

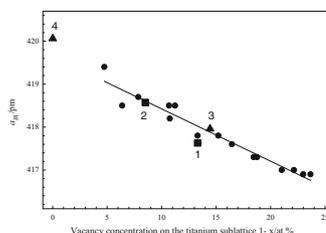
# Elimination of vacancies in titanium monoxide under high pressure in combination with high temperature

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Received: 13 January 2015 / Accepted: 8 March 2015 / Published online: 8 April 2015  
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**Abstract** The material design with controlled structure was performed on titanium monoxide with structural vacancies on both sublattices. The polycrystalline powder of disordered titanium monoxide  $\text{TiO}_{0.98}$  with *B1* structure was subjected to high pressures up to 60 kbar and high temperatures up to 2273 K. The X-ray powder diffraction of as-prepared and treated powders revealed cubic single-phase crystals. The lattice constant of this phase increased from 417.6(3) to 418.5(3) pm due to decreasing vacancy concentration on the titanium sublattice from 13.3 to 8.5 at.% after a highest pressure-highest temperature treatment for 1 h.

*Graphical abstract*



**Keywords** XRD · Non-stoichiometry · Structural vacancy · Vacancy elimination

## Introduction

A possibility of controlling vacancy defects in crystals and latent properties of substances is of special interest for material design [1]. A great number of structural vacancies were found in non-stoichiometric titanium monoxide  $\text{TiO}_y$  by using a positron annihilation technique [2–4] and TEM [5]. They are assumed to substantially contribute to the stabilization of  $\text{TiO}_y$  [6–8].  $\text{TiO}_y$  with vacancies on both sublattices is unique, because the way of vacancies distribution affects the structure of the compound [9–12].

There is some recent interest in  $\text{TiO}_y$  as a thin film coating material due to its promising mechanical properties [13, 14]. The design of the vacancy defect-controlled microstructures of titanium monoxides as promising high-temperature thermoelectric materials is discussed in [1]. Moreover,  $\text{TiO}_y$  is highly efficient as a diffusion barrier against the interdiffusions of Al and Si [15, 16]. Due to these properties, conductive  $\text{TiO}_y$  could be used as a thin film material for applications in nanoelectronic layered structures. In all the examples it is important to understand the role of structural vacancies in  $\text{TiO}_y$  since they are an inherent part of the crystal structure and influences not only the structure but also the properties of the material.

Experiments on  $\text{TiO}_y$ , which was subjected at ambient temperature to a pressure of 60–70 kbar by using a tetrahedral anvil press [17, 18] and to a pressure of 140 kbar by using a diamond anvil press [19], showed no significant differences between the compression behavior of the samples rich in oxygen vacancies and that of the samples rich in titanium vacancies. The crystal structure of the

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samples was shown to recover and have *B1* structure with the initial lattice constant after shock loading at a dynamic pressure of 600 kbar [20].

From [21] it is known that vacancy concentration in  $\text{TiO}_y$  can be reduced exclusively by applying both high pressure and high temperature simultaneously. It has been found that the number of vacancies decreases from 14.4 % to zero when  $P \times \Delta T > 90,000$  kbar K, where  $P$  is the applied pressure and  $\Delta T$  is the temperature above the ambient one at which the pressure is applied [21]. The resulting phase was metastable under ambient conditions. The decreasing vacancy concentration on both sublattices from 14.4 to 0 % was accompanied by rising lattice constant from 417.9 to 420.6 pm after exposure to a high pressure of 77.4 kbar and high temperature of 1923 K or the same pressure and lower temperature of 1823 K for 1 s. Any number of vacancies, ranging from 14.4 to 0.0 %, could be obtained by the correct selection of  $P \times \Delta T$ . The process is completely reversible by annealing the samples in the absence of the applied pressure, which results in the original vacancy level of 14.4 %. It was suggested in [21] that elimination of vacancies does not change the physical properties significantly.

Vacancy-free  $\text{TiO}_{1.00}$  with *B1* structure was prepared by annealing monoclinic  $\text{TiO}_{1.00}$  at 1938 K and a pressure of 80 kbar for 1 min using a multi-anvil apparatus [22]. The samples were then quenched to an ambient temperature at a rate over 200 K/s at an approximately constant pressure. Then, the pressure was released over a period of several hours. The X-ray powder diffraction (XRD) of the treated samples revealed *B1* structure with the lattice constant of  $420.43 \pm 0.03$  pm. The lattice constant of the compacted vacancy-free cubic samples is in good agreement with that found in [21].

The high pressure and high temperature experiments were performed by annealing titanium monoxide in a wide homogeneity region from  $\text{TiO}_{0.86}$  to  $\text{TiO}_{1.24}$  at pressures ranging from 50 to 60 kbar and high temperatures ranging from 1373 to 1573 K for 2 h [11]. According to [11], 11–22 % of the vacancies on both sublattices were removed depending on the pressure and temperature. The density of the  $\text{TiO}_y$  samples increased by 0.6–2.5 %. The lattice constant increased by 0.4 % on average. It was suggested in [11] that it might be possible to remove all the vacancies in  $\text{TiO}_{1.00}$  by applying higher temperatures and higher pressures.

In [23] the hexagonal phase  $\delta\text{-Ti}_3\text{O}_2$  with lattice constants of  $a_h = 499.0$  and  $c_h = 287.8$  pm was found in the in situ observations after treatment of titanium monoxide  $\text{TiO}_{1.04}$  at a pressure of 77 kbar and a temperature of 1073 K for 2 h. The unit cell of this hexagonal phase is clearly connected with the structure of the original cubic *B1* phase, and can be expressed in terms of the  $a_{B1}$  lattice

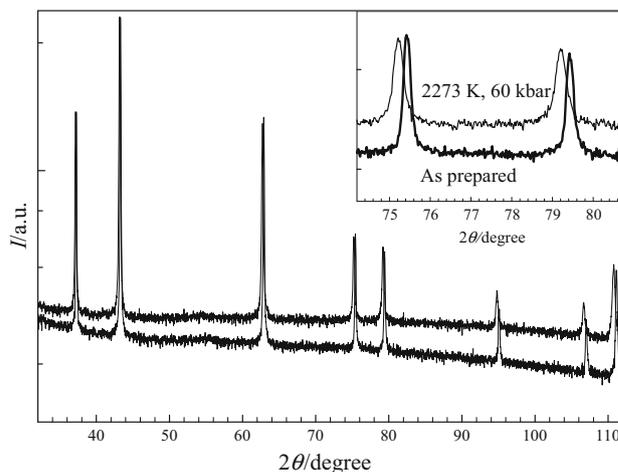
constant. Taking this into account, one can compare the initial lattice constant ( $a_{B1} = 418.0$  pm) with the lattice constant after annealing treatment, which has increased by 0.7 pm. This change can be attributed to a partial filling of vacancies.

Taking into account the above mentioned discrepancies in literature data, the aim of this work was to analyze more precisely the influence of all three factors, i.e. high pressure, high temperature, and treatment time, on the elimination of vacancies in titanium monoxide  $\text{TiO}_y$ .

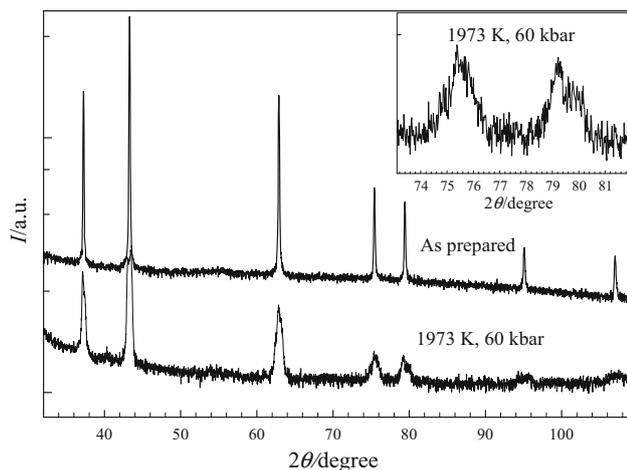
## Results and discussion

In the present work the experiments were performed at 1973 and 2273 K and pressures of 30 and 60 kbar. All treatments were performed during 60 min. The XRD of as-prepared and treated powders at 2273 K of  $\text{TiO}_y$  showed reflections exclusively of cubic phase with *B1* structure. There were no additional reflections observed which correspond to the material of the capsule (Fig. 1). The reflections were symmetric and not broadened. In contrast, the XRD for the experiment at 60 kbar and at a lower temperature of 1973 K showed that the powder became inhomogeneous, i.e. the gradient of concentration of vacancies in the treated powder was observed. XRD of Fig. 2 and in the inset show much more broadened cubic reflections. This inhomogeneity is obviously due to insufficient time for diffusion at this temperature. Thus, time is very important for elimination of vacancies.

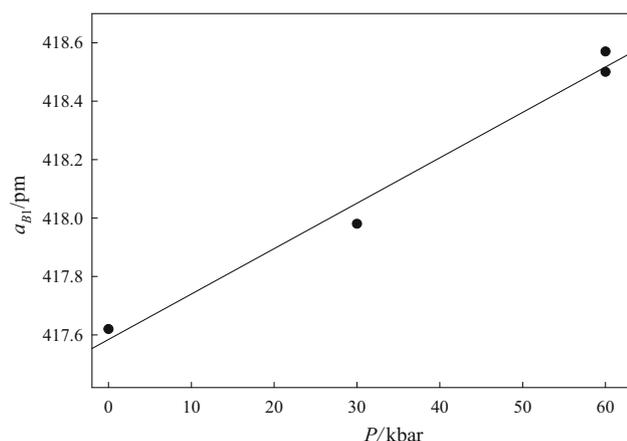
Full profile analysis of the XRD pattern shows that the lattice constant of  $\text{TiO}_y$  increases due to decreasing



**Fig. 1** XRD of as-prepared and treated (2273 K, 60 kbar) powders of  $\text{TiO}_y$  revealed single-phase material without any superstructure. The reflections are shifted (see also the *inset*) and the lattice constant of  $\text{TiO}_y$  is increased from 417.6(3) to 418.5(7) pm after a high temperature–high pressure treatment



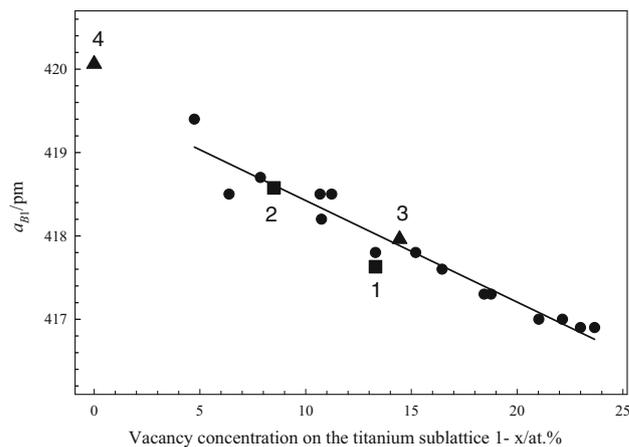
**Fig. 2** XRD of  $\text{TiO}_y$  powders: as-prepared powder contains exclusively one cubic phase with sharp reflections, and powder subjected to high pressure 60 kbar and high temperature 1973 K annealing has much broadened reflections. See also much broadened cubic reflections in the *inset*



**Fig. 3** Increasing lattice constant of  $\text{TiO}_{0.98}$  in dependence on pressure  $P$  at 2273 K

vacancy concentration in  $\text{TiO}_y$ . The increasing lattice constant of  $\text{TiO}_y$  depending on pressure  $P$  is shown in Fig. 3. It can be seen that the best results are obtained under pressure of 60 kbar and temperature of 2273 K.

Figure 4 shows the changes in concentrations of vacancies on the metal sublattice of as-prepared powder of  $\text{TiO}_y$  and after the treatment at a high pressure of 60 kbar and a high temperature of 2273 K. Experimental points of the present work are shown as squares. According to the lattice constant and chemical composition data, the vacancy concentration on the titanium sublattice decreases from 13.3 down to 8.5 at.%. The concentrations of vacancies were determined from the empirical dependence (solid line in Fig. 4) of the lattice constant versus chemical



**Fig. 4** The dependence of the lattice constant on vacancy concentration on Ti sublattice (shown by *closed circles* and *solid line*). Experimental points of the present work are shown by *squares*: 1—*as-prepared* sample, 2—*treated at high pressure 60 kbar and high temperature 2273 K* sample. Two experimental data points received by Taylor [21] for vacancy-rich (3) and vacancy-free (4)  $\text{TiO}_{1.00}$  samples are shown by *triangles*

composition as suggested in [12]. The decreasing vacancy concentration on the titanium sublattice is due to elimination of vacancies by applying high pressures in combination with high temperatures and rapid quenching. In [21] the decreasing vacancy concentration from 14.4 down to 0 % is accompanied by a rising lattice constant from 417.9 to 420.6 pm after exposure to a high pressure of 77.4 kbar and a high temperature of 1923 K. Thus, in the present experiment the zero vacancy concentration on the titanium sublattice in  $\text{TiO}_y$  is not reached, the expression for removing vacancies  $P \times \Delta T > 90,000$  kbar K suggested by Taylor [21] was found to be not valid. Removing vacancies seems to be a more complex process and there are more factors which affect the results.

The questions arise: how do the elastic and inelastic deformations affect the compound? Why does the lattice constant change after simultaneous applying of high pressures and temperatures? It is known that under normal conditions structural vacancies in  $\text{TiO}_y$  reduce the average bond length and, hence, the size of the unit cell. At high pressures structural vacancies in the crystal lattice have an unfavorable trend to reduce the total volume. Due to a good mobility at high temperatures, structural vacancies migrate through the crystal lattice to the surface, while atoms fill vacancies in the lattice without changing significantly the symmetry of the crystal structure, which leads to a decrease in total volume and an increase of the interatomic distances. Thus, the observed changes of the lattice constant are result of inelastic deformation, and are due to the mobility of vacancies at high temperatures, their migration to the surface, reduction of the number of vacancies in the

crystal lattice, an increase in the atomic density and, as a result, an increase of the interatomic distance.

During the elastic compression the volume of the lattice decreases due to the pressure and, therefore, reduces the volume, occupied by one atom, which results in decreasing interatomic distances and lattice constant. After release of elastic compression the lattice constant increases back and regain their value.

It is clear that to remove vacancies from  $\text{TiO}_y$ , a very high pressure is necessary, i.e. the higher the pressure is, the lower the concentration of structural vacancies in the end product. However, the value of temperature cannot be predicted theoretically at present. Indeed, on the one hand, high temperatures are necessary for high mobility of vacancies. On the other hand, high temperatures make freezing of the vacancy-free state difficult, because it requires a very high quenching rate from high temperatures. Thus, both high pressures and a long time of annealing are equally important for elimination of vacancies in  $\text{TiO}_y$ , whereas the temperature of annealing is less important.

## Conclusions

In the present work we managed to decrease vacancy concentration on the titanium sublattice of  $\text{TiO}_y$  from 13.3 to 8.5 at.% by applying a high pressure of 60 kbar in combination with a high temperature of 2273 K and consequent rapid quenching of 200 K/s. The lattice constant increased from 417.6(3) to 418.5(3) pm with an increasing pressure without changing the crystal structure symmetry. The data under discussion reveal that the pressure and time are more important for elimination of vacancies than the temperature. The study of the defect structure and the influence of high-pressure treatment on structural vacancy concentration of  $\text{TiO}_y$  enable the synthesis of novel TiO material with controlled vacancy concentration and properties.

## Experimental

In the present work the high pressure experiments in combination with high temperature and consequent rapid quenching were performed on non-stoichiometric  $\text{TiO}_{0.98}$ . The samples were synthesized by using a high temperature vacuum solid phase sintering from titanium dioxide  $\text{TiO}_2$  and titanium Ti powders. The details on the preparation of the samples and the descriptions of the characterization are given in [12].

An analysis of the data obtained in the present work and the data from [12] shows that the vacancy concentrations on the titanium sublattice  $V_{\text{Ti}}$  linearly increase with

increasing oxygen content  $y$  in  $\text{TiO}_y$  according to the formula  $V_{\text{Ti}} = (14 \pm 1) + (34 \pm 2) \times (1 - y)$ . In contrast, the vacancy concentrations on the oxygen sublattice  $V_{\text{O}}$  decrease according to the formula  $V_{\text{O}} = (14 \pm 1) - (48 \pm 2) \times (1 - y)$ . These formulas are useful for determining the dependence of lattice constant of  $\text{TiO}_y$  on the vacancy concentration on the titanium sublattice.

The experiments with high pressures in combination with high temperatures and consequent rapid quenching were performed in a modified belt apparatus. As-prepared powder of  $\text{TiO}_{0.98}$  with  $13.3 \pm 0.3$  at.% vacancy concentration on the titanium sublattice and  $14.7 \pm 0.3$  at.% vacancy concentration on the oxygen sublattice was put into a cylindrical capsule made of boron nitride BN, which was placed in the center of the belt apparatus. Pyrophyllite  $\text{Al}_2(\text{OH})_2(\text{Si}_2\text{O}_5)_2$  served as a pressure transmitting medium for high pressure annealing and quenching experiments. High pressure annealing and quenching experiments were made by fixing pressures at 30 or 60 kbar for 1 min and temperatures of 1973 or 2273 K for 1 min. The pressure and temperature was kept constant for 60 min. After that the temperature rapidly decreased to the ambient temperature at a rate of about 200 K/s at approximately constant pressure. Then, the pressure was released during several seconds. Heating for as many as 60 min was chosen for a complete process of diffusion in the sample. The experiments were repeated under the same conditions, and reproducibility was proved by the full profile analysis of XRD pattern.

XRD studies of  $\text{TiO}_y$  were carried out with a STOE STADI P transmission diffractometer equipped with a linear PSD, a Ge-monochromator, and a Mythen 1 K detector at 293 K. The measurements were performed in  $\text{CuK}\alpha_1$  radiation, the  $2\theta$  range was  $10^\circ$ – $116^\circ$  with a step-width of  $0.015^\circ$ .  $\text{LaB}_6$  was used as an external standard. The XRD patterns were measured both in a short run and a longer run with better statistics. Four XRD powder patterns were summed up for better statistics and were used for a full profile analysis. The error of the lattice constant determination was about 1 pm.

**Acknowledgments** We are grateful to Dr. M. Andratschke, F. Rau, and U. Schiessl for their help during the experiments. This work was financially supported by the AvH Foundation, RFBR Nos. 14-03-00869 and 15-03-00453.

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