



# Nonstoichiometric orthorhombic titanium oxide, $\text{TiO}_{2-\delta}$ and its thermochromic properties

Isao Tsuyumoto<sup>\*</sup>, Hiroshi Uchikawa

*Department of Environmental Chemistry, College of Environmental Engineering and Architecture,  
Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan*

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## Abstract

Redox relationship among anatase, rutile, and a new nonstoichiometric orthorhombic titanium oxide was elucidated. Single crystal of nonstoichiometric orthorhombic titanium oxide  $\text{TiO}_{1.94}$  was prepared by reducing a single crystal of rutile  $\text{TiO}_2$  at 950 °C in  $\text{H}_2$  for 1 h based on this relationship. The single crystallinity was demonstrated by both the Laue and the Debye–Scherrer methods. Temperature dependence of the conductivity and the reflectance spectrum was measured for the single crystal of  $\text{TiO}_{1.94}$ , and it was found that the reflectivity in near-infrared region over 1700 nm gradually increased with increasing temperature. “Smart windows” using this titanium oxide was proposed.

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## 1. Introduction

Window glass whose reflectivity increases with increasing temperature controls room temperature automatically because it shades sunlight at high temperature. This is called “smart window” and many researchers have tried to apply thermochromism of some transition metal oxides accompanied by a semiconductor-to-metal transition. For example, the monoclinic form of  $\text{VO}_2$  is transformed into the rutile form at  $T_c = 67$  °C, and this semiconductor-to-metal transition brings about an abrupt reduction of transmittance at near-infrared region. Kudo and co-workers [1] have reported that the thin film of  $\text{VO}_2$  was prepared by a wet process of sol–gel techniques, and that the  $T_c$  of 67 °C was lowered by doping tungsten or molybdenum.

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<sup>\*</sup> Corresponding author.

*E-mail address:* [tsuyu@neptune.kanazawa-it.ac.jp](mailto:tsuyu@neptune.kanazawa-it.ac.jp) (I. Tsuyumoto).

The reflectivity change due to thermochromism is explained by using the plasma frequency  $\omega_p$  as follows.

$$\omega_p^2 = \frac{4\pi ne^2}{m} \quad (1)$$

where  $n$  is the density of conduction electrons and  $m$  is the mass of electron. In general, light below the frequency of  $\omega_p$  is reflected by the substance, and thus it is effective to increase  $\omega_p$ , i.e.,  $n$  to expand the wavelength range in which light is reflected. There are two methods to increase  $n$ . One is to use a semiconductor-to-metal transition. This brings about an abrupt increase in  $n$ , i.e.,  $\omega_p$  at  $T_c$ . The reported reflectivity change of  $\text{VO}_2$  in near-infrared region at  $T_c$  is based on this idea. The other is to use gradual increase in  $n$  with increasing temperature, and this results in a gradual increase in reflectivity. Here we paid attention to nonstoichiometric compounds and their electrical properties.

The structure and electrical properties of nonstoichiometric compounds such as  $\text{Ti}_n\text{O}_{2n-1}$  ( $n = 2-10$ ),  $\text{V}_n\text{O}_{2n-1}$  ( $n = 3-9$ ),  $\text{K}_x\text{WO}_3$  ( $x = 0.17-0.33$ ) have been intensively investigated because the lattice defect accompanied by the nonstoichiometry is closely associated with various functional properties: ionic conduction, gas-sensitivity, magnetism, etc. [1–3]. Tremendous reports have appeared on  $\text{TiO}_2$  with regard to photocatalyst, and the structure and electrical properties of its reduced form  $\text{Ti}_n\text{O}_{2n-1}$  have been the subject of many previous researches [4–6]. The  $T_c$  of  $\text{Ti}_n\text{O}_{2n-1}$  have been reported to be 660, 450, 150, 125, and 133 K for  $n = 2, 3, 4, 5, 6$ , respectively. Thus, we have investigated synthesis of new titanium oxide with reduced form  $\text{TiO}_{2-\delta}$ , and have reported that a new titanium oxide of orthorhombic system with a nonstoichiometric composition of  $\text{TiO}_{1.94}$  is obtained by reducing anatase  $\text{TiO}_2$  in  $\text{H}_2$  at 950 °C [7]. It is highly desirable to use an environment-friendly material like titanium oxides to keep mild room temperature automatically and at the same time to decompose harmful chemical species. The goal of this study is to develop thermochromic windows using the new titanium oxide. Here we present the preparation of its single crystal, and its electrical and optical properties.

## 2. Experimental

### 2.1. Preparation of materials

Nonstoichiometric orthorhombic titanium oxide  $\text{TiO}_{1.94}$  ( $a = 0.938$  nm,  $b = 0.919$  nm,  $c = 0.588$  nm) was prepared according to our previous paper [7].  $\text{TiO}_2$  powder with anatase form was used as starting material. After grinding in an agate mortar, the sample powder was transferred in an alumina boat and placed in a quartz tube. After purging the tube with  $\text{N}_2$  gas,  $\text{H}_2$  gas was introduced. The temperature was increased at 15 °C/min, and heating was performed at 950 °C for 1 h.  $\text{TiO}_2$  powder with rutile form and a single crystal (10 mm × 10 mm × 0.5 mm) with rutile form were also used as starting materials and the products were investigated.

### 2.2. Structural aspects

Laue photographs were taken to verify the single crystallinity of the product from the rutile single crystal. Exposure time was 180 s under backscatter configuration (Cu  $K\alpha$ , 40 kV, 20 mA, MX-Labo, MAC Science Co.).

Single crystallinity of the product was also checked using a Debye–Scherrer diffractometer with monochromatized Cu  $K\alpha$  radiation (Miniflex, Rigaku Corporation).

### 2.3. Conductometry

The resistivity was measured by the conventional d.c. four-probe method in  $N_2$  stream. A constant current flow was made to flow from two outside electrodes with a current source (R6144, Advantest Corporation), and the electric potential difference between the two inside electrodes induced by the current was measured with an electrometer (HP34401A, Hewlett–Packard Corporation).

### 2.4. Optical measurement

The reflectance spectra in the wavelength range of 200–2500 nm was measured as a function of temperature using a spectrophotometer (Ubest V-570DS, JASCO Corporation).

## 3. Results and discussion

### 3.1. Structure and redox properties

It was found that the orthorhombic titanium oxide was also obtained by reducing the rutile  $TiO_2$  in  $H_2$  at  $950\text{ }^\circ\text{C}$  for 1 h, and that heating the orthorhombic titanium oxide in air at  $950\text{ }^\circ\text{C}$  yields the rutile  $TiO_2$ . In a word, the redox reaction between the orthorhombic titanium oxide and the rutile  $TiO_2$  was reversible at  $950\text{ }^\circ\text{C}$ . Since it is well-known that heating the anatase  $TiO_2$  at  $950\text{ }^\circ\text{C}$  in air yields the rutile  $TiO_2$ , redox reactions among these three compounds are schematically depicted by a relationship in Fig. 1.

Single crystals of rutile  $TiO_2$  are found in a wide variety of rocks and also produced artificially for optical materials. We investigated a product obtained by reducing the rutile single crystal at  $950\text{ }^\circ\text{C}$  in  $H_2$ , because the redox reaction between the two was reversible as for powder sample. A dark blue opaque sample (201.1 mg,  $\rho = 4.002\text{ g/cm}^3$ ) was formed by reducing a transparent rutile single crystal (1 0 0) (10 mm  $\times$  10 mm  $\times$  0.5 mm, 203.7 mg,  $\rho = 4.074\text{ g/cm}^3$ ). The color of the product was similar to that of the powder sample, and the size was almost same as that of the starting material. The chemical formula of the product was approximately estimated from the

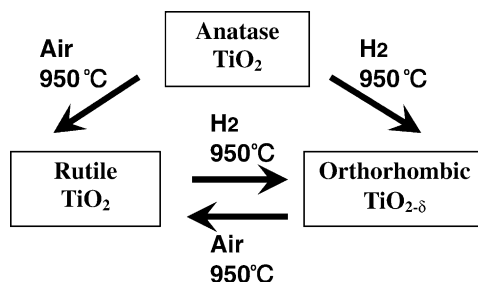


Fig. 1. Redox reactions among the anatase, the rutile, and the orthorhombic titanium oxides.

mass change in the reduction at  $\text{TiO}_{1.94}$ . The product showed metallic shine after polishing the surface.

Laue photographs were taken to verify the single crystallinity of the product. Fig. 2a and b show Laue photographs for the rutile single crystal and its reduced form, respectively. Exposure time was 180 s under backscatter configuration (Cu  $K\alpha$ , 40 kV, 20 mA, MX-Labo, MAC Science Co.). Definite spots observed for the reduced form indicates single crystallinity similar to the rutile. Some spots observed with streaks may reflect heterogeneous distribution of oxygen composition in depth direction.

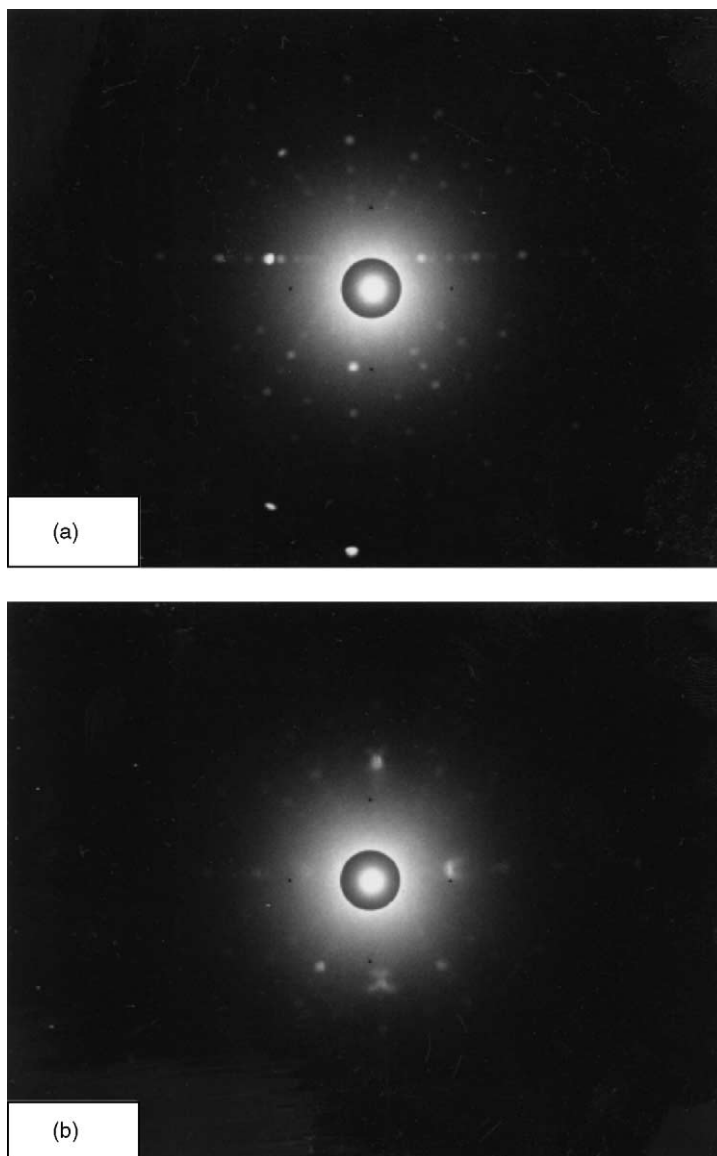


Fig. 2. Laue photographs from the rutile single crystal (a) and its reduced form (b).

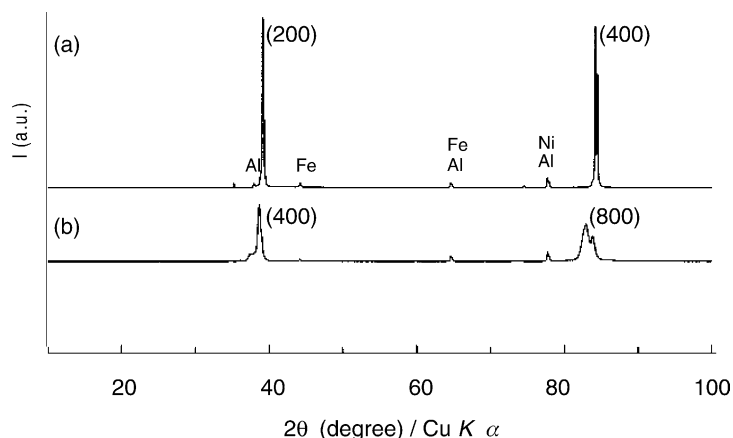


Fig. 3. Debye–Scherrer X-ray diffraction patterns from the rutile single crystal (1 0 0) (a) and its reduced form (b).

Single crystallinity of the product was also investigated using an X-ray diffractometer with monochromatized Cu K $\alpha$  radiation. Fig. 3a and b show Debye–Scherrer X-ray diffraction patterns from the rutile single crystal and its reduced form, respectively. The plane of incidence was normal to (1 0 0), and thus single crystals exhibit diffraction spots definitely from planes parallel to (1 0 0). The rutile single crystal showed only two diffraction peaks from (2 0 0) and (4 0 0) planes except for those from sample holders (Fe, Ni, Al), and the lattice parameter  $a$  was calculated at 0.460 nm. Similarly the reduced form showed only two diffraction peaks from (2 0 0) and (4 0 0) planes, and the lattice parameter  $a$  was calculated at 0.931 nm.

These results indicate that the rutile single crystal was transformed into the single crystal of its reduced form, orthorhombic titanium oxide TiO $_{2-\delta}$ . The lattice parameters of powder sample of the orthorhombic titanium oxide TiO $_{1.94}$  were  $a = 0.938$  nm,  $b = 0.919$  nm,  $c = 0.588$  nm, as reported previously [7]. It is interesting to note that the calculated lattice parameter of the reduced form,  $a = 0.931$  nm, was close to  $a = 0.938$  nm for the powder sample rather than  $b = 0.919$  nm. In a word, an increase in lattice parameter by reduction occurred normal to the surface where hydrogen gas was in contact. The directivity of the reduced single crystal appears to be dependent on the direction of diffusion of hydrogen.

Furthermore, scanning electron microscope (SEM) observation of the reduced form showed smooth surface with almost no cracks as shown in Fig. 4. This indicates that the transformation between the rutile and the reduced form occurs through topochemical process such as diffusion of hydrogen or oxygen.

### 3.2. Electrical and optical properties

Temperature dependence of the conductivity of the single crystal sample of TiO $_{1.94}$  is shown in Fig. 5. The conductivity at 25 °C was 17.2 S m $^{-1}$ , and it increased monotonously with increasing temperature. The temperature dependence was semiconductive in the range of 25–300 °C, and the activation energy was estimated at 2.75 kJ/mol ( $2.85 \times 10^{-2}$  eV). The semiconductor-to-metal transition was not observed in the temperature range. This result predicts that the sample shows a gradual reflectivity change in the temperature range.

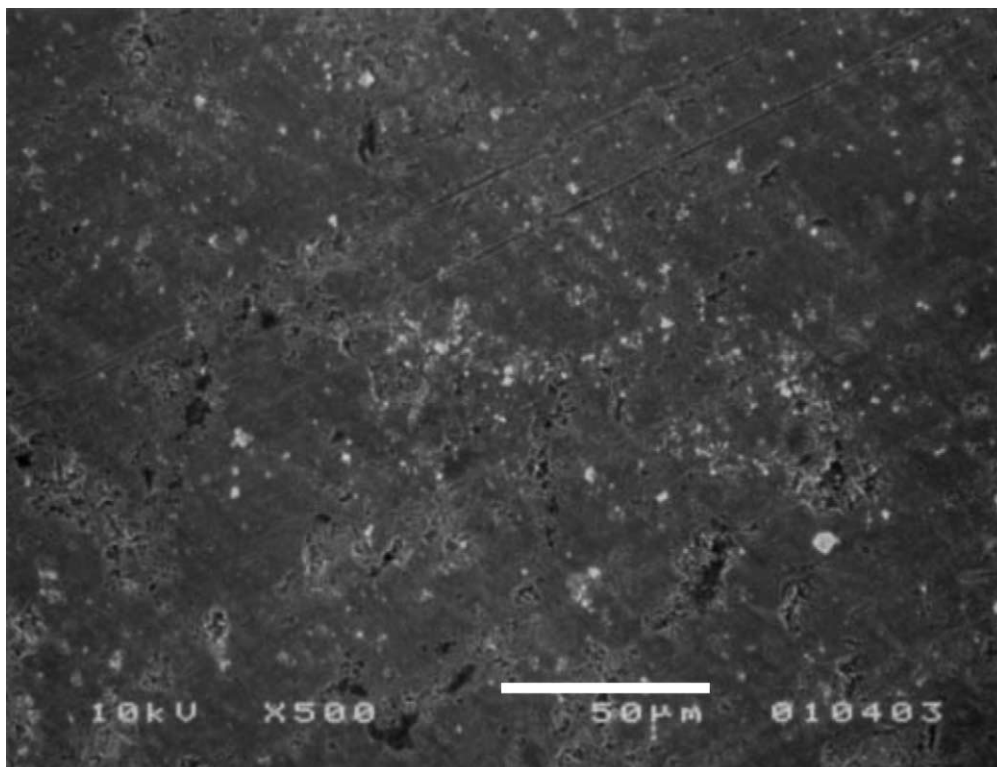


Fig. 4. SEM picture of the reduced form obtained by heating the rutile single crystal in  $H_2$  at  $950^\circ C$  for 1 h.

Reflectance spectra for the single crystal samples of the rutile and of the orthorhombic  $TiO_{1.94}$  are shown in Fig. 6a and b, respectively. Absorption at 400 nm observed for the rutile is due to the photoexcitation of electron–hole pairs, which contribute to the photocatalytic function. This peak at 400 nm disappeared after reduction because high electrical conductivity of the reduced form depresses the generation of the electron–hole pairs. This suggests that the photocatalytic function is unexpected as

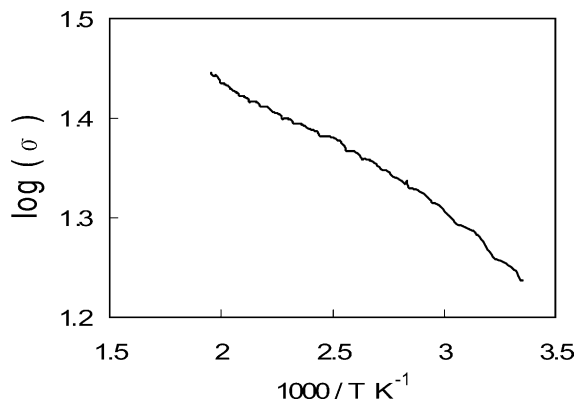


Fig. 5. Conductivity of the single crystal of  $TiO_{1.94}$  in the range of  $25\text{--}300^\circ C$ .

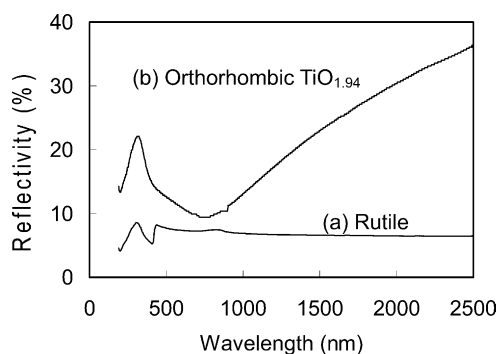


Fig. 6. Reflectance spectra for the single crystal samples of the rutile (a) and of the orthorhombic  $\text{TiO}_{1.94}$  (b).

for the orthorhombic  $\text{TiO}_{1.94}$ . It is interesting to note that the reflectivity of the orthorhombic  $\text{TiO}_{1.94}$  increases with increasing wavelength above 900 nm, whereas that of the rutile decreases. Near-infrared light from the sun largely affects temperature rise in room. Glass window which transmits visible light and simultaneously shades the near-infrared light is desirable because heat ray can be shaded with transparency.

Reflectance spectra of the orthorhombic  $\text{TiO}_{1.94}$  at 25–120 °C are shown in Fig. 7. It was found that the reflectivity in near-infrared region over 1700 nm gradually increased with increasing temperature, whereas it was almost the same below 1700 nm. In general, optical properties are strongly correlated with electrical properties, and thus this spectrum change is correlated with the increase of the conductivity, i.e., the density of conduction carriers shown in Fig. 5. Theoretical study on the correlation between the spectrum and the carrier density is needed to provide details. In application to “smart window”, it is essential to reflect near-infrared light at high temperature, because near-infrared light from the sun contributes greatly to the temperature rise in the room. Our results indicate that the orthorhombic titanium oxides satisfy this requirement. It can be said that “smart windows” are achieved by fabricating thin film of the orthorhombic titanium oxides on glass or dispersing the fine powders in glass matrix. It will be possible to achieve a drastic resistivity change of the material by preparation of complex oxides with the other transition metal oxides which exhibit phase transitions.

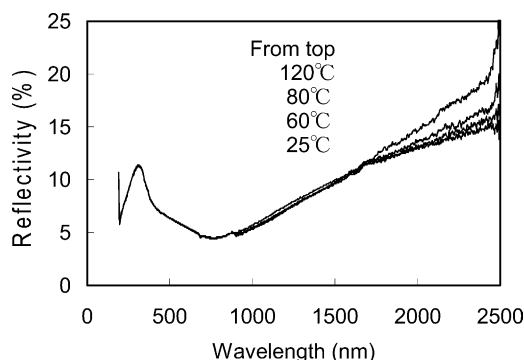


Fig. 7. Reflectance spectra for the single crystal sample of the orthorhombic  $\text{TiO}_{1.94}$  at 120, 80, 60, and 25 °C from top.

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## **References**

- [1] I. Takahashi, M. Hibino, T. Kudo, *Jpn. J. Appl. Phys.* 35 (1996) L438–L440.
- [2] I. Tsuyumoto, T. Kudo, *Mater. Res. Bull.* 31 (1996) 17–28.
- [3] R. Marchand, L. Brohan, M. Tournoux, *Mater. Res. Bull.* 15 (1980) 1129–1133.
- [4] A.L. Linsebigler, G. Lu, J.T. Yates, *Chem. Rev.* 95 (1995) 735–758.
- [5] R.F. Bartholomew, D.R. Frankl, *Phys. Rev.* 187 (1969) 828–833.
- [6] J.M. Honig, T.B. Reed, *Phys. Rev.* 174 (1968) 1020–1026.
- [7] I. Tsuyumoto, H. Uchikawa, *J. Mater. Sci. Lett.* 19 (2000) 2075–2076.