

# New orthorhombic titanium oxide, TiO<sub>1.94</sub>

I. TSUYUMOTO, H. UCHIKAWA

Department of Environmental Systems Engineering, Kanazawa Institute of Technology, 7-1 Ohgigaoka, Nonoichi, Ishikawa 921-8501, Japan

E-mail: tsuyu@neptune.kanazawa-it.ac.jp

The structure and electrical properties of the titanium oxides, having the composition of Ti<sub>n</sub>O<sub>2n-1</sub> where *n* is 2–10, have been the subject of much previous research [1–3]. Most of these compounds exhibit a semiconductor-metal transition at a critical temperature *T<sub>c</sub>*. This transition accompanies a significant change in optical properties, i.e., light is transmitted through a semiconductor phase below *T<sub>c</sub>* and reflected by a metal phase above *T<sub>c</sub>*. The *T<sub>c</sub>*s of Ti<sub>n</sub>O<sub>2n-1</sub> have been reported to be 660 K, 450 K, 150 K, 125 K, and 133 K for *n* = 2, 3, 4, 5, 6, respectively. Materials, having *T<sub>c</sub>* around room temperature, can be applied to thermochromic windows which shade radiation from the sun above *T<sub>c</sub>*. Thus, titanium oxide, having *T<sub>c</sub>* around room temperature, is highly desirable. As for some other compounds such as VO<sub>2</sub> and V<sub>1-x</sub>M<sub>x</sub>O<sub>2</sub> (M = W or Mo), trial applications to thermochromic windows have been reported [4, 5]. However, these include deleterious heavy metal, vanadium and may cause environmental pollution. Titanium oxide is known to act as a photocatalyst which decomposes deleterious chemical species. It can be expected that thermochromic windows using titanium oxide would be an environment-friendly material which keeps mild room temperature automatically and at the same time decomposes harmful chemical species. In this study, we focus on synthesis of new titanium oxide with reduced form TiO<sub>2-δ</sub>, aiming at *T<sub>c</sub>* around room temperature. We present here a new orthorhombic titanium oxide with the composition of TiO<sub>1.94</sub>.

Starting material was TiO<sub>2</sub> powder with anatase form (reagent grade). 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 completely with N<sub>2</sub> gas, H<sub>2</sub> gas was introduced. Heating was performed in a H<sub>2</sub> 100% stream at 600 °C, 800 °C, and 950 °C for 1 h, respectively. The temperature was increased at 15 °C/min. For comparison, the same experiment was performed in a N<sub>2</sub> 100% stream.

Crystalline phases were determined using an X-ray diffractometer with monochromatized Cu K<sub>α</sub> radiation.

TABLE I Compounds derived from anatase titanium oxide

Heating conditions		Products
H <sub>2</sub> 100% 1 h	600 °C	Anatase
	800 °C	Anatase
	950 °C	Dark blue TiO <sub>1.94</sub> (New)
N <sub>2</sub> 100% 1 h	600 °C	Anatase
	800 °C	Anatase
	950 °C	Rutile

As shown in Table I, a dark blue titanium oxide was formed in H<sub>2</sub> at 950 °C. We found that this is a new crystalline phase, which has not been reported so far. Because the products at 800 °C and 600 °C were the same as the starting materials, the transition of the crystal structure is considered to occur from 800 °C to 950 °C. In contrast, the rutile TiO<sub>2</sub> was obtained in N<sub>2</sub> at 950 °C. This indicates that the removal of oxygen atoms in

TABLE II X-ray powder diffraction data for orthorhombic TiO<sub>1.94</sub>. Lattice parameters *a* = 0.938 nm, *b* = 0.919 nm, *c* = 0.588 nm

<i>hkl</i>	<i>d</i> <sub>obs</sub> (nm)	<i>d</i> <sub>cal</sub> (nm)	<i>I</i> / <i>I</i> <sub>0</sub> obs
201	0.3673	0.3667	21
021	0.3617	0.3619	18
121	0.3354	0.3377	61
220	0.3266	0.3282	21
300	0.3176	0.3126	71
030	0.3080	0.3063	60
002	0.2934	0.2938	14
131	0.2621	0.2609	29
230	0.2559	0.2564	33
202	0.2506	0.2490	65
022	0.2492	0.2475	61
400	0.2360	0.2344	25
040	0.2322	0.2297	22
222	0.2204	0.2189	67
330	0.2177	0.2188	34
	0.2120		18
420	0.2086	0.2088	23
240	0.2063	0.2063	15
	0.2010		12
501	0.1783	0.1787	14
422	0.1700	0.1702	91
242	0.1685	0.1688	100
440	0.1637	0.1641	72
060	0.1532	0.1531	13
620	0.1471	0.1480	45
004	0.1451	0.1469	20
260	0.1438	0.1456	40
204	0.1389	0.1402	38
024	0.1382	0.1399	36
602	0.1371	0.1380	34
062	0.1362	0.1358	35
224	0.1327	0.1341	20
404	0.1250	0.1245	17
044	0.1237	0.1238	15
424	0.1208	0.1202	13
244	0.1194	0.1197	16
800	0.1175	0.1172	22
	0.1159		20
080	0.1151	0.1149	19
444	0.1100	0.1094	30
660	0.1080	0.1094	27
624	0.1043	0.1043	31
264	0.1035	0.1034	26

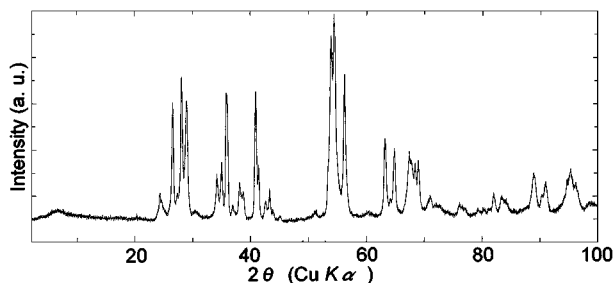


Figure 1 Powder X-ray diffraction pattern of new orthorhombic titanium oxide,  $\text{TiO}_{1.94}$ .

reducing atmosphere is essential for the formation of the new crystalline phase. Powder XRD pattern of the new crystalline phase is shown in Fig. 1. As shown in Table II, the crystal system of the new compound was found to be orthorhombic and the lattice parameters were calculated as  $a = 0.938$  nm,  $b = 0.919$  nm,  $c = 0.588$  nm using the least square method. Although the similar XRD pattern has not been reported so far, it seems that this structure arises from the lack of symmetry in the rutile structure [6].

The composition of the new compound was determined by using thermogravimetry (TG) and differential thermal analysis (DTA). In heating the sample in air from room temperature to  $1000^\circ\text{C}$  at  $10^\circ\text{C}/\text{min}$ , an oxidation from the  $\text{TiO}_{2-\delta}$  to  $\text{TiO}_2$  took place in the range of  $430^\circ\text{C}$  to  $570^\circ\text{C}$  and the weight of the sample was increased by 1.17%. This weight change corresponds to the incorporation of 0.06 mol of oxygen atoms. Therefore, the composition of the new compound was esti-

mated as  $\text{TiO}_{1.94}$ . Furthermore, the possibility of formation of hydrogen-doped  $\text{TiO}_2$  ( $\text{H}_\delta\text{TiO}_2$ ) can be ruled out, because the transition from the reduced form to the oxidized form accompanied the weight increase.

Resistivity of the pellet was measured by the DC two-probe technique. The product was pressed into powder compact with diameter of 2.5 mm, reheated in  $\text{H}_2$  at  $950^\circ\text{C}$  for 1 h, and used for the measurement. The resistivity was ca.  $16 \Omega \text{ cm}$ . This value includes possible ambiguities due to its strong dependence on the relative density of pellet. It can be considered that this compound shows electronic conductivity due to the mixed valence of titanium.

In conclusion, new titanium oxide with orthorhombic structure was formed in hydrogen atmosphere at  $950^\circ\text{C}$ . The composition was found to be  $\text{TiO}_{1.94}$  by TG and DTA measurement. Electronic conductivity can be expected from the preliminary conductometry.

## References

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