

## Electrical properties of Nb-doped titanium dioxide TiO<sub>2</sub> at room temperature

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Nb-doped TiO<sub>2</sub> (0–15 at. % Nb) polycrystalline specimens were prepared by the sol-gel method. Below 10 at. % of Nb, materials were homogeneous and exhibited rutile structure, their lattice parameters changing with Nb concentration according to the Vegard's law. Above 10 at. % of Nb, the second phase TiNb<sub>2</sub>O<sub>7</sub> was formed, detected by X-ray diffractometry. Materials were heated at 1273 K for 3 h in air ( $p_{\text{O}_2} = 210$  kPa) and in flow of Ar + 3 vol. % H<sub>2</sub> gas mixture ( $p_{\text{O}_2} = 10^{-15}$  Pa) and then cooled down. Electrochemical impedance spectroscopy within the frequency range 0.01 Hz–2 MHz has been used to determine electrical properties of the materials. An equivalent circuit composed of a resistor  $R_{\text{gb}}$ , a capacitor  $C$  connected parallel and a resistor  $R_{\text{b}}$  connected in series, well represents the electrical properties of reduced samples. On the other hand, non-Debye elements should be taken into account in construction of the equivalent circuit of oxidized materials. The mechanism of the Nb incorporation has been proposed.

Key words: *titanium dioxide; Nb-doping; solid solution; defect structure; impedance spectroscopy*

### 1. Introduction

Titanium dioxide (rutile) has a wide range of applications due to its interesting electrical and photo-electrical properties [1, 2] determined by nonstoichiometry and related point defect structure. Metal ion doping (by both acceptor- or donor-type elements) can significantly modify these properties [1, 3–5]. High-temperature semiconducting properties of undoped [6, 7], acceptor- [3, 7, 8] or donor- [7, 9] doped TiO<sub>2</sub> have been the subject of numerous reports. On the other hand, little is known about the electrical properties of these materials at room temperature (i.e., at the conditions in which they are used as electrodes, electronic devices, etc.). The purpose of the pre-

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sent paper is to examine the effect of Nb doping on structural and electrical properties of polycrystalline  $\text{TiO}_2$  at room temperature.

## 2. Experimental

*Sample preparation.* Materials were prepared by thermal decomposition of oxide precursors. Titanium tetraisopropoxide,  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ , (Aldrich, 97 %) and niobium pentachloride,  $\text{NbCl}_5$ , (Aldrich, 99 %) were used as starting materials. Anhydrous  $\text{C}_2\text{H}_5\text{OH}$  was mixed with  $\text{H}_2\text{O}$  and  $\text{HCl}$  (as a catalyst) at 273 K and then added drop by drop to solution of  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$  in  $\text{C}_2\text{H}_5\text{OH}$  under continuous stirring at room temperature. The molar composition of the solution was  $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4/\text{C}_2\text{H}_5\text{OH}/\text{H}_2\text{O}/\text{HCl} = 1/8/5/0.02$ . The Nb-containing solution was prepared by dissolution of 4 g of  $\text{NbCl}_5$  in 100  $\text{cm}^3$  of anhydrous ethanol.

Both solutions were mixed by dropping a suitable amount of  $\text{NbCl}_5$  solution into stirred tetraisopropoxide solution at temperature close to 273 K. Time of sol-gel transformation varied from 1 day to 3 weeks, for undoped specimen and 15 at. % Nb-doped, respectively. After the evaporation of solvents, the remaining powders were dried in air (273–373 K), ground in an agate mortar and then calcined at 873 K during 2 h. Pellets were formed by uniaxial pressing under 100 MPa followed by isostatic pressing under 250 MPa and then sintered at 1600 K during 5 h in air.

*Impedance measurements.* The impedance measurements were performed using a frequency response analyser Solartron 1294. Frequency range was 1 Hz–2 MHz, the amplitude of the sinusoidal voltage signal was 20 mV. The best-fit values of the equivalent circuit components were determined using the ZPLOT software included in the Solartron impedance equipment.

## 3. Results and discussion

*XRD analysis.* X-ray diffraction was done using Philips X'Pert Pro diffractometer with  $\text{CuK}_\alpha$  filtered radiation in the  $2\theta$  range from  $10^\circ$  to  $80^\circ$ . Phase identification was performed using the data base ICDD. The analysis revealed that the samples containing 10 at. % of Nb and less are homogeneous and crystallize in the rutile phase. On the other hand, apart rutile phase, the traces of the  $\text{TiNb}_2\text{O}_7$  have been detected in the specimen  $\text{TiO}_2 + 15$  at. % of Nb. The lattice parameters were determined by means of Rietveld's method using the Fullprof program [10]. Figure 1 illustrates calculated lattice parameters  $a$  and  $b$  of the rutile unit cell as a function of the concentration of Nb. As it can be seen, a linear dependence is observed within the range 0–10 at. % of Nb, predicted by Vegard's law. The increase of both parameters,  $a$  and  $b$ , can be explained by substitution of smaller  $\text{Ti}^{4+}$  ions ( $r_{\text{Ti}^{4+}} = 68$  pm) by larger  $\text{Nb}^{5+}$  ( $r_{\text{Nb}^{5+}} = 69$  pm [11]). Departure from the linearity presented in Figure 1 indicates that the Nb-solubility limit is between 10 and 15 at. % of Nb.

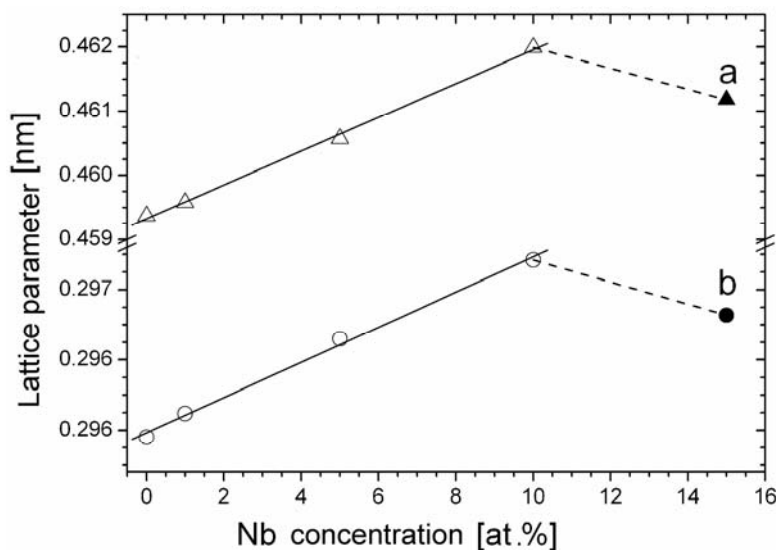


Fig. 1. Lattice parameters  $a$ ,  $b$  of the Nb- $\text{TiO}_2$  rutile cell as a function of the concentration of Nb

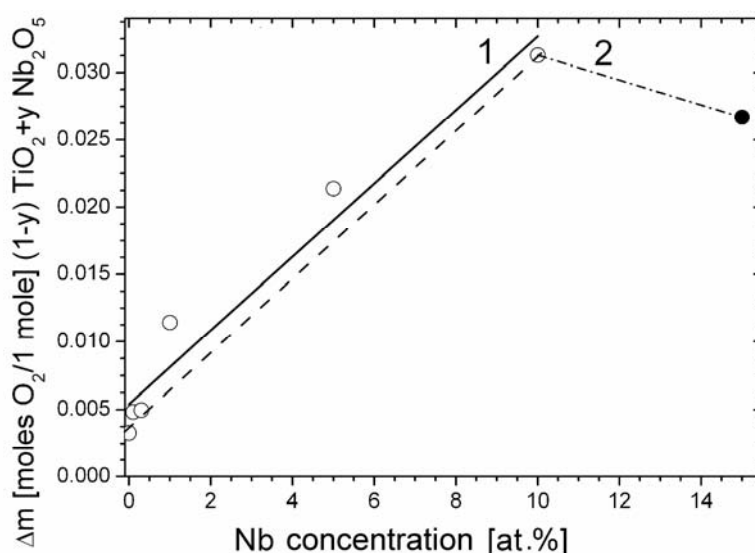


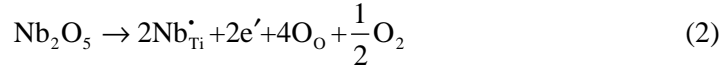
Fig. 2. Maximum reversible weight change of Nb-doped  $\text{TiO}_2$  accompanying  $p(\text{O}_2)$  changes between 210 kPa and  $10^{-15}$  Pa as a function of the concentration of Nb. The dashed line 2 illustrates the best linear dependence; the solid line 1 corresponds to the theoretical dependence resulting from the reaction (3)

*Thermogravimetric studies.* Figure 2 shows weight changes of the samples, accompanying their reduction at 1273 K for 3 h. The observed weight losses may be ex-

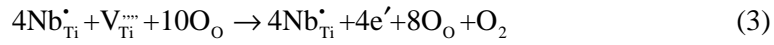
plained by the existence of two forms of Nb-doped  $\text{TiO}_2$  resulting from different reactions of the Nb incorporation into  $\text{TiO}_2$  lattice occurring either in oxidizing or reducing conditions. In Kröger and Vink [12] notation, the following reaction occurs at oxidizing conditions:



where  $\text{V}_{\text{Ti}}^{\text{'''}}$  denotes titanium vacancy having the charge 4– with respect to the lattice. At reducing conditions:



Transition between the above forms may be described by the following equation:



Solid line 2 in Figure 2 illustrates the weight change corresponding to reaction (3) (“theoretical dependence”). As can be seen, there is a good agreement between the experimental data and the theoretical dependence.

*Impedance measurements.* Figures 3 and 4 illustrate impedance spectra presented in a complex impedance plane of undoped  $\text{TiO}_2$  reduced and oxidized, respectively. In

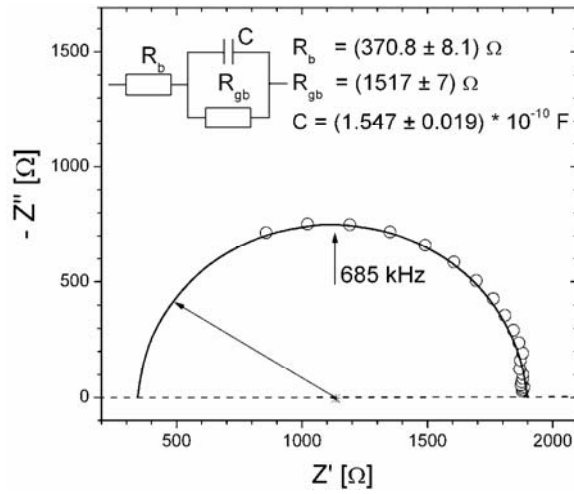


Fig. 3. Complex impedance spectrum and the equivalent circuit of reduced undoped  $\text{TiO}_2$ . The asterisk shows the centre of the semicircle

Figures 5 and 6, analogous spectra are shown for  $\text{TiO}_2$  containing 10 at. % of Nb reduced and oxidized, respectively. For other compositions the impedance spectra are similar. The experimental points of reduced samples (Figs. 3 and 5) lie on semicircles

with the centre placed on the  $Z'$  axis. The simplest equivalent circuit of such plots is composed with a resistor  $R_b$  and a parallel  $R_{gb}$ - $C$  branch in series.

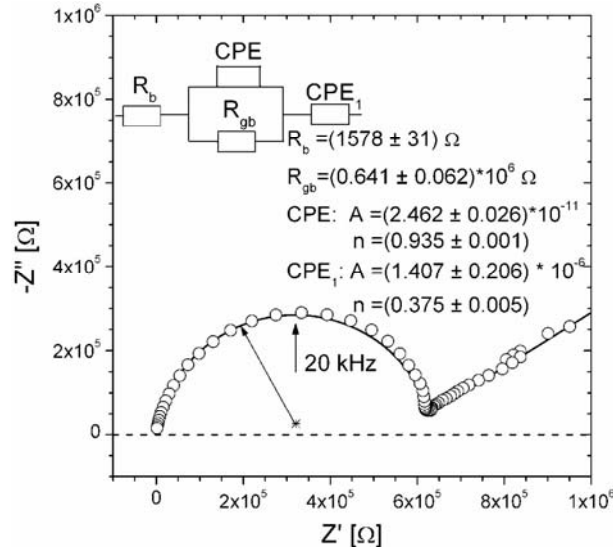


Fig. 4. Complex impedance spectrum and the equivalent circuit of oxidized undoped  $\text{TiO}_2$ .

The asterisk shows the centre of the semicircle

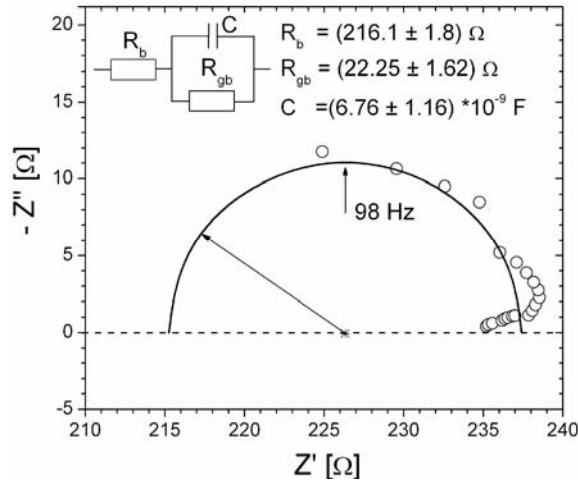


Fig. 5. Complex impedance spectrum and the equivalent circuit of reduced  $\text{TiO}_2 + 10$  at. % Nb. The asterisk shows the centre of the semicircle

Based on general rules [13], we can ascribe  $R_b$  to the bulk resistivity,  $R_{gb}$  and  $C$  to the grain boundaries parameters. The impedance spectra of the oxidized samples show a more complex character. The centres of the arcs are placed below the  $Z'$  axis. More-

over, spur is observed at higher frequencies. The non-Debye constant phase elements (CPE) defined by the admittance formula:

$$Y_{\text{CPE}} = A(j\omega)^n \quad (4)$$

had to be included into an equivalent circuit in order to describe properly the experimental results. Similar behaviour was observed for polycrystalline  $\text{TiO}_2$  materials prepared by coprecipitation method [14].

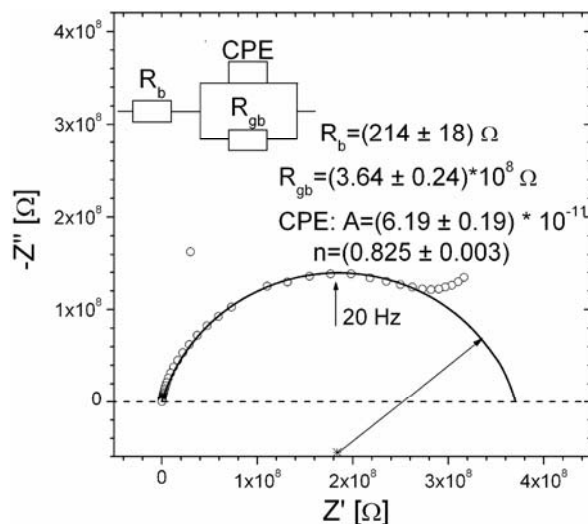


Fig. 6. Complex impedance spectrum and the equivalent circuit of oxidized  $\text{TiO}_2 + 10$  at. % Nb. The asterisk shows the centre of the semicircle

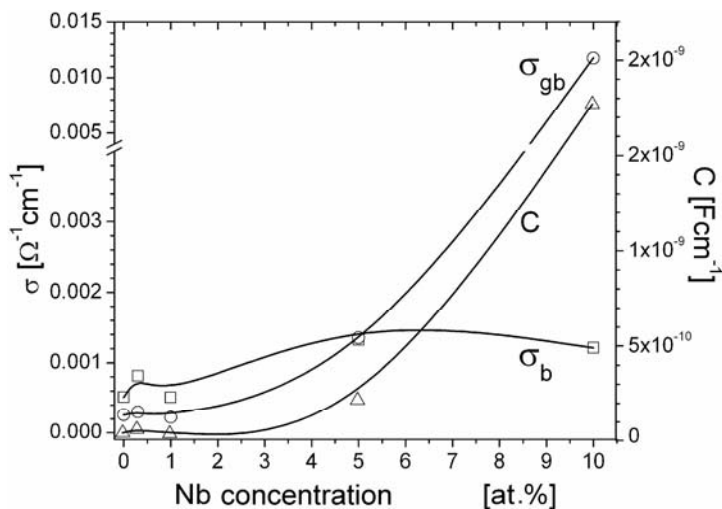


Fig. 7. Dependences of the electrical conductivity (left axis) and capacitance (right axis) of the Nb- $\text{TiO}_2$  system on the concentration of Nb

Figure 7 shows the compositional dependences of the electrical conductivity  $\sigma_b$  (bulk) and  $\sigma_{gb}$  (grain boundaries) (left axis), and capacitance  $C$  (right axis) of the reduced samples. Below 5 at. % of Nb, the electrical conductivity of grain boundaries is lower than that of the bulk. Poor conductivity of grain boundaries can result from enrichment of the grain boundaries with niobium. There are two possible explanations of this enrichment resulting from very slow rate of incorporation of Nb in TiO<sub>2</sub> lattice due to extremely low diffusion of Nb [14] or by the occurrence of segregation processes [16].

#### 4. Conclusions

Polycrystalline Nb-doped TiO<sub>2</sub> specimens (0–15 at. % Nb) were the subject of this study. Below doping level of 10 at. % of Nb, materials exhibit rutile structure and lattice parameters change with Nb concentration according to Vegard's law. Above dopant concentration of 10 at. % of a second phase, TiNb<sub>2</sub>O<sub>7</sub>, was detected.

Electrochemical impedance spectroscopy within the frequency range 0.01 Hz–2 MHz has been used to determine electrical properties of the studied materials at room temperature. The impedance spectra differ substantially from those of oxidized ones. The equivalent circuit of the reduced materials is composed of a resistor  $R_{gb}$ , a capacitor  $C$  connected in parallel and a resistor  $R_b$  connected in series, well represents the impedance of studied samples. On the other hand, non-Debye elements should be taken into account in construction of the equivalent circuit of oxidized materials.

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