment of the experimental data for titanates

The experimental results obtained allowed us to evaluate a number of parameters for SrTiO₃. The calculation was performed in the following manner. The slopes of the low-temperature portions of $\log \sigma = f(1/T)$ dependences in figure 4 give the activation energy values of about 0.33 eV. The increase of the $\log \sigma = f(1/T)$ curve slope can be thought to be a switch from the case of the weakly compensated donors to the case of the strongly compensated ones.

The horizontal portions of $\log \sigma = f(1/T)$ dependences can be considered as a result of donor depletion. All the carriers other than those compensated by acceptors are thermally excited to the conduction band. If the region of depletion was observed in a fixed sample the evaluation of N_a and N_d would become available in a simple way.

The V_O can accept two electrons. As a consequence the system with the vacancy concentration N_d has $2N_d$ additional electrons in the unity volume. On account of the compensation by acceptors $2N_d - N_a$ electrons are localized on V_O at $T = 0$. If the inequality

$$N_a < (2N_d - N_a) < N_d \quad (3)$$

is valid then the lower level of V_O with a depth of several tenths of an eV is filled. If the

following is valid

$$(2N_d - N_a) > N_d \quad (4)$$

then the upper level of V_O becomes filled. The depth of this level is about 0.01 eV. So one could expect that the thermal activation of this level takes place at low temperature.

In such a case (the strongly reduced sample) the carrier concentration is a constant and equals $N_d - N_a$. Consequently, the ability to observe the temperature dependence of conductivity controlled by the second ionization energy is restricted by the very rigid restriction (4). Considering the region of depletion (figure 4, curves 4, 5 and 6) one can obtain the electron's concentration, n , in the conduction band by the expression

$$\sigma = |e|\mu_n n \quad (5)$$

where e is the electron charge and μ_n is the electron mobility. Regarding the temperature dependence of the electron mobility it should be noted that, according to experimental data [25], the activation energy of the electron mobility is very small: W_μ is of 0.023 eV in n-type barium titanate and is likely to be even less in n-type strontium titanate. Due to this fact we neglected the temperature dependence in our computation. Assuming μ_n to equal $5 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ [15] we found

$$n(4) = 2.6 \times 10^{22} \text{ m}^{-3} \quad (6)$$

$$n(5) = 6.0 \times 10^{21} \text{ m}^{-3} \quad (7)$$

$$n(6) = 5.4 \times 10^{19} \text{ m}^{-3}. \quad (8)$$

The numbers in the brackets correspond to the curve numbers in figure 4. The data obtained can be expressed via the defect's concentrations as follows

$$n(4) = N_d - N_a. \quad (9)$$

(Here the higher level of V_O is partially filled at $T = 0$.)

$$n(5) = 2N_d - N_a \approx N_d. \quad (10)$$

(The lower level of V_O is weakly compensated while the higher level is empty at $T = 0$.) With the use of (3) to (9) we evaluated the acceptor concentration and found it to equal

$$N_a \approx 6 \times 10^{21} \text{ m}^{-3}.$$

To justify this evaluation we performed the computation of the $\log \sigma = f(1/T)$ dependence over a wide range of temperature and compared the results with those obtained with the experiment.

The calculation was carried out in the framework of the statistics of carriers on the multiple-charged centres [8]. The following is devoted to a brief description of the theory. It was supposed that

$$\sigma = |e| \sum_i \mu_i n_i \quad (11)$$

where μ_i is the mobility for carriers of the type i and n_i is the concentration of these carriers.

The concentration of electrons in the conduction band and holes in the valence band are given by

$$n = \int_{\text{conduction band}} \rho_c(E) f(E, T) dE \quad (12)$$

$$p = \int_{\text{valence band}} \rho_v(E) f_p(E, T) dE \quad (13)$$

where ρ_c and ρ_v are the density of states in the bands; f and f_p are the Fermi–Dirac distributions for the electrons and holes

$$f(E, T) = \left[1 + \exp\left(\frac{E - F}{kT}\right) \right]^{-1} \quad (14)$$

$$f_p = 1 - f \quad (15)$$

F is the electrochemical potential and k is the Boltzmann constant. The F value can be found from the electroneutrality condition at $T = \text{constant}$

$$n(F, T) + n_t(F, T) - p(F, T) - p_t(F, T) = 0 \quad (16)$$

where n and p are the electron and hole concentrations in the conduction and valence bands while n_t and p_t are the concentrations of the electrons and holes bound to the donor and acceptor centres, respectively. We assume the donor centres (the oxygen vacancy) to have both the shallow and comparatively deep levels. Because of this circumstance we are to use the grand canonical distribution together with the mean field theory. Within this theory the probability for j electrons to be on a multiple charged centre is given by the expression

$$f_m^{(j)} = A \exp \frac{jF - E_m^{(j)}}{kT} \quad (17)$$

where $E_m^{(j)}$ is the energy of the m th quantum state of the centre. The constant A can be calculated from the normalization rule

$$\frac{1}{A} = \sum_{j=0}^M \sum_m \exp \frac{jF - E_m^{(j)}}{kT} \quad (18)$$

where M is the maximal number of electrons that the defect can accept. If the centre with j electrons has excited states, it is convenient to write

$$E_m^{(j)} = E^{(j)} + \varepsilon_{jm} \quad (m = 1, 2, \dots). \quad (19)$$

Here $E^{(j)}$ is the energy of the centre with j electrons in the ground state, ε_{jm} is the energy of the m th excited state (with respect to the ground state). The energy level of the point-defect, E_j , is related to the many-electron energy, $E^{(j)}$, as follows

$$E^{(j)} = E_1 + E_2 + E_3 + \dots + E_j. \quad (20)$$

The probability of finding the centre in a state with j electrons is defined by the equation

$$f^{(j)} = \sum_m f_m^{(j)}. \quad (21)$$

Let us introduce the degree of the degeneration, β_{jm} , for various excited states of the centre with j electrons. After that, from (17)–(19), one has

$$f^{(j)} = \frac{g_j \exp((jF - E^j)/kT)}{\sum_{j=0}^M g_j \exp((jF - E^{(j)})/kT)} \quad (22)$$

where

$$g_j = \beta_j + \sum_m \beta_{jm} \exp\left(-\frac{\varepsilon_{jm}}{kT}\right). \quad (23)$$

Here β_j is the degeneration of the ground state.

For the multiple-charged donors having M electrons in the electroneutral state the positive charge can be defined as

$$p_t = N_d \sum_{j=1}^{M-1} (M - j) f^{(j)}. \quad (24)$$

Similarly, for the multiple-charged acceptors which can accept M holes to become electroneutral the negative charge is

$$n_t = N_a \sum_{j=1}^M j f^{(j)} \quad (25)$$

where N_d and N_a are the donor and acceptor concentrations, respectively.

Equations (12) to (25) are sufficient for determining F and the carrier concentrations. After obtaining these quantities one can calculate $\sigma(T)$ on the basis of equation (11). Below we represent the parameters and results of the particular calculation for SrTiO₃.

The density of states in the conduction band of OPFs is well known [26]

$$\rho_c(E) = \frac{6|E|}{\pi^2 D^2} K'(k) \quad (26)$$

where $K(k)$ is the full elliptic integral of the first kind,

$$K'(k) = K(\sqrt{1-k^2}) \quad k = \frac{4D^2 - E^2 + \Delta^2}{4D^2}.$$

Here D and Δ are the (pd π)-type hopping integral and the half width of the forbidden gap, respectively.

From (16) and (12) one can obtain the following evaluation for N_c

$$N_c = \frac{3\Delta kT}{\pi a^3 D^2}.$$

Concerning N_v , it can only be mentioned that it must be somewhat higher than N_c due to the existence of non-bonding states at the top of the valence band. Knowing the number of the non-bonding states (six) one can write the inequality

$$N_v < 6/a^3 \quad (27)$$

where a is the lattice constant. In the computation we used the following assumptions

$$\mu_n = \mu_p = 5 \times 10^{-4} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$$

$$\rho_v(E) = 2\rho_c(-E)$$

$$M_a = 1 \quad M_d = 2 \quad g_a = 1 \quad g_d = 12$$

$$E_1^a = -1.0 \text{ eV} \quad E_1^d = 1.35 \text{ eV} \quad E_2^d = 1.65 \text{ eV} \quad D = -1.12 \text{ eV}$$

$$\Delta = 1.70 \text{ eV}.$$

Here the upper index refers to the acceptor (a) and donor (d) levels, respectively. With these assumptions taken into account we have $N_d = 3.2 \times 10^{22} \text{ m}^{-3}$ (curve 4, figure 4); $N_d = 6.0 \times 10^{21} \text{ m}^{-3}$ (curve 5) and $N_d = 3.0 \times 10^{21} \text{ m}^{-3}$ (curve 6).

All acceptors were supposed to be singly-charged and non-degenerated and their energies were taken rather arbitrarily. Only the total acceptor concentration, N_a , had an impact on the result (we only studied the case of the n-type conductivity which is true for the reduced samples of strontium titanate). The N_a and N_d obtained were found to satisfy equations (4) to (10). The energy parameters for V_O in SrTiO₃ were taken in the same manner as in [1] and in [24]. It must be noted that, in the references cited, the energy levels of the V_O were calculated with respect to the boundary of the conduction band. In the present notation it corresponds to the quantity $\Delta - E_i^d$, i.e. in our case 0.35 eV and 0.05 eV. At the parameters described above the solutions of (12) to (16) faithfully reproduce the experimental curves 4, 5 and 6 in figure 4. So the use of the theoretical data regarding the electronic structure of V_O allows the defect concentrations in perovskites to be evaluated rather exactly.

3.3. $A^{1+}B^{5+}O_3$ compounds

As already mentioned, during vacuum annealing at $T_a \geq 800^\circ\text{C}$ the $A^{1+}B^{5+}O_3$ compounds lose not only oxygen but also alkali metal ions. As the result of this fact the procedure for obtaining the set of the $\log \sigma = f(1/T)$ curves used in the case of titanates is not applicable to the $A^{1+}B^{5+}O_3$ oxides. Therefore in order to determine the activation energy of the V_O levels in the $A^{1+}B^{5+}O_3$ compounds we investigated the $\sigma(T)$ dependences of ceramic samples annealed in vacuum at temperatures not exceeding the temperature of the maximum in the $\sigma(T_a)$ dependence. Measurements were carried out in air using electrodes from rubbed In–Ga alloy.

According to differential thermal analysis data [22,23], the oxidation of reduced NaNbO_3 ceramics in air begins at $200\text{--}250^\circ\text{C}$ at a heating rate of 15 K min^{-1} , i.e. at substantially lower temperatures than in titanates. One may expect that at lower heating rate oxidation begins even at lower temperatures. In order to elucidate the influence of oxidation on the result, the upper border of the measured interval was limited by $100\text{--}150^\circ\text{C}$. Prior to first measurement a sample was heated up to the maximal temperature. The $\sigma(T)$ curves were reproducible both for heating and cooling the sample.

Figure 7 shows the $\log \sigma = f(1/T)$ dependences for KTaO_3 ceramics. The slope of the $\log \sigma = f(1/T)$ dependence decreases by a factor of two with the increase of T_a from 700 to 800°C (figure 7 curves 1 and 2).

The slope of the $\log \sigma = f(1/T)$ dependence for the most conductive vacuum-reduced sample of nominally pure NaNbO_3 was practically the same as in the less conductive samples (figure 8, curve 1). We supposed that under the experimental conditions employed it is impossible to obtain a concentration of donor centres in NaNbO_3 large enough to achieve the state with the weak degree of the donor/acceptor compensation. Therefore we investigated the $\log \sigma = f(1/T)$ dependences of Ca-doped NaNbO_3 ceramics $\text{Na}_{1-x}\text{Ca}_x\text{NbO}_3$ reduced

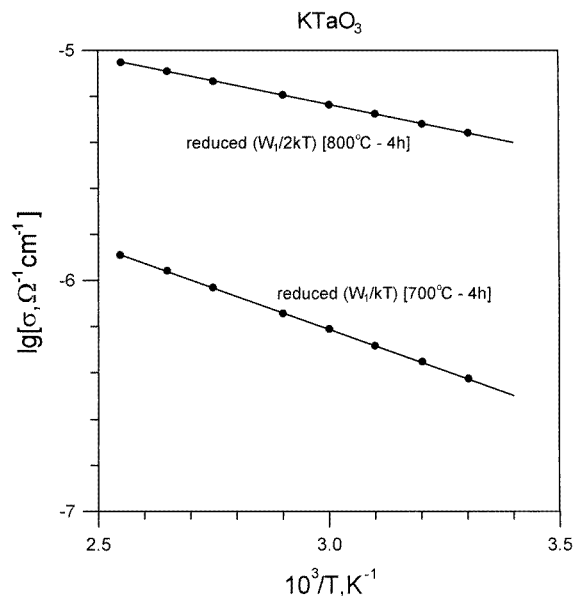


Figure 7. $\log \sigma = f(1/T)$ dependences for KTaO_3 measured in air after vacuum annealing for 4 h at 700°C and 800°C .

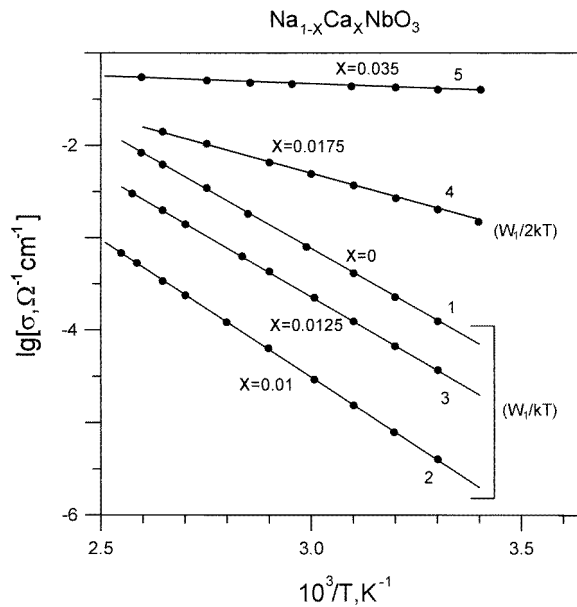


Figure 8. $\log \sigma = f(1/T)$ dependences for NaNbO_3 (1) and $\text{Na}_{1-x}\text{Ca}_x\text{NbO}_3$ (2–5) measured in air after vacuum annealing for 4 h at 800°C (1) and 1000°C for 2 h (2–5). 2. $x = 0.01$; 3. $x = 0.0125$; 4. $x = 0.0175$; 5. $x = 0.035$.

in vacuum at 1000°C for 2 h. For such ceramics the σ values at room temperature increase dramatically with x (figure 3). For the samples with $0 < x \leq 0.015$ the increase of x is not accompanied by changes of the $\log \sigma = f(1/T)$ slope (figure 8, curves 2 and 3). The activation energy value calculated using expression (1) is about 0.55 eV, i.e. is the same as in the non-doped ceramics. The slope of the $\log \sigma = f(1/T)$ dependence for a sample with $x = 0.0175$ is smaller by a factor of two as compared to the samples with the lower x values. Such behaviour is likely to be caused by the transition to the state with the weak degree of the donor/acceptor compensation. For the samples with $x \geq 0.030$ the activation energy is found to be of about a few hundredths of an eV (figure 8, curve 5).

4. Discussion

The results obtained are consistent with the data from other investigators and show that there are two types of donor levels in reduced OPFs. The shallow one has the activation energy of several hundredths of an eV while for the deeper one it is of about several tenths of an eV. Based on the results of computations published in the first part of this work [1] we attribute the shallow level to the neutral V_O and the deeper one to the singly-charged V_O capturing an electron.

As we have mentioned the activation energies of several hundredths of an eV have been reported for heavily reduced perovskites in many works [2–7, 27]. Besides, there are several works in which the activation energies observed were similar to ours. For example, according to [28], BaTiO_3 ceramics reduced in vacuum at 700°C and 800°C had conductivity activation energies of about 0.5 eV (deduced using expression (1)). For the same ceramics reduced at 900°C the $\log \sigma = f(1/T)$ slope was approximately half that which is likely to be caused by a transition between the states with the strong and

weak degrees of the donor/acceptor compensation ratio. The activation energies of oxygen vacancy levels determined in [29] from the temperature dependence of the secondary electron emission current were of the order of 0.35–0.50 eV for both SrTiO₃ and BaTiO₃ vacuum-reduced single crystals. Investigations of thermostimulated currents spectra and volt–ampere characteristics in Ba_{0.4}Sr_{0.6}TiO₃ thin films revealed the trap energies distributed at 0.4–0.5 eV which were ascribed to oxygen vacancies [30]. In KTaO₃ crystals with different degrees of reduction, the investigation of thermostimulated currents revealed activation energies, the values 0.08 eV and 0.13–0.18 eV of which were supposed to correspond to the neutral and singly-charged V_O , respectively [31]. An activation energy of 0.55 eV was detected in NaNbO₃ crystals by the same method [32].

In the present study samples of several perovskites were prepared so that they proved to be in the states of both the strong and weak degree of the donor/acceptor compensation. A study of the temperature dependence of conductivity has given us the possibility to determine the energy of the lowest electronic level in the singly-charged V_O .

Table 1 collects the experimental values of the forbidden gap, E_g , the activation energies of the donor centres obtained with the use of the experimental treatment of the samples described in the present work ($\Delta W_e = \Delta W_1$) and the activation energies calculated in [1] without taking into account the polaronic effect (ΔW_c). The last column represents the polaron energies for several OPFs obtained experimentally in [33].

It is worth noting that for the given OPFs the same ΔW_e values were obtained irrespectively of the prehistory and initial defect structure (including impurities) of the samples. For example in the case of SrTiO₃ both the reduction of the as-sintered dielectric sample having p-type conductivity (curves 2 and 3 in figure 4) and oxidation of the heavily-reduced sample having n-type conductivity (curves 5 and 6 in figure 4) gave the same ΔW_e values. The same was true for nominally pure NaNbO₃ annealed in vacuum at temperatures where predominantly V_O were formed (curve 1 in figure 8) and for donor-doped NaNbO₃ (Na_{1-x}Ca_xNbO₃, $0 < x \leq 0.015$) annealed in vacuum at 1000 °C where both V_O and V_A were formed, the latter being acceptors (curves 2 and 3 in figure 8). These facts are in agreement with usual theory of semiconductors [8] according to which only the donor/acceptor ratio (not the absolute values of either the donor or acceptor concentration) has an impact on the temperature dependence of conductivity.

Experimentally determined ΔW_e includes both W_n and W_μ , the activation energies of carrier concentration and mobility, respectively. In turn, W_n includes both W_t , the desired trapping energy of electron at V_O , and W_f , the formation energy of V_O (activation energy for carrier formation by reduction). We have already mentioned that, under the experimental conditions used, the condition of constant composition was fulfilled and thus the influence of W_f was circumvented. Besides the reproducibility of the $\log \sigma = f(1/T)$ dependences in the course of heating and cooling there are some additional arguments supporting the fulfilment of the condition of constant composition in our experiments. The portions of the $\log \sigma = f(1/T)$ dependences with the desired slopes are observed at temperatures substantially lower than 600 K where, in titanates, changes of the total concentrations of the defects may be neglected [9]. Wide horizontal portions of $\log \sigma = f(1/T)$ dependences observed in some SrTiO₃ and BaTiO₃ samples are likely to be a result of donor depletion. The existence of donor depletion regions on the $\log \sigma = f(1/T)$ curves may also serve as evidence of the condition of constant composition fulfilment. The main reason for the constant composition is that the samples were, at first, thermally treated up to an equilibrium V_O concentration and, then, the measurements were made at lower temperatures in vacuum. This procedure does not allow the V_O concentration to change at cooling because of the circumstances mentioned in section 1. In other words, within the framework

of our experiment, the period of time needed for changing the V_O concentration is much higher than the measuring time while the measuring time is much higher than the electron and local lattice relaxation time. The fact that the curves obtained at cooling and heating coincided each with the other in some temperature interval supports the assumption that the V_O concentration did not change not only at cooling but also at heating.

Let us try to estimate the W_μ contribution into the measured ΔW_e values. In the OPFs studied the current carriers are likely to be small polarons [7, 25, 33–35]. According to existing models [34–36] at low temperatures small polarons move via a band mechanism and their mobility temperature dependence is non activated. At temperatures exceeding $\Theta_D/2$, where Θ_D is the Debye temperature, the transport mechanism changes to thermally activated hopping. The mobility activation energy in this case equals one half of the polaron energy. For NaNbO_3 Θ_D is about 1400 K [34], so at temperatures below 450 K, where the conductivity of NaNbO_3 was measured in the present study (see figure 8), the carrier mobility in this OPF seems to be non activated. The extensive studies of charge transport in BaTiO_3 and some other OPFs have shown [25, 27, 36] that in the samples with n-type conductivity the activation energy of the electron mobility is very small in comparison with the polaron energy extracted from optical measurements. The nature of this discrepancy is complex and was under discussion in [25, 27, 36]. Thus one may expect that the W_μ values for the reduced samples of all the OPFs investigated are much lower than the experimentally measured conductivity activation energies ΔW_e which are therefore close to the desired electron activation energy from the singly-charged oxygen vacancy level (assuming the condition of constant composition is fulfilled and the formation energy of the V_O contribution to W_n may be neglected). However, when calculating the electronic structure of V_O one should take into account the polaronic effect due to the well localized nature of an electron at a singly-charged V_O . This was a major point of Part I [1]. It can be seen that the difference between the values given in the third (ΔW_e) and fourth (ΔW_c) columns of table 1 is nicely fitted by the values in the last column (ΔE_p). This confirms the idea presented in Part I, that the interaction between the lattice polarization and the electron trapped by the vacancy, leads to a lowering of the energy levels of the singly-charged V_O . Indeed, the polaronic contribution vanishes if the electronic state of V_O is well delocalized.

Besides the electric measurements already mentioned, one can find some supporting data in optical measurements. For example in [37] it was shown that the reduction of cubic KTaO_3 leads to the appearance of local dipole distortions that can be associated with the dipole state of V_O . The same tendency is observed in the luminescence spectra.

5. Conclusions

The experimental study of OPFs carried out in the present work confirms the results obtained in Part I [1] theoretically. A special treatment of the as-sintered samples having the p-type of conductivity, i.e. containing an excess of acceptors, was employed. The oxygen vacancy concentration was varied by vacuum annealing so as to obtain the samples in the state with either a strong or weak degree of the donor/acceptor compensation.

The present experimental investigation has shown that the neutral V_O has a shallow level of several hundredths of an electronvolt. Owing to this the neutral V_O has to be ionized at not very high temperature, often even at room temperature. The singly-charged V_O already has a comparatively deep level with an energy of several tenths of an electronvolt.

The results of the investigation of the influence of the vacuum annealing temperature on the conductivity of the $A^{1+}B^{5+}O_3$ samples are consistent with the results of the calculation carried out in Part I of this work which predicted the acceptor character of the energy levels

formed in OPFs by the A-sited vacancies. Note that this point of view does not contradict the results of the computation performed in the framework of the shell model [20]. According to this computation holes are comparatively weakly bound to the Ba-vacancy in BaTiO₃. The same result was obtained in [1].

In conclusion we want to stress that the main object of our study was V_O . As the result of this we were generally interested in the n-type conductivity samples. Obtaining reliable information concerning V_O^+ was possible because these point defects are main in the n-type OPFs. The question regarding the nature of the main point defects in the p-type OPFs (or main carriers) is not so clear. New studies are required to answer this question.

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