研究

On the Defect Structure of Rutile

II. Dependence of the Electrical Conductivity of High Purity Polycrystalline Rutile on Equilibrium Oxygen Pressure and Temperature*

Kazumasa Hirajima,** Tomoaki Sasaki** and Kenzo Hijikata**

An investigation has been conducted in order to gain "nearly intrinsic" character on the defect structure of high purity polycrystalline rutile (ca 6 nine), prepared from titanium tetrabutylate as a starting material, in the high oxygen pressure range $10^{-2} \sim 10^3$ mmHg and at the temperature 800° and 900°C. Measurement has been made by electrical conductivity (dc and ac) and thermoelectric power techniques. Since the frequency dispersion of the conductivity was not observed above 800°C at the frequency range 1~100 KHz and dc conductivity data correspond to those of ac and the sign of the thermo-emf indicates negative, it seems that the carrier is electronic rather than ionic. Over the oxygen pressure range $10^{-2} \sim 10^3$ mmHg, the electrical conductivity in nearly intrinsic region accorded well to the relation $\sigma \propto P_{O_2}^{-1/6}$, which is attributed to the predominance of fully ionized oxygen vacancies. It seems that p-type conduction did not belong to the intrinsic character of rutile below atmospheric pressure. The apparent activation energy was found ca 1.48 eV in pure oxygen atmosphere at 600°~1000°C.

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I. Introduction

The defect structure of oxygen-deficient rutile has been extensively investigated. There is, however, no agreement among published results. Namely, experimental results have usually been interpreted in terms of either vacancies¹⁻⁴⁾ or interstitial ions.⁵⁻⁹⁾ Kofstad¹⁾ measured the weight loss ΔW of rutile to 1227°C and concluded that oxygen vacancies are formed from the observed dependence of oxygen pressure $\Delta W \propto P_{O_2}^{-1/6}$. Förland²⁾ also observed a $P_{O_2}^{-1/6}$ dependence on thermogravimetric measurements in rutile. Bussem and Butler³⁾ confirmed the $P_{O_2}^{-1/6}$ dependence by weight loss determination. On the other hand, the previous measurements of Assayag⁵⁾ gave an exponent $-1/5$, indicating titanium interstitials. Hurlen⁶⁾ proposed that titanium interstitials predominate, however, his experimental evidence was scanty. Electron spin resonance experiments were analyzed by Frederikse⁷⁾ who concluded that at room temperature the main defects are Ti^{3+} interstitials. When the electrical conductivity of rutile are plotted as a function of oxygen pressure, $\sigma \propto P_{O_2}^{-1/m}$, several investigations, close to atmospheric pressure, have given values of m ranging 4~6.^{4, 8-13)} These differences of the values are attributed to reflect the presence of varying amounts of impurities in the rutile used by the different investigators. It might be noted that defect structure of rutile is very dependent on the individual conditions of experiments, such as on impurities in the rutile specimens used and on atmosphere contamination especially

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** Inst. Inorg. Chem., Depart. Chem., Nihon Univ., 3-25-40 Sakurajosui Setagaya-ku Tokyo Japan.

at low temperatures. The reported results have not been carried out under extremely high purity of specimen and atmosphere. In order to gain precise information for "nearly intrinsic" character of rutile, it is essential either to use extremely high purity material or to conduct experiments in which the impurity content can be shown to have little effect. The object of the present investigation is to study the influence of oxygen partial pressure on the electrical conductivity of high purity specimen, prepared from titanium tetra-butylate, at low temperatures and high oxygen pressures.

II. Experimental Procedures

II-1 Specimens

The powder of high purity oxide (rutile) was prepared from titanium tetra-butylate (T.B.T.-100; Nihon Soda Co. Ltd., Tokyo, Japan).

The white precipitate, which was obtained by hydrolysis of titanium tetra-butylate with pure water, was filtered, washed with triply distilled water, dried in air at ca 200°C, and calcined in a quartz crucible at 1000°C for 1 hr in air, and then cooled slowly in an electric furnace with Kanthal heater.

The X-ray diffraction patterns of the powders indicated a well crystallized structure of rutile.

Table 1 Spectrographic analysis of rutile from T.B.T.

Ti	Cr	Si	V	Fe	Ca	Mg	Mn	Ni	Mo
V.S.	N.D.	V.V.W.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.	N.D.

N.D.: not detected, p.p.m. under

With a small addition of ethyl alcohol as a binder, the powders were compacted into tablets at ca 2000 kg/cm². After removing the binder and the contamination from the steel mould, the compacts were packed in the same rutile powders, and sintered in a mullite tube with a SiC heater at 1400°C for 20 hr in air. The apparent densities of sintered specimens were greater than 80% of theoreticals. The specimens were polished and shaped into disks ca 8 mm in diameter by 3 mm thick. The spectrographic analysis* of the sintered specimen indicated that the silicon contaminated from an agate mortar only increased to v.v.w., and yet the remaining impurities were unchanged (Table 1).

Platinum was evaporated in vacuum on the both sides of the disk as electrodes.

II-2 Apparatus and Atmosphere Control

Fig. 1 shows the schematic diagram of the apparatus for the measurements of electrical conductivity and thermoelectric power. All measurements were made in a specially designed alumina tube. The platinum-evaporated specimen disk sandwiched between the platinum plates is shown in Fig. 2. Two thermocouples (0.3 mm ϕ Pt-Pt13%Rh) with platinum wires as current

* J.A. CO., Emission Spectrograph with a diffraction grating, Ebert mount 3.4 m.

Fig. 1 Schematic diagram of apparatus for electrical conductivity.

Fig. 2 Specimen holder.

leads were contacted to each electrode. The platinum arms of the thermocouples are used to determine ac conductivity, dc conductivity and Seebeck voltage.

The specimen temperature could be controlled within $\pm 0.3^\circ\text{C}$. For the high oxygen pressure (e.g. oxygen partial pressure: 150 and 760 mmHg), an oxygen-nitrogen gas mixture was used. Each gas was dried (dew point: -50°C) by molecular sieves,* and after passing through the calibrated flow-meters, gases were mixed and introduced into the chamber for the electrical measurements (ca 250 cc/min). For low oxygen pressure, a vacuum pumping system with a Pirani gauge was used.

II-3 Measurements

The electrical conductivity measurements (both ac and dc) based on a two-terminal method. The ac conductivity was measured directly by an impedance bridge** applying 1 KHz to the specimens in all runs. All the dc fields used were below 6 V/cm to ensure ohmic behavior and the

* molecular sieves 5A.

** Model AS-7130, Ando Electric Co., Ltd., Tokyo, Japan.

dc readings were taken in both direction and averaged. The ac and dc conductivities were obtained on heating and cooling with a good reproducibility. The measurements were approached in the direction of both increasing and decreasing oxygen pressures at each constant temperature. Equilibrium points were taken after specimen resistance stabilized for 1 hr. Their values, however, remained constant even in 20 hr or more in all experimental conditions.

The thermoelectric power Q is defined as the proportionality factor between the electrical field and the temperature gradient existing in a specimen with the condition that electrical current density is zero. Thus Q is given by the following equation:

$$\Delta V = Q \cdot \Delta T$$

where ΔV , ΔT , Q are respectively the specimen emf, the temperature difference between the two ends of the specimen, and the thermoelectric power of the specimen. Plot of ΔV vs ΔT were made at various temperatures at fixed P_{O_2} and Q obtained from the slope using the expression. Usually three data points were used to determine the slope. The temperature gradient varied ca $5^\circ \sim 20^\circ \text{C/cm}$ was established by moving the furnace. After moving the furnace, ca 1 hr had to be allowed for the specimen to reach to equilibrium. Temperatures and emf of the specimen were both measured with a digital millivolt meter.*

III. Results

The electrical conductivity of the sintered rutile compact was observed to follow the form $\sigma \propto \exp(-\Delta H/KT)$. A plot of $\log \sigma$ vs the reciprocal of absolute temperature at 760 mmHg of the oxygen pressure is displayed in Fig. 3. The reproducibility was obtained in all used atmospheres on heating and cooling and the thermal hysteresis was not observed. The data are well represented by a straight line having a 1.48 eV slope in the temperature ranges $600^\circ \sim 1000^\circ \text{C}$ except at 500°C . The frequency dispersion of the conductivity was observed at 700°C as shown by isobar

Fig. 3 The electrical conductivity vs. the reciprocal of absolute temperature at 760 mmHg of oxygen partial pressure for rutile.

* Type 2805, 0.1 μV (max. sensitivity/1 digit), Yokogawa Electric Works, Ltd., Tokyo, Japan.

Fig. 4 Frequency dispersion for rutile.

relation in Fig. 4. Above 800°C, the dc conductivity data corresponded to those of ac, while below 700°C the ac conductivity were slightly higher than dc values on the same run. When the dc conductivity measurements were performed at 760 mmHg oxygen pressure under 500°C, the dc voltage between both ends of specimen changed slowly for ca 6 min from the time that the current was turned on. In the case of specimen without platinum-evaporated electrodes, voltage changes occurred over much longer periods, usually ca 50 min or more.

In the thermoelectric power measurements, the cooler end of the specimen was always negative with respect to hotter end. This fact indicates negative charge carriers in pure oxygen, but the quantitative values could not be obtained with a reproducibility.

The electrical conductivity as a function of oxygen partial pressure was found to obey the relation $\sigma = K \cdot P_{O_2}^{-1/m}$, as given in Fig. 5. Both the 800° and 900°C curves are characterized by $m=6.0$.

Fig. 5 The logarithms of electrical conductivity vs. the logarithms of oxygen partial pressure for rutile.

IV. Discussion

IV-1 Defect Structure

The conductivity curve of Fig. 3 indicates that there is only a conduction mechanism in the high oxygen partial pressure (760 mmHg O₂).

The negative sign of the thermo-emf indicates that the defects are either electrons which are free to move through the crystal or are negatively charged ionic defects. The fact that frequency dispersion is not observed above 800°C suggests that the conduction is electronic rather than ionic. In addition, free electrons are associated with donor-type defects which are oxygen deficient defects. The electrical conductivity increased with decreased oxygen pressures, which indicates oxygen deficient defects are responsible. In the observed pressure dependence, the slope $-1/6$ is attributed to the predominance of doubly ionized oxygen vacancies according to the following equation:

therefore, by the chemical equilibrium theory,

$$P_{\text{O}_2}^{-1/2} = K(T) \cdot [\text{AV}] \cdot [e^-]^2.$$

If the neutrality condition can be simplified to

$$\begin{aligned} [\text{AV}] &= 2[e^-], \quad \text{then} \\ P_{\text{O}_2}^{-1/2} &= K'(T) \cdot [e^-] \cdot [e^-]^2, \\ &= K(T) \cdot [e^-]^3, \\ \sigma &= [e^-] \cdot q \cdot \mu(T) = K''(T) \cdot P_{\text{O}_2}^{-1/6}, \end{aligned}$$

where e^- is an electron in the conduction band, AV is an oxygen vacancy from which both electrons have been exited, q is carrier concentration, and μ is mobility, respectively.

A plot of the electrical conductivity as a function of the reciprocal absolute temperature gives a value for the activation energy of the intrinsic conductivity. An approximately straight line relation was obtained with an activation energy of 1.48 eV. This indicates that the intrinsic energy gap in rutile is equal to 2.96 eV. As a comparison it has been found that intrinsic energy gap in rutile has a value of 3.04~3.12 eV.^{12,14,15} Winter¹⁶ studied the kinetics of exchange of oxygen-18 for the several oxides, and the activation energy of exchange reaction for rutile was found 35 kcal/mol $\approx$ 1.52 eV) in the temperature range 500°~750°C.

Studies of electrical conductivity as a function of oxygen pressure (1 atm~CO-CO₂ mixtures) at 1000°~1500°C by Tannhauser⁸) and Blumenthal *et al*⁹), have shown that the oxygen pressure dependence, $\sigma \propto P_{\text{O}_2}^{-1/m}$, is characterized by values of m ranging from 4~5 in CO-CO₂ mixtures to 5~6 at atmospheric and subatmospheric pressures. The results in the CO-CO₂ mixtures have been interpreted in terms of a defect structure model involving tri- and tetra-valent interstitial titanium ions. By Blumenthal *et al*,⁹) however, the electrical conductivity of rutile in air below ca 950°C appears on the basis of his investigation to be impurity-controlled due to the presence of aluminum rather than intrinsic conduction. Yahia¹³) reported that the oxygen ion vacancy model seemed to predominate at pressure above 10 mmHg in the temperature range 950°~1212°C, while at lower oxygen pressures a model involving titanium interstitial was dominant. It seems likely to be questionable that specimen used in his investigation contained total impurity ca 700 ppm. Delmaire *et al*¹⁷) also reported $-1/6$ dependence, however, it was not clearly described at all for the experimental details. Ludolph¹²) obtained values of m ranging 4.9~5.7 at 719°~944°C, but impurity of specimen used was not indicated. Thus, it is unreasonable to compare the present results with theirs above mentioned. From the results of conductivity measurement of rutile by Greener *et al*,⁴) impurity-controlled defects were dominant in the lower temperature region 600°~900°C.

It seems that the authors could succeed in measuring "nearly intrinsic" conductivity of rutile, because the relation $\log \sigma$ vs $1/T$ was well represented by a straight line having a slope 1.48 eV as shown in Fig. 3 in the temperature range $600^\circ\sim 1000^\circ\text{C}$, and the sign of the thermo-emf indicated negative in all temperature ranges. As to the possibility of coexistence with interstitial ions shown by Kofstad²⁷⁾, the authors did not carry on the electrical conductivity measurements above 1000°C , because the diffusion of platinum electrode into specimen was observed remarkably in higher temperatures. Thus the authors could not make out whether interstitial titanium ions coexist at the same time or not.

Recently, Innami *et al*²⁸⁾ has found that the linear shrinkage and the specific resistance during sintering for the same rutile powders used for the present experiment were very affected by the oxygen partial pressure. At N_2 atmosphere ($\approx 10^{-3}$ mmHg oxygen partial pressure), the linear shrinkage and the electrical conductivity increased rather than at air atmosphere. These consistent with the present results of electrical conductivity measurements. Therefore, it may be noted that the defect structure of high purity rutile involved oxygen vacancies.

IV-2 Impurity Effect

Earlier studies, by the authors,¹⁸⁾ of the electrical properties of polycrystalline rutile from TiCl_4 indicates the p-conduction. The results are shown in Fig. 6. The curves are shown to be an amphoteric semiconductor with the region of predominant hole conduction shifting to higher pressures at lower temperatures. About this p-conduction, Kofstad¹⁹⁾ and Pearson²⁰⁾ also found. It is of interest to note that iron-doped rutile exhibits an amphoteric semiconductor in a certain pressure range at high temperatures¹²⁾. A similar p-type character was found in aluminium-doped rutile by Yahia,¹³⁾ Haufler¹¹⁾ and Hurlen⁶⁾ also observed the p-type conductivity of chromium-doped rutile, and the authors¹⁸⁾ also confirmed similar behavior of chromium-doped rutile from the thermoelectric power and pressure dependence of conductivity below 1000°C .

Fig. 6 Isothermal relation between the logarithms of the conductivity and the logarithms of P_{O_2} in the temperature range $770^\circ\sim 1000^\circ\text{C}$.

Table 2 Spectrographic analysis of rutile from TiCl_4 .

Ti	Cr	Si	V	Fe	Ca	Mg	Mn	Ni	Mo
V.S.	N.D.	W.	N.D.	N.D.	V.W.	V.W.	N.D.	N.D.	N.D.

N.D.: not detected, p.p.m. under

It seems that p-type behavior, observed in the case of previous work,¹⁸⁾ happened on the interaction of the defects produced by the various impurities. P-type character was not found in the present case of high purity rutile. Therefore, it appears that p-type conduction did not belong to the intrinsic behavior of rutile below atmospheric pressure. Results of spectrographic analysis of rutile powders prepared from TiCl_4 are given in Table 2.

Recently, there are some reports for the influence of the atmosphere contamination on the experiments. Aronson²¹⁾ and Kofstad and Ruzicka²²⁾ examined oxygen deficiency in ZrO_2 as a function of temperature ($<1300^\circ\text{C}$) and of oxygen partial pressure, using H_2 - H_2O and CO - CO_2 gas mixtures, and both studies produced uncertain results. Hussey and Smeltzer²³⁾, who studied the oxidation of Zr by CO - CO_2 , indicated that this gas mixture may give unreliable results with ZrO_2 . By Carniglia *et al.*,²⁴⁾ consistent results were obtained when O_2 -inert gas mixtures were used, but use of H_2 - H_2O and CO - CO_2 at $1000^\circ\sim 1200^\circ\text{C}$ gave abnormal and, in the latter case, erratic data. Iguchi and Yajima²⁵⁾ reported that the rutile specimens reduced in vacuum with diffusion pump are contaminated by pump oil. Any carbon introduced with pump oil might influence on the electrical properties near-stoichiometric region or in the n-type region, as suggested by Pope and Simkovich.²⁶⁾ The side reactions in these atmospheres are inferred.

IV-3 Homogeneous Range of Rutile

The general problem of the stability of compounds which exhibit an apparently large deviation from the stoichiometric composition has been reviewed by Anderson *et al.*²⁹⁾ and Wadsley.³⁰⁾ A continuous series of phases of rutile having the basic rutile structure has been identified for compositions corresponding to $\text{Ti}_n\text{O}_{2n-1}$, where possibly $n \rightarrow \infty$. Anderson *et al.*³¹⁾ put the limit of homogeneity at higher than $\text{TiO}_{1.96}$. More recently, Straumanis *et al.*³²⁾ have placed the limit at $\text{TiO}_{1.983}$ for the specimens quenched from 1400°C . Bursil and Hyde³³⁾ suggest the existence of a new family of ordered phases, probably $\text{Ti}_n\text{O}_{2n-1}$ ($n = 15\cdots 36$) derived from quenched rutile (ca 99.9%) by means of electron microscopic observation. These studies were made for the quenched samples but a thermodynamic information is very scarce. By Bulmenthal and Whitmore³⁴⁾, electromotive forces on galvanic cells which utilized solid electrolytes were measured to determine the homogeneous range of rutile at 900° and 1000°C . The cell voltage is plotted as a function of the O/Ti ratio at the two temperatures. In the case of electrode compositions with O/Ti ratios ca 1.998~1.992, the cell emf is a function of specimen composition, signifying the existence of a single-phase region (probably nonstoichiometric rutile) and specimens with O/Ti ratio lying ca 1.992~1.968 exhibited essentially constant emf's, providing further evidence that a two-phase region exists over this compositional range. In a large number of these studies, the O/Ti ratio has been determined by the thermogravimetric method. In this kind

of investigation, no experiments have yet been made in order to determine the homogeneous range as a function of oxygen partial pressure in a certain temperature.

V. Summary

- 1) The electrical conductivity of high purity polycrystalline rutile prepared from T.B.T. was determined as a function of the oxygen partial pressure ($10^{-2}\sim 10^3$ mmHg) at 800° and 900°C . The electrical conductivity has been found proportional to $P_{\text{O}_2}^{-1/6}$.
- 2) The frequency dispersion of the conductivity was not observed at 800° and 900°C , and the dc conductivity data corresponded to those of ac.
- 3) The relation $\log\sigma$ vs $1/T$ was well represented by a straight line having a slope 1.48 eV in pure oxygen gas and in the temperature range $600^\circ\sim 1000^\circ\text{C}$.
- 4) In the thermoelectric power measurements, the cooler end of the specimen was always negative with respect to the hotter end indicating negative charge carriers, electrons, but the quantitative values could not be obtained with a reproducibility.
- 5) It may be concluded that the defect of rutile with a "nearly intrinsic" character involves oxygen vacancies at 800° and 900°C in the oxygen partial pressure $10^{-2}\sim 10^3$ mmHg, and it appears to imply that p-type conduction did not belong to the intrinsic behavior of rutile below atmospheric pressure.

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会 告

第11回 窯業基礎討論会プログラム

日	時	昭和48年1月25日(木), 28日(金)	
会	場	岡山県総合文化センター (岡山市天神町8-54, 電話 (0862)24-1286)	
共	催	粉体粉末冶金協会 他	
討 論 主 題		1. 相変化-雰囲気, 異種成分の影響
2. セラミックスの微構造と物性	
特 別 講 演		1月25日	固相の反応における雰囲気や異種成分の影響
(東工試) 小 寺 嘉 秀
		1月26日	セラミックスの加工と強度
(東工大工材研) 齊 藤 進 六
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