

The Crystal Structures of Ti_2O_3 , A Semiconductor, and $(Ti_{0.900}V_{0.100})_2O_3$, A Semimetal

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The crystal structures of the semiconductor Ti_2O_3 and the semimetal $(Ti_{0.900}V_{0.100})_2O_3$ were determined from X-ray diffraction data collected from single crystals. The compounds are isostructural with Al_2O_3 of rhombohedral unit cell dimensions of $a = 5.4325(8)$ Å and $\alpha = 56.75(1)^\circ$ for Ti_2O_3 , and $a = 5.4692(8)$ Å and $\alpha = 55.63(1)^\circ$ for the doped system. The effect of substitution of V^{+3} is to increase the metal-metal distance across the shared octahedral face from 2.579 Å in Ti_2O_3 to 2.658 Å in $(Ti_{0.900}V_{0.100})_2O_3$, while decreasing the metal-metal distance across the shared octahedral edge from 2.997 to 2.968 Å. The metal-oxygen distances exhibit only small changes. These structural changes are consistent with the band theory proposed by Van Zandt, Honig, and Goodenough (9) to explain changes in electrical and other properties with increasing vanadium content in $(Ti_{1-x}V_x)_2O_3$.

Introduction

The resistivity of Ti_2O_3 first diminishes almost exponentially with increasing temperature, then drops rather abruptly to a minimum after which it rises with further increases in temperature (1-6). The drop in resistivity occurs in the temperature region of 400-600°K, and is accompanied by a rapid change in the unit cell parameters (5, 7), although the point group symmetry of Ti_2O_3 remains unchanged through the transition (8). The deformation of the cell is apparently accompanied by an alteration of the band structure such that the narrow band gap, which originally separated a filled band from higher lying empty bands, narrows down and is eventually replaced by an overlapping set of bands (9, 10).

Doping with V_2O_3 also decreases the band gap (11). The magnitude of the change from semiconducting to metallic behavior in $(Ti_{1-x}V_x)_2O_3$ decreases with increasing vanadium content until, at $x = 0.100$, the material is metallic over the entire temperature range 150-500°K with a resistivity equal to that of Ti_2O_3 above its transition temperature. Since the lattice parameters of $(Ti_{0.900}V_{0.100})_2O_3$ at room temperature are virtually identical with those of pure Ti_2O_3 above the transition range (7), we felt that crystal

structure determinations of Ti_2O_3 and $(Ti_{0.900}V_{0.100})_2O_3$ at room temperature would provide the positions of the metal atoms and the oxygens in the semiconducting and semimetallic forms of these materials and serve as a check of the model proposed for the transition.

Experimental

Samples of Ti_2O_3 and $(Ti_{0.900}V_{0.100})_2O_3$ from single crystal boules were provided by Professor J. M. Honig of this department (11). A Ti_2O_3 sphere with a radius of 0.0097 cm was ground from fragments of the boule. Due to pronounced cleavage planes, spheres of the vanadium-doped system could not be ground, so a rectangular parallelepiped with dimensions $0.0064 \times 0.0104 \times 0.0246$ cm was used. This crystal was mounted along the long dimension. Weissenberg and precession photographs of both of these crystals exhibited $\bar{3}m$ diffraction symmetry, and the systematic absences observed (hkl ; $-h + k + l = 3n$; $hh2hl$; $(l = 3n)$; $h\bar{h}0l$; $(h + l = 3n)$, $l = 2n$) were consistent with the space groups $R\bar{3}c$ or $R3c$.

Both crystals were mounted along non-principal crystallographic directions in order to reduce the effects of multiple diffraction (12).

Unit cell parameters and intensities were measured using an Enraf-Nonius fully automated CAD-4 diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation. An incident beam collimator of 0.8-mm dia. at a takeoff angle of 4.0° was used with a receiving aperture located 173 mm from the crystal. The pulse height analyzer used with the scintillation counter was set to admit approximately 95% of the diffraction intensity. Following optical centering of the crystal, 15 reflections were located by a systematic search. These reflections were widely separated in the reciprocal lattice, and were located at $60^\circ < 2\theta < 65^\circ$. Accurate values of the diffractometer angles 2θ , ω , κ , and ϕ were determined by scanning ω , κ , and 2θ , and locating the peak at the average positions of the half heights. Both the search and alignment procedures were under the control of the computer using programs supplied by Enraf-Nonius. Following X-ray centering of the crystals, the reflection centering procedure was repeated, and the reflections were indexed from the known cell constants and the relative positions of the reflections. The orientation matrix was determined from these reflections using a least-squares program provided with the instrument. Precise unit cell parameters were determined by centering the $K\alpha_1$ ($\lambda = 0.70926 \text{ \AA}$)

reflection at both positive and negative 2θ and taking the average as the diffraction angle. The cell was treated as triclinic in the refinement so three values for each rhombohedral parameter were obtained. The errors in the following parameters are the rms deviations from the three values thus obtained. For Ti_2O_3 , $a = 5.4325 \pm 0.0008 \text{ \AA}$ and $\alpha = 56.75^\circ \pm 0.01^\circ$, for $(\text{Ti}_{0.900}\text{V}_{0.100})_2\text{O}_3$, $a = 5.4692 \pm 0.0008 \text{ \AA}$ and $\alpha = 55.63^\circ \pm 0.01^\circ$.

All reflections in a hemisphere of reciprocal space with $2\theta < 90^\circ$ were collected for both samples. The θ - 2θ scanning technique with a variable scanning speed was used with a 2θ range of $1.6 + \tan\theta$ degrees centered about the average peak position. The aperture was set at 3 mm wide by 4 mm high. Each reflection was first scanned at a rate of $20.1^\circ \text{ min}^{-1}$ to determine its approximate intensity. Reflections were then scanned twice at a slower rate necessary to accumulate a minimum net count of 1000 counts above background. The maximum rate for the slower scan was set at $6.7^\circ \text{ min}^{-1}$, with the majority of reflections counted at this rate. Those reflections which were too weak to give the desired net count were scanned twice at a rate of $1.3^\circ \text{ min}^{-1}$. The intensities of 85% of the reflections were well above the minimum net

TABLE I
CRYSTALLOGRAPHIC DATA FOR Ti_2O_3 AND $(\text{Ti}_{0.900}\text{V}_{0.100})_2\text{O}_3$

Parameters	Ti_2O_3		$(\text{Ti}_{0.90}\text{V}_{0.10})_2\text{O}_3$	
	Ti	O	M	O
x^a	0.34464(4)	0.5624(2)	0.34614(3)	0.5614(2)
y	0.34464	-0.0624	0.34614	-0.0614
z	0.34464	0.2500	0.34614	0.2500
B_{11}^b	0.0077(1)	0.0090(5)	0.0033(2)	0.0040(4)
B_{22}	0.0077	0.0090	0.0033	0.0040
B_{33}	0.0077	0.0066(7)	0.0033	0.0037(6)
B_{12}	-0.0028(1)	-0.0003(5)	-0.0013(2)	-0.0014(4)
B_{13}	-0.0028	-0.0047(4)	-0.0013	-0.0016(3)
B_{23}	-0.0028	-0.0047	-0.0013	-0.0016
R_1	0.031		0.027	
R_2	0.027		0.030	
a	5.4325(8) \AA		5.4692(8) \AA	
α	56.75(1) $^\circ$		55.63(1) $^\circ$	
a_{hex}	5.163 \AA		5.104 \AA	
c_{hex}	13.624 \AA		13.822 \AA	
c/a	2.64		2.71	

^a In fractions of the rhombohedral unit cell edges. Numbers in parentheses are the estimated standard deviations of the least significant figures.

^b The form of the temperature factor approximation is $f = f_0 \exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$.

count required, although the counting rates were such that no coincidence corrections were required. For no observed reflections were the results of the two slow scans statistically different. Background counts were made for 1/4 of the scan time at each end of both scans. Several reflections were monitored alternately every 20 min and did not change significantly during the course of the data collection period.

Integrated intensities, I , were obtained using the expression $I = C - 2B$, where C is the sum of the counts collected during the two slower scans, and B is the sum of the background counts during these scans. A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = [C + 4B]^{1/2}$. The data were corrected for Lorentz-polarization effects. The crystals were measured using a microscope with a micrometer eyepiece and the appropriate absorption corrections applied (13, 14). The linear absorption coefficient for Ti₂O₃ was 75.2 cm⁻¹; for (Ti_{0.900}V_{0.100})₂O₃, 78.5 cm⁻¹. Averaging of equivalent reflections gave 134 observed independent reflections ($I/\sigma(I) \geq 3.0$)

TABLE II
INTERATOMIC DISTANCES (Å) AND BOND ANGLES
(DEGREES)^a

	Ti ₂ O ₃	(Ti _{0.900} V _{0.100}) ₂ O ₃
M ₁ -M ₂	2.579(0)	2.658(0)
M ₁ -M ₃	2.997(0)	2.968(0)
M ₁ -O ₁	2.065(1)	2.072(1)
M ₁ -O ₅	2.030(1)	2.012(1)
O ₁ -O ₂	2.794(1)	2.753(1)
O ₄ -O ₅	3.079(1)	3.048(1)
O ₁ -O ₄	2.792(1)	2.805(1)
O ₁ -O ₅	2.884(1)	2.899(2)
O ₁ -M ₁ -O ₂	85.14(4)	83.28(4)
O ₄ -M ₁ -O ₅	98.61(2)	98.50(5)
O ₁ -M ₁ -O ₄	85.94(4)	86.77(5)
O ₁ -M ₁ -O ₅	89.51(1)	90.44(5)
O ₁ -M ₁ -O ₆	169.94(2)	168.78(10)
M ₁ -O ₁ -M ₂	77.27(1)	79.79(1)
M ₁ -O ₂ -M ₃	94.06(2)	93.23(4)
M ₁ -O ₅ -M ₄	123.02(4)	122.83(9)
M ₂ -O ₂ -M ₃	132.41(4)	132.68(8)

^a Numbers in parentheses are the estimated standard deviation of the least significant digit rounded up to the next significant figure.

TABLE III
ROOT-MEAN-SQUARE THERMAL DISPLACEMENTS (Å)

	Atom	rms Displacement		
Ti ₂ O ₃	Ti	0.0791	0.0843	0.0843
	O	0.0477	0.0795	0.1111
(Ti _{0.900} V _{0.100}) ₂ O ₃	M	0.0458	0.0553	0.0553
	O	0.0497	0.0595	0.0615

for Ti₂O₃ and 145 independent reflections for (Ti_{0.900}V_{0.100})₂O₃.

The initial values for refinement of the positional parameters were those of Newnham and de Haan (15). Five weighted refinement cycles (16) of the scale factor, all variable atomic parameters, and anisotropic temperature factors, reduced R_1 ($R_1 = \sum |F_o - F_c| / |F_o|$) to 0.031 and R_2 ($R_2 = \{w|F_o - F_c|^2\}^{1/2} / \{\sum w|F_o|^2\}^{1/2}$) to 0.027 for Ti₂O₃, and R_1 to 0.027 and R_2 to 0.030 for (Ti_{0.900}V_{0.100})₂O₃. Final shifts in the parameters were less than 10% of the estimated standard deviations of the individual parameters. The standard deviation of an observation of unit weight was 1.13 for Ti₂O₃ and 1.08 for the doped system. Weights were assigned as $w = 1/\sigma^2(F) = 4F_o^2/\sigma^2(F_o^2)$. The scattering factors were those of Ibers (17) for Ti^o, V^o, and O^o with real and imaginary anomalous scattering corrections (18) applied for the metals. Weighted averages of the Ti and V scattering factors and the anomalous scattering corrections were used with the doped system.

The final atomic parameters listed in Table I were used to calculate the interatomic distances and bond angles reported in Table II as well as the rms thermal displacements in Table III. Structure factor amplitudes are reported in Table IV.

Results

Both Ti₂O₃ and (Ti_{0.900}V_{0.100})₂O₃ are isostructural with Al₂O₃ (15), space group $R\bar{3}c$, with approximate hexagonal close packing of the oxygens and metal ions in 2/3 of the octahedral sites. Within the standard deviations of the determinations, the structure of Ti₂O₃ was found to be identical to that reported by Newnham and de Haan (15). There is no evidence for ordering of Ti and V in the doped system. The effect of the added vanadium is to increase the M₁-M₂ distance (see Table II and Fig. 1) across

TABLE V
LEAST-SQUARES PLANES

Ti ₂ O ₃					
(a) Equations of planes ^a					
Plane No.	Atoms in plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
1	O ₁ -O ₃	4.541	4.541	4.541	7.947
2	O ₄ -O ₆	4.541	4.541	4.541	10.218
(b) Distance of atoms from planes					
	plane 1-M ₁	1.289 Å			
	plane 1-O ₄	2.271 Å			
	plane 2-M ₁	0.981 Å			
(Ti _{0.900} V _{0.100}) ₂ O ₃					
(a) Equations of planes					
Plane No.	Atoms in plane	<i>l</i>	<i>m</i>	<i>n</i>	<i>p</i>
3	O ₁ -O ₃	4.607	4.607	4.607	8.063
4	O ₄ -O ₆	4.607	4.607	4.607	10.367
(b) Distance of atoms from planes					
	plane 3-M ₁	1.329 Å			
	plane 3-O ₄	2.304 Å			
	plane 4-M ₁	0.975 Å			

^a The equations of the planes are $lX + mY + nZ = p$ relative to the rhombohedral unit cell axes in Å.

the shared octahedral face from 2.597 Å in Ti₂O₃ to 2.658 Å in (Ti_{0.900}V_{0.100})₂O₃. This is accompanied by an extension of the rhombohedral cell body diagonal (the *c* axis of the hexagonal cell) from 13.624 to 13.822 Å and an increase in the separation of the oxygen planes (Table V) perpendicular to this axis from 2.271 Å in Ti₂O₃ to 2.304 Å in (Ti_{0.900}V_{0.100})₂O₃. In addition, a decrease in the M₁-M₃ distance across the shared octahedral edge from 2.997 to 2.968 Å is observed. This is accompanied by a reduction of the hexagonal cell edge *a* from 5.163 to 5.104 Å. There are only minor changes in the various M-O distances with a maximum change of 0.018 Å. The increased M₁-M₂ distance coupled with only a 0.006 Å change in the M₁-O₁ and M₂-O₁ distances results in an increase in the M₁-O₁-M₂ angle from 77.27 to 79.79° with a concomitant reduction of the O₁-O₂ distances from 2.794 to 2.753 Å. This reduction in O₁-O₂ is also consistent with the

reduction in *a*_{hex}. All of the various changes could result from the 0.061 Å change in the M₁-M₂ distance coupled with reorganization of the lattice in order to maintain constant M-O distances.

The shift in the M₁-M₂ and M₁-M₃ distances are consistent with the scheme (9, 10) advanced to explain changes in the electrical (1-6, 11), thermoelectric (3, 19), optical (8), magnetic properties (20), and the specific heats (21) of pure Ti₂O₃ with increasing temperature and of vanadium-doped Ti₂O₃ with increasing vanadium content. The model postulates a lower lying valence band of *a*_{1g} symmetry derived from *d* orbitals of the metal atoms with large lobes extending primarily along the threefold axis and a higher lying conduction band of *e*_g(*π*) symmetry resulting from overlap of *d* orbitals of *π* symmetry directed primarily parallel to the 001 plane of the hexagonal cell. The *a*_{1g} band which is bonding with respect to M₁-M₂ is exactly filled at 0°K while the *e*_g(*π*) band is empty. As the temperature of pure Ti₂O₃ is increased, not only are electrons transferred across the band gap from the *a*_{1g} band to the *e*_g(*π*) band, but the band gap is decreased by the shifting of the atoms noted above until the two bands overlap. The shift of electron density from the valence band to the conduction band would result in an increase in the M₁-M₂ distance with consequent reorganization of the lattice.

In the vanadium-doped systems, vanadium is known to function as an acceptor (*p*-type dopant). This behavior would also remove electrons from the valence band and result in an increased M₁-M₂ distance.

It should be noted that there are only small changes in the positional parameters of M and O upon going from pure Ti₂O₃ to (Ti_{0.900}V_{0.100})₂O₃ (7). Heating Ti₂O₃ through the transition also produces little change in the positional parameters of the atoms (22). Since changes in the unit cell dimensions resulting from heating Ti₂O₃ above the transition temperature or doping with 10% V₂O₃ are virtually identical, this suggests that the structure of Ti₂O₃ above the transition should be quite similar to that of (Ti_{0.900}V_{0.100})₂O₃.

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