Zeitschrift für Kristallographie 194, 305–313 (1991)

The crystal structure of rutile as a function of temperature up to 1600° C

Kazumasa Sugiyama* and Yoshio Takéuchi

Mineralogical Institute, Faculty of Science, University of Tokyo,
Hongo, Tokyo 113, Japan

Received: September 5, 1990

Rutile* / TiO₂ / *High temperature crystal chemistry

Abstract. The crystal structure of rutile (TiO_2) has been studied at high temperatures up to about 1600° C based on sets of single crystal X-ray diffraction intensities collected on a four-circle diffractometer. The thermal expansion coefficients for the *a*- and *c*-axes in the measured temperature range were $\alpha_a = 8.9(1) \times 10^{-6}$ °C^{-1} and $\alpha_c = 11.1(1) \times 10^{-6}$ °C^{-1}, respectively. The thermal response of the octahedra about Ti is such that the thermal coefficient for the four short equatorial Ti–O bonds was $8.4(3) \times 10^{-6}$ °C^{-1} and for the two long apical Ti–O bonds $11.5(3) \times 10^{-6}$ °C^{-1}. The rate of thermal expansion of the octahedral shared edge is relatively large under ~ 1200° C, while it becomes small above ~ 1200° C. An l to l_o ratio, which we denote shrinkage index, however, decreases with the raise of temperature (l = the length of the shared edge at a temperature; l_o = the edge length of a regular octahedron having the same volume as the Ti octahedron has at the same temperature).

Introduction

In the series of our high temperature structural studies of oxygen-based crystals, we noted that shared edges of polyhedra about cations tend to show specific thermal responses (Takéuchi et al., 1984). In order to gain further examples of those thermal responses of shared edges, we have undertaken the study of the rutile structure at elevated temperatures. The crystal structure of rutile was first analyzed by Vegard (1916). Refinements of the structure have since been carried out by Cromer and Herrington

---

* *Present address:* Research Institute of Mineral Dressing and Metallurgy (SENKEN), Tohoku University, Sendai 980, Japan.

(1955), Baur (1956), Baur and Kahn (1971), Abrahams and Bernstein (1971), Shintani et al. (1975) and Gonschorek (1982). The thermal response of the structure has been theoretically studied by West and Bruce (1982), while experimentally by Meagher and Lager (1979) up to 900° C and by Seki et al. (1984) up to 1000° C. Since however the melting point of rutile is as high as 1850° C, it is certainly desirable to extend the temperature range close to this temperature to fully elucidate thermal behaviour of crystalline rutile. The present paper is to report the result of our structural study of rutile at temperatures up to 1600° C.

Experimental

The rutile crystal used in this high temperature study has been synthesized by the Czochralski method and kindly provided by Dr. S. Takasu of Toshiba Ceramic Co., Ltd. Out of this crystal, we prepared an X-ray specimen having the shape of a cylinder, the radius of the cross section being 0.15 mm and 15 mm long along *c*. With the use of such a long crystal specimen, we can evade the possible contamination of the diffraction intensities from the crystal with those of a binder such as alumina or zirconia cement, which is generally used to fix the crystal to a rod for high temperature X-ray studies. The usefulness of this method was confirmed in the high temperature crystal structural study of danburite $CaB_2Si_2O_8$ (Sugiyama and Takéuchi, 1985).

The crystal specimen was mounted on a goniometer head on a four-circle single-crystal diffractometer (Rigaku AFC5) with its cylindrical axis parallel to the ϕ axis. As a heat sources, we used a small electric resistance furnace such as the one described by Brown et al. (1973) for the studies up to 900° C, while a gas flame furnace (Yamanaka et al., 1981) for the studies of higher temperatures. Details of the temperature measurement have been provided by Yamanaka et al. (1981).

The cell dimensions were calculated by the least-squares procedure applied to the 2θ values of $20 \sim 25$ reflections measured on the diffractometer using pylolitic graphite monochromated Mo$K\alpha$ radiation, $\lambda = 0.70926$ Å. The ω-2θ scan technique was used to collect the one sixteenth of the graphite monochromated intensities. Since we used a collimator having a diameter 0.5 mm for the incident X-ray beam, the cylindrical crystal specimen was not fully bathed in the X-ray beam, thus giving rise to a change in effective volume of the crystal depending upon its orientation with respect to the incident beam. Due corrections were therefore made for the effective volume and absorption using the procedure developed by Haga and Takéuchi (1983) after correction for Lorentz and polarization factors. During all the intensity measurements, intensities of three reference reflections were monitored every 100 reflections at each temperature; the fluctuation of those intensities was less than one $\sigma|F\text{obs}|$. Details of the intensity study data are summarized in Table 1 with the obtained cell dimensions.

Table 1. Variation of cell dimensions with the intensity-study data.

Temperature (°C)	a (Å)	c (Å)	V (Å^3)	2 θ maximum (°)	No. reflections used	R (%)	Rw (%)
25	4.5924(2)	2.9575(2)	62.38(1)	150	352	2.69	3.65
250	4.6001(3)	2.9654(4)	62.76(1)	80	119	5.17	6.48
460	4.6083(4)	2.9737(5)	63.15(1)	80	130	4.42	5.77
670	4.6172(5)	2.9803(7)	63.54(2)	80	119	4.75	6.37
890	4.6252(3)	2.9878(5)	63.92(1)	80	112	3.38	4.88
1060	4.6344(3)	2.9919(2)	64.26(1)	150	248	5.25	5.77
1190	4.6392(3)	2.9967(2)	64.50(1)	150	219	5.53	6.69
1350	4.6452(3)	3.0017(2)	64.77(1)	130	190	5.44	5.41
1480	4.6499(3)	3.0057(2)	64.99(1)	130	184	5.68	5.68
1610	4.657(1)	3.0093(2)	65.26(2)	100	152	8.02	7.29

Table 2. Atomic coordinates and isotropic temperature factors (Å^2) and anisotropic thermal parameters ($\times 10^4$) of the form $\exp-(\beta_{11}h^2 + \ldots + 2\,\beta_{12}hk + \ldots)$.

Temperature (°C)	Ti				O				
	β_{11}	β_{33}	β_{12}	$B_{eq.}$	$x(=y)$	β_{11}	β_{33}	β_{12}	$B_{eq.}$
25	71.5(7)	95(2)	−0.8(3)	0.513	0.30499(8)	57.9(9)	78(3)	−19.2(9)	0.416
250	127(5)	182(11)	1(1)	0.928	0.3053(3)	109(6)	154(15)	−28(4)	0.796
460	162(4)	255(9)	−2(1)	1.218	0.3056(2)	139(5)	229(14)	−46(4)	1.057
670	202(5)	319(11)	0(2)	1.527	0.3057(3)	180(7)	297(18)	−54(5)	1.376
890	218(4)	358(10)	−3(1)	1.668	0.3056(3)	192(6)	334(16)	−77(4)	1.496
1060	260(2)	401(5)	−4(1)	1.967	0.3056(2)	224(4)	380(10)	−88(4)	1.793
1190	277(3)	441(7)	−4(2)	2.119	0.3056(3)	250(5)	412(14)	−93(5)	1.926
1350	311(3)	494(7)	−3(2)	2.385	0.3061(3)	287(5)	485(14)	−108(5)	2.234
1480	326(3)	513(7)	−4(2)	2.501	0.3060(3)	296(6)	509(15)	−107(6)	2.318
1610	353(5)	547(12)	−8(3)	2.701	0.3063(4)	323(9)	544(23)	−117(10)	2.523

Refinement

Among structure factors thus obtained, those greater than $3\sigma|F\text{obs}|$ were used for the following structural studies. The structural refinement in each case was carried out in the space group $P4_2/mnm$ using the least-squares program LINUS (Coppens and Hamilton, 1970) with a weighting scheme of $1/\sigma^2|F\text{obs}|$. A first trial of an anisotropic refinement revealed the existence of conspicuous extinction effect; the correction factor, y, for the 110 reflection, for example, was as small as 0.36 at room temperature. The correction for the isotropic extinction effect was therefore made using program LINUS. The anisotropic refinement with corrections for extinction at each temperature converged at the values of R and Rw as given in Table 1. The resulting atomic coordinates are listed in Table 2. Neutral atomic form factors and values for dispersion corrections for all atoms were provided by *International Tables for X-ray Crystallography* Vol. IV (1974)[1].

Results and discussion

The temperature dependence of the lattice dimensions and unit cell volume of rutile are shown in Figures 1 and 2, respectively. Linear thermal expansion coefficients in the measured temperature range were obtained to be $\alpha_a = 8.9(1) \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$ and $\alpha_c = 11.1(1) \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$ for the a- and c-axes respectively. That of the c-axis is larger than that of the a-axis, showing a good agreement with the previous results up to 1000°C (Rao et al., 1970; Meagher and Lager, 1979; Fawcett et al., 1983; Seki et al., 1984). The thermal expansion coefficient for the cell volume was determined to be $\alpha_V = 29.1(1) \times 10^{-6}\,{}^\circ\mathrm{C}^{-1}$.

Prior to discuss thermal response of the structure now considered, it is to be reminded that the six Ti–O bonds of the octahedron about Ti may be classified into two categories; one includes four shorter bonds denoted Ti–O(a) parallel to (110), and the other remaining two longer bonds parallel to (001) (Fig. 3). Each octahedron shares a pair of two opposite edges O(a)–O(a′) to form a straight chain of octahedra parallel to the c-axis.

Thermal response of the Ti–O distances

The variations, with the increase of temperature, of two independent interatomic distances Ti–O(a) and Ti–O(b) are compared in Figure 4. Our results are in good agreement with the previous values reported by Seki et al. (1984) for the temperature range up to 1000°C. The thermal expansion

---

[1] Additional material to this paper can be ordered from the Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen 2, FRG. Please quote reference no. CSD 55011, the names of the authors and the title of the paper.

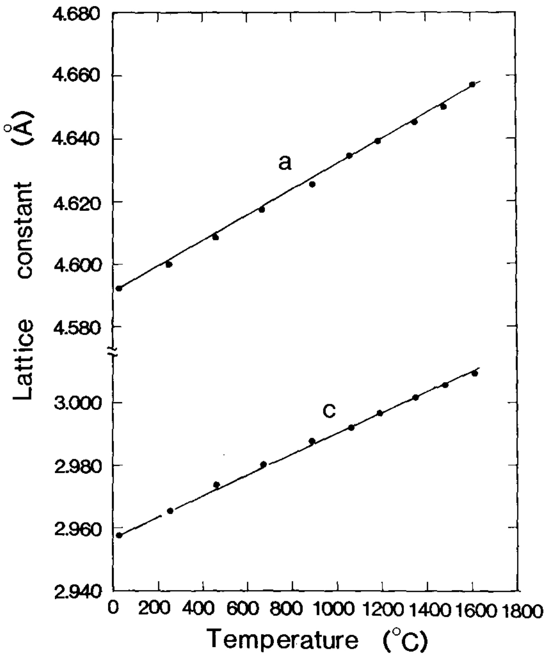

Fig. 1. A plot of lattice constants of rutile versus temperature.

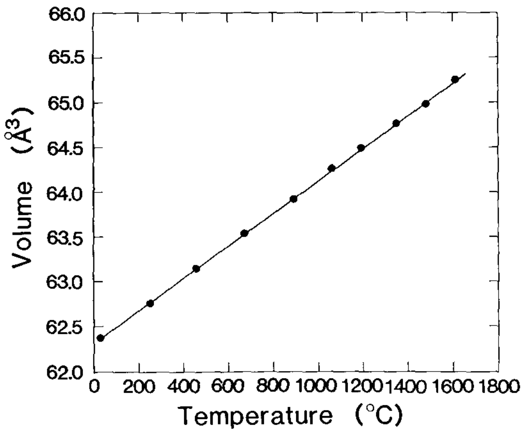

Fig. 2. A plot of unit cell volume of rutile versus temperature.

coefficients for the Ti – O(a) and Ti – O(b) distances were revealed to be $8.4(3) \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$ and $11.5(3) \times 10^{-6}\,{}^{\circ}\mathrm{C}^{-1}$, respectively. Both distances increase uniformly with increasing temperature. However the coefficient for the longer Ti – O(b) distances is slightly larger, showing a trend of increasing the distortion of the titanium octahedron.

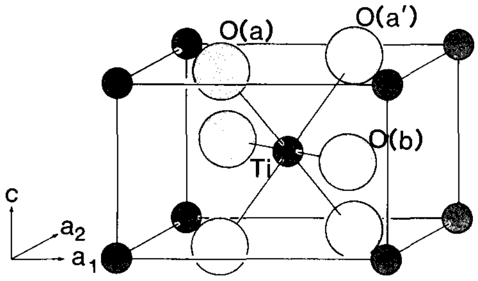

Fig. 3. A perspective view of the rutile structure, showing the notation of the oxygen atoms.

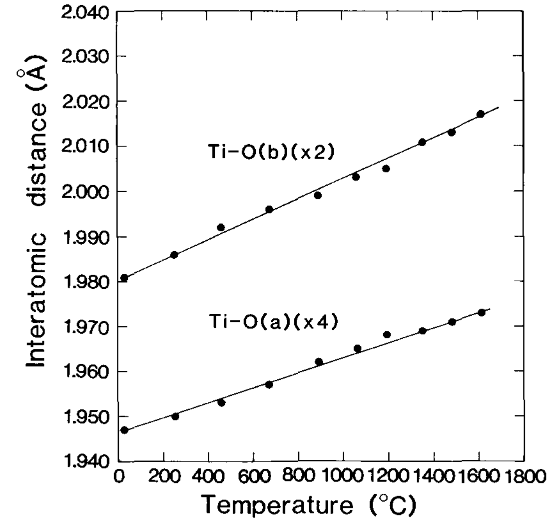

Fig. 4. Variation with increasing temperature of the Ti—O(a) and Ti—O(b) bonds.

Thermal response of the shared edge

The length of about 2.53 Å for the shared edge O(a)—O(a') is significantly small as expected from the strong repulsion between two adjacent Ti atoms. This particular shared edge shows an interesting thermal response with the increase of temperature (Fig. 5 *bottom*), showing a significantly high rate of expansion between ~ 500° C and ~ 1200° C. In order to study further detail of the thermal response of the shared edge, we introduced a shrinkage index $R_s = l/l_o$. Where, l is the length of the shared edge of the Ti octahedron at a given temperature, and l_o the edge length of a regular octahedron having the same volume as the Ti octahedron has at the same temperature.

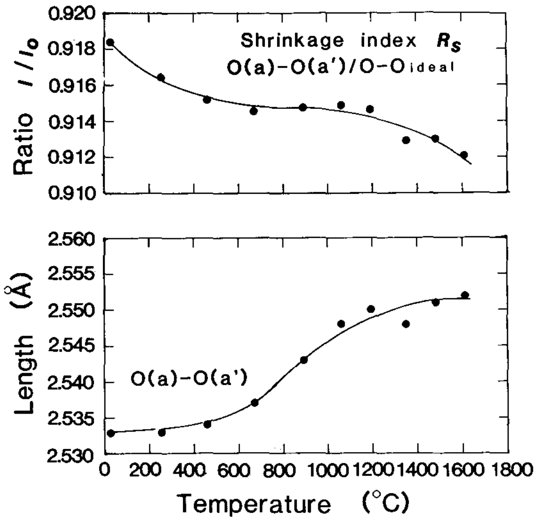

Fig. 5. *(Bottom)* Variation with increasing temperature of the shared edge O(a) – O(a′) length. *(Top)* Variation with increasing temperature of the $O(a) - O(a')/O - O_{ideal}$ ratio (see text).

We then evaluated the values of R_s and plotted versus temperature in the top of Figure 5. In this figure, we observe that the ratio decreases with the increase of temperature though the rate of decreasing is very small in the specific temperature range mentioned above. This result shows a general trend that the shared edge in fact becomes relatively shortened, with the increase of temperature, to shield the increasing repulsive forces between Ti's owing to the increase of effective ionic radius of Ti.

These features characteristic of the change in the octahedra well account for the fact that the thermal expansion of the *c*-axis is large relative to that of the *a*-axis and also for mode of variation of the O(a) – Ti – O(a′) angle. The tendency, with increasing temperature, of the decreasings of both R_s and the O(a) – Ti – O(a′) angle away from 90° (Table 3) indicates the increase of octahedral distortion. The slight decrease, with increasing temperature, of the Ti – O – Ti angle (Table 3) suggests that the geometrical environment around the oxygen atom becomes more regular with the raise of temperature. These thermal responses characteristic of the rutile structure are in line with those theoretically predicted by West and Bruce (1982).

Acknowledgements. We thank Dr. N. Haga of the University of Tokyo for his experimental assistance. Computations were carried out on HITAC M-380H at the Computer Center of the University of Tokyo.

Table 3. Some important interatomic distances and angles in rutile.

Temperature (°C)	Ti – O(a) (Å)	Ti – O(b) (Å)	O(a) – O(a′) (Å)	O(a) – Ti – O(a′) (°)	O(a) – O(b) (Å)	Ti – O – Ti (°)
25	1.9470(2)	1.9808(3)	2.5330(5)	81.16(1)	2.7775(2)	130.58(1)
250	1.950(1)	1.988(1)	2.533(2)	81.01(4)	2.783(1)	130.51(1)
460	1.953(1)	1.992(1)	2.534(2)	80.86(4)	2.790(1)	130.43(2)
670	1.957(1)	1.996(1)	2.537(2)	80.82(5)	2.796(1)	130.41(2)
890	1.962(1)	1.999(1)	2.543(2)	80.81(4)	2.801(1)	130.40(2)
1060	1.9648(4)	2.003(1)	2.548(2)	80.83(3)	2.8059(4)	130.42(1)
1190	1.968(1)	2.005(1)	2.550(2)	80.80(4)	2.809(1)	130.40(2)
1350	1.969(1)	2.011(1)	2.548(2)	80.66(4)	2.814(1)	130.33(2)
1480	1.971(1)	2.013(1)	2.551(2)	80.64(4)	2.817(1)	130.32(2)
1610	1.973(1)	2.017(1)	2.552(3)	80.59(6)	2.821(1)	130.30(3)

References

Abrahams, S. C., Bernstein, J. L.: Rutile: normal probability plot analysis and accurate measurement of crystal structure. J. Chem. Phys. **55** (1971) 3206–3211.

Baur, W. H.: Über die Verfeinerung der Kristallstrukturbestimmung einiger Vertreter des Rutiltyps: TiO_2, SnO_2, GeO_2 und MgF_2. Acta Crystallogr. **9** (1956) 515–520.

Baur, W. H., Kahn, A. A.: Rutile-type compounds. IV. SiO_2, GeO_2 and a comparison with other rutile-type structures. Acta Crystallogr. **B27** (1971) 2133–2139.

Brown, G. E., Sueno, S., Prewitt, C. T.: A new single-crystal heater for the precession camera and four-circle diffractometer. Am. Mineral. **58** (1973) 698–704.

Coppens, P., Hamilton, W. C.: Anisotropic extinction corrections in the Zachariasen approximation. Acta Crystallogr. **A26** (1970) 71–83.

Cromer, D. T., Herrington, K.: The structure of anatase and rutile. J. Am. Chem. Soc. **77** (1955) 4708–4709.

Fawcett, T. G., Kirchhoff, P. M., Newman, R. A.: The measurement of thermally induced structural changes by high temperature (900°C) Guinier X-ray powder diffraction techniques. Adv. X-Ray Anal. **26** (1983) 171–180.

Gonschorek, W.: X-ray charge density study of rutile (TiO_2). Z. Kristallogr. **160** (1982) 187–203.

Meagher, E. P., Lager, G. A.: Polyhedral thermal expansion in the TiO_2 polymorphs: Refinement of the crystal structures of rutile and brookite at high temperature. Can. Mineral. **17** (1979) 77–85.

Haga, N., Takéuchi, Y.: Absorption and volume corrections for a fine cylindrical sample longer than the beam diameter. In: *Structural Studies of Minerals at High Temperatures and High Pressures.* (Ed. Takéuchi, Y.) J. Miner. Soc. Japan **16**, Spec. Issue **1** (1983) 93–98.

International Tables for X-ray Crystallography. Vol. IV, Kynoch Press, Birmingham (1974).

Rao, K. V. K., Naidu, S. V. N., Iyengar, L.: Thermal expansion of rutile and anatase. J. Am. Ceramic Soc. **53** (1970) 124–126.

Seki, H., Ishizawa, N., Mizutani, N., Kato, M.: High temperature structure of the rutile-type oxides, TiO_2 and SnO_2 (in Japanese). J. Ceramic Soc. Jpn. **92** (1984) 219–223.

Shintani, H., Sato, S., Saito, Y.: Electron-density distribution in rutile crystals. Acta Crystallogr. **B31** (1975) 1981–1982.

Sugiyama, K., Takéuchi, Y.: Unusual thermal expansion of a B–O bond in the structure of danburite $CaB_2Si_2O_8$. Z. Kristallogr. **173** (1985) 293–304.

Takéuchi, T., Yamanaka, T., Haga, N., Hirano, N.: High temperature crystallography of olivines and spinels. In: *Materials Science of the Earth's Interior* (Ed. I. Sunagawa). pp. 191–231. Terrapub, Tokyo (1984).

Yamanaka, T., Takéuchi, Y., Sadanaga, R.: Gas-flame high temperature apparatus for single crystal X-ray diffraction study. Z. Kristallogr. **154** (1981) 147–153.

Vegard, L.: Results of crystal analysis-III. Phil. Mag. **32** (1916) 505–518.

West, A. R., Bruce, P. G.: Tetragonal-packed crystal structure. Acta Crystallogr. **B38** (1982) 1891–1896.