

In Situ Study of the Temperature Stability of $\text{TiO}_{1.05}$ Titanium Monoxide Using Synchrotron Radiation

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Abstract—The temperature stability of cubic $\text{TiO}_{1.05}$ titanium monoxide is investigated. An in situ X-ray structural analysis is performed using synchrotron radiation in a high temperature vacuum chamber. It is found that under poor vacuum and at high heating rates of up to 1250°C, the structural transformations in $\text{TiO}_{1.05}$ occur at 630°C. In particular, there is a phase transition from $\text{TiO}_{1.05}$ (space group $Fm-3m$) to rhombohedral Ti_2O_3 (space group $R-3c$) via $\text{Ti}_{2.5}\text{O}_3$ (space group $Immm$).

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INTRODUCTION

The nonstoichiometric titanium monoxide TiO_y is a unique compound, since it contains many structural vacancies simultaneously in two sublattices [1]. The structural vacancies are natural: they are not introduced to the system from without, but formed during synthesis under high temperatures and stabilize the compound [2]. In addition, they influence the order of compound, and can be found in an ordered or disordered distribution, depending on the heating conditions. Variation in the concentration of vacancies in the sublattices and their distribution over the lattice sites change both the structure and properties of titanium monoxide [3].

TiO_y is of interest for thin-film coatings with promising mechanical properties [4, 5]. In addition, TiO_y is very efficient as a barrier to Al and Si mutual diffusion [6, 7]. Due to these properties, Marteev [4] and Grigorenko [5] assumed that TiO_y can be used as a thin-film material for microelectronic structures. It is thus logical to study how the temperature influences the TiO_y structure and properties, and its stability.

EXPERIMENTAL

The nonstoichiometric titanium monoxide $\text{TiO}_{1.05}$ was synthesized by solid phase sintering from a mixture of powders: metallic titanium Ti and titanium dioxide TiO_2 under vacuum at a pressure of 10^{-5} mbar and at a temperature of 1500°C. After synthesis, the sample contained two phases: disordered (cubic) and ordered (monoclinic) phases. To obtain the disordered state, the sample was annealed in evacuated ampoule for 3 hours at 1057°C; after that, an ampoule with a sample was put into water. The quenching rate was 200°C/s. The sample was fully certified using chemi-

cal, spectral, pycnometric, and X-ray structural and phase methods. Information on the heating procedure for obtaining disordered and ordered states, and on the results from certifying the samples, can be found in [2].

Structural in situ investigations were performed using the disordered cubic titanium monoxide $\text{TiO}_{1.05}$. The experiment was conducted on Channel 6 of the VEPP-3 storage ring at the Siberian Center of Synchrotron and Terahertz Radiation (Novosibirsk). The X-ray structural analysis was performed during in situ investigations with synchrotron radiation using a Bruker D8 Advance diffractometer and an Anton Paar HTK-2000 high temperature vacuum chamber. Heating was performed in the range from room temperature to 1250°C over two hours, in the vacuum chamber under a pressure of 1.4×10^{-4} mbar. The furnace was cooled from 1250°C to room temperature over two hours as well. The X-ray diffraction spectra were recorded in steps of 25°C.

Diffraction investigations of the powders for the initial $\text{TiO}_{1.05}$ titanium monoxide, and for the powder after temperature tests, were conducted on the synchrotron using $\text{CuK}_{\alpha,2}$ radiation and a Shimadzu automatic diffractometer with Bragg-Brentano recording geometry. We employed step-by-step scanning at $\Delta(2\theta) = 0.02^\circ$ for a range of angles 2θ that varied from 10° up to 160° with a high degree of accuracy.

The microstructure of both the initial powder and the powder after temperature investigations were examined by SEM (scanning electron microscopy) on a JEOL JSM-6390 LA electron microscope. To overcome charge accumulation on a sample's surface during recording with the electron microscope, the investigated powder was put onto a strip of carbon tape.

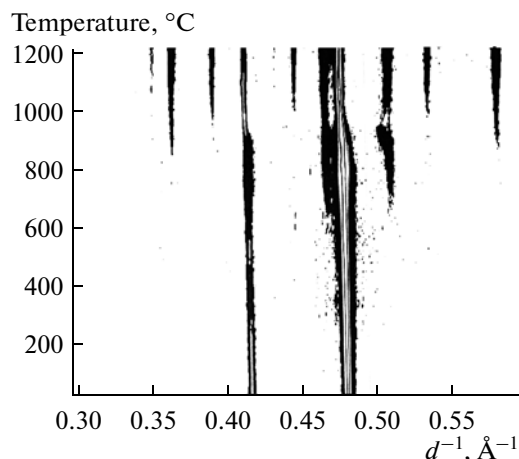


Fig. 1. Relationship between X-ray reflection intensity and inverse interplane distance and temperature. It was generated for heating TiO_{1.05} titanium monoxide powder from 25 to 1250°C in vacuum at a pressure of 1.4×10^{-4} mbar.

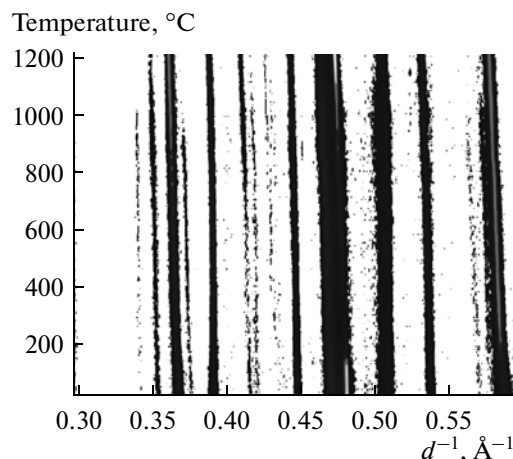


Fig. 2. Relationship between X-ray reflection intensity and inverse interplane distance and temperature. It was generated for cooling TiO_{1.05} titanium monoxide powder from 1250 to 25°C in vacuum at a pressure of 1.4×10^{-4} mbar.

RESULTS AND DISCUSSION

From the experimental relationship between X-ray reflection intensity and inverse interplane distance and temperature (Fig. 1), we can see that at temperatures higher than 630°C, the initial phase becomes unstable. For temperatures varying from room temperature to 630°C, we see only two reflections, corresponding to cubic phase peaks (111)_{B1} and (200)_{B1}. At higher temperatures, reflection (200)_{B1} becomes wider and additional low intensity reflections appear. Figure 2 presents the plot generated for sample cooling from 1250 down to 25°C. It can be seen that the cubic structure intrinsic to titanium monoxide before the experiment is not restored.

Phase analysis shows that after heating at high temperatures, the sample contains three phases: cubic (space group *Fm-3m*), 76.5 wt % of mass; the orthorhombic phase of Ti_{2.5}O₃ [8] (space group *Immm*), 9.8 wt % of mass; and the rhombohedral phase of Ti₂O₃ [9, 10] (space group *R-3c*), 13.7 wt % of mass.

We may conclude that upon fast heating under mean vacuum, titanium monoxide is a temperature-unstable compound. Structural variations in TiO_{1.05} occur even below 630°C: there is a phase transition from cubic titanium monoxide TiO_y (space group *Fm-3m*) to rhombohedral Ti₂O₃ (space group *R-3c*) via Ti_{2.5}O₃ (space group *Immm*). The phase transitions are evidently caused by the increased sensitivity of this system to residual oxygen in the vacuum chamber at temperatures higher than 630°C, or to the water absorbed on the powder's surface.

Figure 3 shows the diffraction spectra before and after the experiment. The initial sample (Fig. 3, 1) has cubic structure of the B1 type. After heating, two additional phases with increased oxygen content are formed (Fig. 3, 2). In addition, at high temperatures we see that the position of phase B1 peaks is shifted due to titanium oxide heat expansion.

We determined the heat expansion coefficient for TiO_{1.05} titanium monoxide from the experimental [200]_{B1} X-ray reflection spectra. To determine the precise lattice constant for the cubic phase, the experimental X-ray spectra were approximated using the pseudo-Voigt function

$$V(\theta) = ca \left[1 + \frac{(\theta - \theta_0)^2}{\theta_L^2} \right]^{-1} + (1-c)a \exp \left[-\frac{(\theta - \theta_0)^2}{2\theta_G^2} \right], \quad (1)$$

where c is the relative contribution from the Lorentz function to the total reflection intensity; θ_L and θ_G are Lorentz and Gauss distribution parameters, respec-

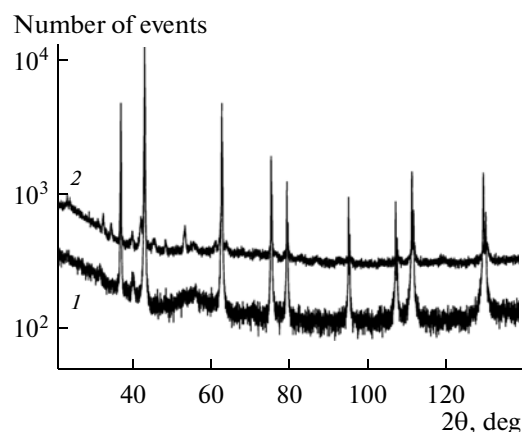


Fig. 3. Spectra from X-ray diffraction for titanium monoxide obtained at room temperature: (1) initial sample, (2) after heating and cooling.

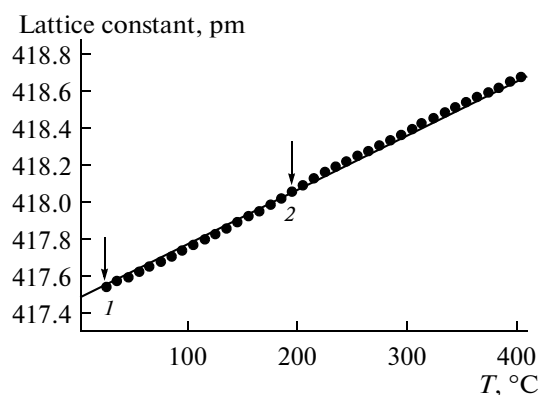


Fig. 4. Relationship between lattice constant a_{B1} and temperature for $\text{TiO}_{1.05}$ cubic titanium monoxide, determined from reflection $[200]_{B1}$. For segment 1–2, the curve is approximated by a straight line.

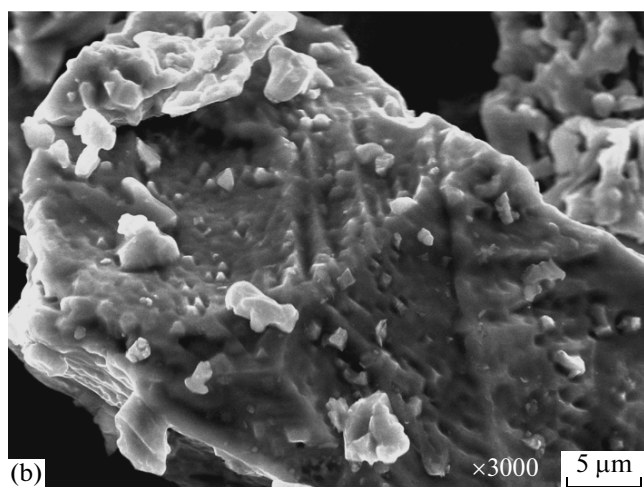
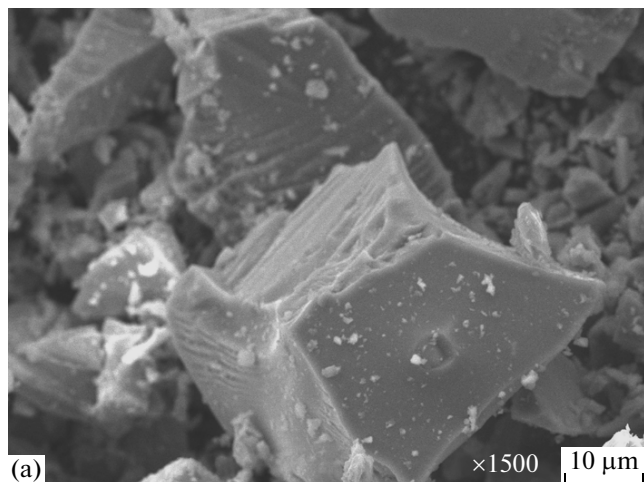


Fig. 5. Powder microstructure for titanium monoxide: (a) is the initial powder of cubic $\text{TiO}_{1.05}$; (b) is the powder after heating to 1250°C and cooling to room temperature. It can be seen that the sample structure and morphology change.

tively; a is the normalizing coefficient for intensity; and θ_0 is the maximum position of the function and reflection. A complete profile of the experimental data was compiled according to the procedure described in [11]. The numerical values for a , c , θ_0 , θ_L and θ_G for each reflection were determined by approximating the experimental spectra using the mean-least-square method. Interplane distances d_{hkl} were calculated using the maximum position for each diffraction reflection θ_0 . To exclude errors caused by incorrect sample position during X-ray pattern recording, the value of a_{B1} determined for each reflection were extrapolated by the Nelson–Riley function: $0.5[(\cos^2\theta)/\sin\theta + (\cos^2\theta)/\theta]$ [12, 13] for $\theta = 90^\circ$. A lattice constant determined from reflection $[200]_{B1}$ at different temperatures is presented in Fig. 4. The curve is approximated by a straight line in the temperature range of 25 to 200°C (segment 1–2 in Fig. 4). Using the slope of this line, we found the thermal expansion coefficient: $6.78 \times 10^{-6} \text{ deg}^{-1}$. This value is close to the thermal expansion coefficient: $6.67 \times 10^{-6} \text{ deg}^{-1}$ determined for $\text{TiO}_{1.00}$ by X-ray diffraction [14]. At higher temperatures, we see deviation from the straight line, due possibly to oxygen stoichiometry variation during heating as a result of absorbed water interacting with the titanium monoxide.

Electron microscopy revealed that the initial powder of $B1\text{-TiO}_{1.05}$ titanium monoxide is characterized by changing of the structure (Fig. 5a), and the grain size varies from 0.1 to $100 \mu\text{m}$. In addition, we can see steps that are cross-foliated. After temperature experiments, the powders' morphology changes. In particular, it is seen in the microphotos that the degree of foliation decreases and melt bumps organized in rows form on the surface. The results from electron microscopic analysis verify the phase transitions revealed by diffraction.

CONCLUSIONS

Our experiments showed that the cubic $\text{TiO}_{1.05}$ titanium monoxide is temperature unstable even under mean vacuum. In addition, this compound is very sensitive to absorbed water both in the vacuum chamber and in the powder. It was found that the structural variations in titanium monoxide caused by oxidation start at temperatures under 630°C . In the temperature range of 630 to 1250°C , there is a phase transition from cubic titanium monoxide TiO_y (space group $Fm-3m$) to rhombohedral Ti_2O_3 (space group $R-3c$) via $\text{Ti}_{2.5}\text{O}_3$ (space group $Immm$). In addition, the thermal expansion coefficient for cubic titanium monoxide $\text{TiO}_{1.05}$ was determined to be $6.78 \times 10^{-6} \text{ deg}^{-1}$. This value is in good agreement with the earlier experimental data.

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