

(Tranqui, Tordjman, Averbuch-Pouchot & Bassi, 1970) et les composés isotypes.

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High-Temperature Crystal Chemistry of V_2O_3 and 1% Chromium-Doped V_2O_3

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The crystal structures of V_2O_3 at 23, 115, 212, 300, 400, and 600°C, of the low-temperature, α , form of $(Cr_{0.01}V_{0.99})_2O_3$ at 23°C, and of the high-temperature, β , form of $(Cr_{0.01}V_{0.99})_2O_3$ at 23, 113, and 310°C have been determined from X-ray diffraction data collected on a single-crystal diffractometer with graphite-monochromated Mo $K\alpha$ radiation and have been refined by least-squares techniques to weighted residuals of 0.025 to 0.048 using about 100 reflections at each temperature. All systems were found to be rhombohedral, space group $R\bar{3}c$, and are isomorphous with α -alumina. At room temperature the structures of V_2O_3 and α $(Cr_{0.01}V_{0.99})_2O_3$ are essentially identical. Changes in the structure of V_2O_3 with increasing temperature are sigmoidal with the uncorrected metal-metal distance across the shared octahedral edge increasing smoothly from 2.880 (1) Å at 23° to 2.924 (1) Å at 600°C as the a axis of the hexagonally indexed unit cell increases. The c axis decreases over this temperature range but the metal-metal vector, which is parallel to c , across the shared octahedral face increases from 2.697 (1) Å to 2.738 (1) Å. The metal-oxygen distances increase by 0.013 Å or less. These changes in dimensions occur over the same temperature interval as the change in resistivity of metallic V_2O_3 . The differences in interatomic distances in the α and β forms of $(Cr_{0.01}V_{0.99})_2O_3$ are quite close to the corresponding differences in V_2O_3 at 23° and 600°C. The effect of heating β $(Cr_{0.01}V_{0.99})_2O_3$ is to increase most of the interatomic distances and unit-cell dimensions in a linear fashion by only small amounts. The exception is the uncorrected metal-metal distance across the shared octahedral face which decreases from 2.747 (1) Å at 23° to 2.739 (1) Å at 310°C. The net effect of these changes in V_2O_3 and β $(Cr_{0.01}V_{0.99})_2O_3$ is an asymptotical convergence of the structures of these materials at elevated temperatures.

Introduction

A variety of interesting structural and electrical phenomena are observed upon heating rhombohedral V_2O_3 and the rhombohedral chromium-doped systems $(Cr_xV_{1-x})_2O_3$. Pure V_2O_3 exhibits a continuous electrical transition in the range 225° to about 400°C which results in an increase in electrical resistance of about one order of magnitude in this metallic material (Föex, 1946; Morin, 1959). This resistivity change is accompanied by a change in lattice parameters with a smooth nonlinear increase in the a dimension of the hexagonally indexed unit cell and a smooth nonlinear decrease of the c dimension (McWhan & Remeika, 1970). Recent studies of very pure V_2O_3 (Chandrashekar, Sinha & Honig, 1974) have suggested that V_2O_3 exists at least in two rhombohedral forms over this temperature range.

Between about 30 and 230°C the resistivity of $(Cr_{0.01}V_{0.99})_2O_3$ increases abruptly with temperature by one to two orders of magnitude then falls off gradually to its original value. The powder diffraction work of Honig, Chandrashekar & Sinha (1974) suggests that this behavior may be an extrinsic effect resulting from the presence of two phases rather than a Mott transition as originally proposed (McWhan & Remeika, 1970). The room-temperature structure of α $(Cr_{0.01}V_{0.99})_2O_3$ was found to undergo a gradual transition to an isomorphous high-temperature form with both forms present over the temperature interval where the anomalous electrical behavior was observed. The transformation from the α form of $(Cr_{0.01}V_{0.99})_2O_3$ to the β form occurred with an increase in the a dimension of the unit cell and a decrease of the c dimension of about the same magnitudes as those reported by McWhan & Remeika (1970) for V_2O_3 upon heating.

Chromium-doped samples containing more than 2% chromium do not appear to exhibit either the electrical anomaly or two different rhombohedral phases.

In view of the similarity of the unit-cell dimensions of V₂O₃ at 23°C and the α form of the chromium-doped system and the similarity of the dimensions of V₂O₃ at 400°C, the β form of (Cr_{0.01}V_{0.99})₂O₃ and (Cr_{0.038}V_{0.962})₂O₃ (Dernier, 1970), we thought it interesting to examine V₂O₃ and (Cr_{0.01}V_{0.99})₂O₃ at a variety of different temperatures using single-crystal X-ray diffraction techniques. Consequently we have determined the crystal structure of V₂O₃ at six temperatures between 23 and 600°C, the structure of α (Cr_{0.01}V_{0.99})₂O₃ at 23°C, and the structure of β (Cr_{0.01}V_{0.99})₂O₃ at 23, 113, and 310°C.

Experimental

Samples of V₂O₃ (Chandrashekar *et al.*, 1974) and of unannealed (Cr_{0.01}V_{0.99})₂O₃ (Chandrashekar & Sinha, 1974) were provided by Professor J. M. Honig. A right elliptical prism of (Cr_{0.01}V_{0.99})₂O₃, hereinafter referred to as Cr-V₂O₃, with dimensions 0.06 × 0.08 × 0.25 mm and an irregular chip of V₂O₃ with maximum dimensions 0.18 × 0.19 × 0.21 mm and with flat faces were selected for examination. Preliminary studies on a precession camera indicated that both samples had been mounted along the 210 reciprocal direction and that the chromium-doped sample was in the high-temperature form (β Cr-V₂O₃). The systematic absences observed ($hkil$; $-h+k+l \neq 3n$ and $hh0l$; $l \neq 2n$) were consistent with the rhombohedral space group $R\bar{3}c$ (No. 167) previously reported for V₂O₃ and (Cr_{0.038}V_{0.962})₂O₃ (Dernier, 1970; Newnham & de Haan, 1962). Long exposures on a precession camera with no screen showed no deviation from $\bar{3}m$ symmetry.

Both crystals were transferred to silica capillaries with retention of orientation using the procedure described by Brown, Sueno & Prewitt (1973). The capillaries were sealed under vacuum. From consideration of the volume and pressure of the residual air in the capillaries and the masses of the samples, if oxidation of the samples occurred during subsequent heating (see below), the maximum deviation from stoichiometry of an ideal starting sample would have been of the order of M₂O_{3.001}. It is not possible to ascertain the effect of volatile materials released from the quartz during sealing of the capillary, but no change in room temperature unit-cell parameters was observed before or after transfer and before or after the heating experiments.

The unit-cell dimensions reported in Tables 1 and 2 were determined by least-squares refinement of the 2θ values of 18 to 21 reflections, principally of the type hkl , lying in the region $50^\circ < 2\theta < 57^\circ$. The 2θ values were determined on a Picker diffractometer equipped with a single-crystal heater (Brown *et al.*, 1973). Peak locations were measured at positive and negative 2θ using the quarter-height technique with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$).

Chandrashekar, Sinha & Honig (1974) have reported the observation of two phases in powdered samples of very pure V₂O₃ under gettered helium between about 225 and 425°C. They observed splittings of about $0.25^\circ 2\theta$ in their powder diffraction data at 2θ values of 54° with the intensity ratios of the split peaks varying from about 0:1 at 127°C to as much as 3:1 at 427°C in some cases. The effective widths of their peaks at quarter height also increased about 25%. We see no evidence for such behavior in our single-crystal sample. Our peak widths at quarter height, for

Table 1. Crystallographic data for V₂O₃ with standard deviations in parentheses

	23°C	115°C	212°C	300°C	400°C	600°C
a_{hex} (Å)	4.9492 (2)	4.9605 (1)	4.9776 (2)	4.9912 (2)	5.0013 (1)	5.0140 (2)
c_{hex} (Å)	13.998 (1)	13.9857 (6)	13.9647 (7)	13.9489 (6)	13.9416 (5)	13.9427 (7)
V (Å ³)	296.94 (2)	298.04 (2)	299.64 (2)	300.94 (2)	302.00 (2)	303.56 (2)
c/a	2.828	2.819	2.805	2.794	2.788	2.780
Metal parameters						
z	0.34634 (4)	0.34671 (4)	0.34733 (4)	0.34782 (5)	0.34805 (5)	0.34819 (4)
β_{11}^*	56.7 (61)	69.7 (54)	82.1 (55)	88.7 (55)	99.6 (50)	119.8 (49)
β_{33}^*	1.9 (7)	3.6 (6)	4.5 (7)	6.5 (7)	7.2 (6)	9.8 (6)
Oxygen parameters						
x	0.3122 (5)	0.3114 (4)	0.3103 (5)	0.3095 (5)	0.3094 (4)	0.3087 (4)
β_{11}^*	49 (10)	64 (10)	85 (10)	88 (10)	105 (9)	124 (9)
β_{22}^*	76 (14)	99 (13)	97 (13)	110 (13)	114 (12)	154 (12)
β_{33}^*	5.0 (10)	6.6 (9)	7.7 (10)	10.0 (10)	11.0 (10)	13.0 (10)
β_{13}^*	4 (2)	4 (1)	5 (1)	5 (2)	5 (1)	7 (1)
R	0.039	0.036	0.034	0.036	0.035	0.035
R_{wt}	0.048	0.045	0.046	0.046	0.041	0.040
n	98	100	101	101	101	101
$s (\times 10^{-5})$	3.11	3.17	3.09	3.10	3.39	3.79
S	2.38	2.25	2.26	2.29	2.03	1.95

* Times 10^4 . For the metal $\beta_{11} = \beta_{22}$, $\beta_{12} = \frac{1}{2}\beta_{11}$, and $\beta_{23} = \beta_{13} = 0$; for oxygen $\beta_{12} = \frac{1}{2}\beta_{22}$ and $\beta_{23} = 2\beta_{13}$. The form of the anisotropic temperature factor T is $T = \exp(-\sum_i \sum_j h_i h_j \beta_{ij})$.

example, remained constant within 7% over the range 23 to 600°C, and there was no systematic broadening of peaks in this range. These differences may reflect small differences in stoichiometry in the two samples.

At each temperature indicated in Tables 1 and 2, X-ray intensity data for $\pm h, k, l$ reflections of the hexagonally indexed rhombohedral unit cell were collected using the PDP 15/35-controlled Picker diffractometer in the Department of Earth and Space Sciences, State University of New York, Stony Brook, N.Y. Only minor changes of the goniometer head arcs were required to maintain the orientation of both the V_2O_3 and $Cr-V_2O_3$ crystals as the temperature was changed. These changes reflected expansion of the quartz fiber and capillary rather than a change in the orientation of the unit cells. The diffractometer was operated in a θ - 2θ mode using a graphite monochromator with $Mo K\alpha$ radiation. A scan range of 2° plus the α_1 - α_2 separation was used with a scan rate of 1° min^{-1} . 10 s background counts were collected on both ends of each scan. Data collection was terminated at $2\theta = 62^\circ$ for V_2O_3 and $2\theta = 60^\circ$ for $Cr-V_2O_3$. The 030 reflection was monitored after every 30 reflections, and its intensity usually varied by less than one standard deviation. Approximately 360 reflections were measured at each temperature. The data were processed by a routine which corrected for background, Lorentz and polarization effects, and absorption using transmission factors calculated by numerical integration (Prewitt, 1965). The linear absorption coefficient for V_2O_3 was 96.08 cm^{-1} , that for $Cr-V_2O_3$, 94.85 cm^{-1} . Calculated transmission factors varied from 0.328 to 0.443 for V_2O_3 and from 0.520 to 0.633 for $Cr-V_2O_3$. Equivalent reflections were averaged with the larger of the root-mean-square deviation or the average of

the e.s.d.'s of the individual reflections taken as the error in a deliberate attempt to avoid underestimation of the error. Reflections with negative intensity were assigned zero intensity. In no cases did these reflections constitute more than one-third of any set of equivalent reflections so they were averaged with the other members of the set. About 100 averaged reflections (n in Tables 1 and 2) were obtained at each temperature.

Both isotropic and anisotropic refinements were carried out for each set of intensity data using the *RFINE* program written by Finger (1969). The initial atomic parameters in the space group $R\bar{3}c$ were those of Newnham & de Haan (1962) for V_2O_3 . The program minimized $\sum w(F_o - F_c)^2$ using neutral atom scattering factors (Doyle & Turner, 1968) corrected for real and imaginary anomalous scattering (Cromer, 1965), weights based on the errors determined in the averaging process [$w = 1/\sigma^2(F_o) = 4F_o^2/\sigma^2(F_o^2)$], and an extinction correction of the form $F_{\text{corr}}^2 = F_o^2(1 - sF_o^2)$. No weak reflections were rejected from the refinement although the 030, 104, and 110 reflections in all six V_2O_3 data sets showed consistently poor agreement and were given zero weight. Final R values varied from 0.02 to 0.05. Values of the standard deviations of an observation of unit weight are listed in Tables 1 and 2 as S . The final atom parameters listed in these tables were used to calculate the distances and angles reported in Table 3.*

* A list of observed and calculated structure factor amplitudes has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30824 (2 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Crystallographic data for $(Cr_{0.01}V_{0.99})_2O_3$ with standard deviations in parentheses

	α $Cr-V_2O_3$ 23°C	23°C	β $Cr-V_2O_3$ 113°C	310°C
a_{hex} (Å)	4.9540 (2)	4.9974 (1)	5.0018 (1)	5.0052 (1)
c_{hex} (Å)	13.9906 (10)	13.9260 (6)	13.9238 (7)	13.9318 (6)
V (Å ³)	297.36 (3)	301.20 (2)	301.68 (2)	302.26 (2)
c/a	2.824	2.787	2.784	2.783
Metal parameters				
z	0.34648 (3)	0.34864 (3)	0.34861 (3)	0.34831 (3)
β_{11}^*	48.1 (33)	47.7 (31)	56.8 (38)	79.6 (38)
β_{33}^*	2.9 (4)	2.9 (4)	3.9 (4)	6.1 (4)
Oxygen parameters				
x	0.3114 (3)	0.3074 (3)	0.3074 (3)	0.3080 (3)
β_{11}^*	61 (7)	52 (6)	62 (6)	78 (6)
β_{22}^*	81 (9)	65 (7)	70 (8)	105 (8)
β_{33}^*	5.0 (7)	5.8 (7)	7.0 (7)	8.5 (7)
β_{13}^*	5.0 (11)	2.5 (8)	3.0 (9)	4.7 (9)
R	0.020	0.023	0.023	0.023
R_{wt}	0.025	0.026	0.027	0.027
n	102	97	97	97
s ($\times 10^{-5}$)	0.53	1.19	1.21	1.19
S	1.43	2.29	2.34	2.29

* Times 10^4 . For the metal $\beta_{11} = \beta_{22}$, $\beta_{12} = \frac{1}{2}\beta_{11}$, and $\beta_{23} = \beta_{13} = 0$; for oxygen $\beta_{12} = \frac{1}{2}\beta_{22}$ and $\beta_{23} = 2\beta_{13}$. The form of the anisotropic temperature factor T is $T = \exp(-\sum_i \sum_j h_i j \beta_{ij})$.

Table 3. *Uncorrected and corrected interatomic distances (Å) and bond angles (°)*

	V ₂ O ₅							α Cr-V ₂ O ₅			β Cr-V ₂ O ₅			
	23°C	115°C	212°C	300°C	400°C	600°C	23°C	23°C	23°C	113°C	310°C	23°C	23°C	23°C
M(1)-M(2)	2.697 (1) 2.705	2.705 (1) 2.714	2.718 (1) 2.730	2.728 (1) 2.741	2.734 (1) 2.748	2.738 (1) 2.755	2.700 (1) 2.706	2.747 (1) 2.754	2.746 (1) 2.754	2.739 (1) 2.750		2.747 (1) 2.754	2.746 (1) 2.754	2.739 (1) 2.750
M(1)-M(3)	2.880 (1) 2.885	2.888 (1) 2.895	2.900 (1) 2.909	2.910 (1) 2.920	2.916 (1) 2.927	2.924 (1) 2.939	2.884 (1) 2.889	2.917 (1) 2.922	2.919 (1) 2.925	2.920 (1) 2.929		2.917 (1) 2.922	2.919 (1) 2.925	2.920 (1) 2.929
M(1)-O(1)	2.051 (1) 2.061	2.053 (1) 2.065	2.057 (2) 2.072	2.061 (1) 2.078	2.064 (1) 2.083	2.066 (1) 2.090	2.050 (1) 2.060	2.061 (1) 2.070	2.061 (1) 2.072	2.062 (2) 2.078		2.061 (1) 2.070	2.061 (1) 2.072	2.062 (2) 2.078
M(1)-O(5)	1.968 (1) 1.978	1.970 (1) 1.983	1.973 (1) 1.989	1.975 (2) 1.993	1.977 (2) 1.997	1.981 (1) 2.006	1.970 (1) 1.981	1.976 (1) 1.986	1.977 (1) 1.989	1.979 (1) 1.996		1.976 (1) 1.986	1.977 (1) 1.989	1.979 (1) 1.996
O(1)-O(2)	2.676 (3) 2.685	2.675 (3) 2.685	2.675 (4) 2.687	2.676 (3) 2.690	2.680 (3) 2.696	2.681 (3) 2.701	2.673 (3) 2.682	2.661 (2) 2.669	2.663 (2) 2.673	2.670 (2) 2.683		2.661 (2) 2.669	2.663 (2) 2.673	2.670 (2) 2.683
O(1)-O(4)	2.804 (1) 2.813	2.802 (1) 2.813	2.800 (1) 2.814	2.799 (2) 2.814	2.799 (2) 2.815	2.800 (1) 2.821	2.802 (1) 2.813	2.792 (1) 2.801	2.793 (1) 2.803	2.796 (1) 2.810		2.792 (1) 2.801	2.793 (1) 2.803	2.796 (1) 2.810
O(1)-O(5)	2.889 (1) 2.894	2.891 (2) 2.898	2.893 (1) 2.903	2.895 (2) 2.906	2.897 (1) 2.909	2.901 (1) 2.916	2.890 (1) 2.899	2.897 (1) 2.904	2.898 (1) 2.905	2.899 (1) 2.910		2.897 (1) 2.904	2.898 (1) 2.905	2.899 (1) 2.910
O(4)-O(5)	2.952 (1) 2.958	2.962 (2) 2.973	2.978 (1) 2.989	2.990 (1) 3.002	2.997 (2) 3.010	3.007 (1) 3.023	2.958 (2) 2.966	3.004 (1) 3.011	3.006 (1) 3.015	3.006 (1) 3.016		3.004 (1) 3.011	3.006 (1) 3.015	3.006 (1) 3.016
O(1)-M(1)-O(2)	81.45 (7) 88.46 (2)	81.30 (7) 88.27 (2)	81.11 (7) 87.99 (2)	80.95 (7) 87.77 (2)	80.93 (7) 87.67 (2)	80.89 (7) 87.52 (2)	81.36 (5) 88.36 (2)	80.42 (4) 87.51 (1)	80.47 (4) 87.47 (1)	80.70 (4) 87.51 (1)		80.42 (4) 87.51 (1)	80.47 (4) 87.47 (1)	80.70 (4) 87.51 (1)
O(1)-M(1)-O(4)	91.90 (5) 168.62 (8)	91.85 (5) 168.26 (8)	91.74 (5) 167.74 (8)	91.65 (5) 167.33 (8)	91.55 (5) 167.17 (8)	91.52 (5) 167.00 (7)	91.91 (4) 168.43 (6)	91.71 (3) 166.50 (5)	91.68 (3) 166.52 (5)	91.63 (3) 166.81 (5)		91.71 (3) 166.50 (5)	91.68 (3) 166.52 (5)	91.63 (3) 166.81 (5)
O(4)-M(1)-O(5)	97.17 (3) 82.23 (9)	97.49 (3) 82.44 (9)	97.98 (3) 82.69 (9)	98.36 (3) 82.90 (9)	98.56 (3) 82.92 (9)	98.73 (3) 82.98 (9)	97.32 (2) 82.36 (6)	98.93 (2) 83.60 (5)	98.95 (2) 83.54 (6)	98.79 (2) 83.24 (6)		98.93 (2) 83.60 (5)	98.95 (2) 83.54 (6)	98.79 (2) 83.24 (6)
M(1)-O(1)-M(2)	91.54 (3) 133.21 (5)	91.73 (2) 133.18 (4)	92.01 (2) 133.11 (4)	92.23 (2) 133.04 (4)	92.35 (2) 132.98 (4)	92.48 (2) 132.98 (4)	91.64 (2) 133.23 (3)	92.49 (1) 133.05 (2)	92.53 (2) 133.04 (3)	92.47 (1) 133.04 (3)		92.49 (1) 133.05 (2)	92.53 (2) 133.04 (3)	92.47 (1) 133.04 (3)

For a given distance the top entry is the uncorrected distance which is equal to the lower limit or riding distance within experimental error. The bottom entry is the upper limit of the distance. The non-correlated distance is the average of the two entries.

Following data collection from β Cr-V₂O₃, the crystal was aligned on a precession camera, the goniometer head containing the crystal was removed from the

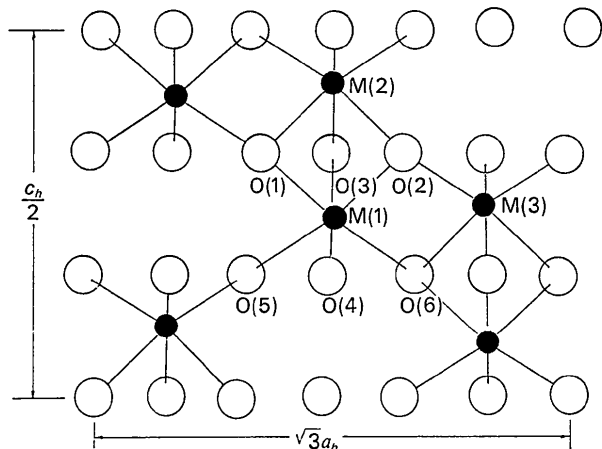


Fig. 1. A projection of the corundum structure on a plane perpendicular to the [110] axis. All oxygen atoms are symmetry-related as are all metal atoms.

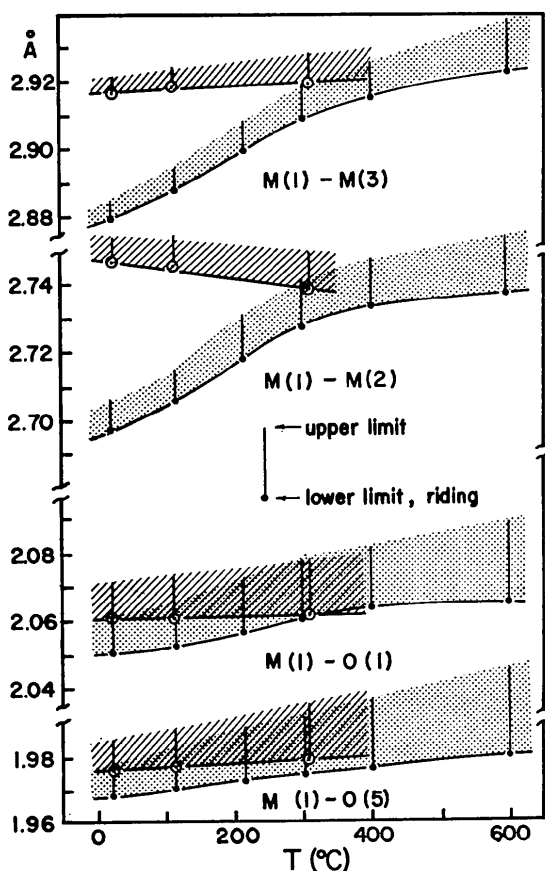


Fig. 2. Variation of uncorrected metal-metal and metal-oxygen distances (solid lines) for V₂O₃, ●, and β Cr-V₂O₃, ○, and ranges of thermal corrections for V₂O₃ (dot shaded) and β Cr-V₂O₃ (line shaded).

camera, and the crystal was cooled to -77° without disturbing the settings of the goniometer arcs. The head was replaced on the camera and crystal alignment reestablished with minor adjustments (30' or less on the arcs). The orientation of the crystal had not changed although the sample had been converted to the low-temperature rhombohedral form, α Cr-V₂O₃. Unit-cell dimensions and a set of intensity data were collected using the Picker diffractometer as described above followed by refinement as indicated.

Results

The samples examined in this study were found to be isomorphous with α Al₂O₃ under all conditions examined. The structures consist of an approximate hexagonally closest packed array of oxide ions with metal ions in two-thirds of the octahedral holes (Fig. 1). Each metal ion has four near metal neighbors; one sharing an octahedral face of the coordination polyhedron [M(1)-M(2) in Fig. 1] and three sharing edges of the octahedron [M(1)-M(3) in Fig. 1].

The thermal expansion of the V₂O₃ system differs from that of α -alumina and other isomorphous compounds. Over the range 23-600°C, Al₂O₃, Cr₂O₃, α Fe₂O₃, and Rh₂O₃ expand by 0.4-0.5% in an approximately linear fashion (Krikorian, 1960; Eckert & Bradt, 1973a). The expansion of V₂O₃ is not linear, but sigmoidal, with the *a* axis of the hexagonally indexed unit cell increasing from 4.9492 (2) Å at 23°C to 5.0140 (2) Å at 600°C (Table 1) while the *c* axis decreases from 13.998 (1) Å at 23°C to 13.9416 (5) Å at 400°C. This axis begins to expand between 400 and 600°C. As nearly as can be determined from their data (which is presented only in a figure), the behavior of V₂O₃ in the 23-400°C range is identical with that reported by McWhan & Remeika (1970). The increase in *c* above about 500°C has also been reported by Eckert & Bradt (1973b). No behavior consistent with the presence of two phases was observed. The difference between the behavior of our sample and that of Chandrashekhar *et al.* (1974) may reflect small differences in stoichiometry. Vanadium sesquioxide samples of the stoichiometry V₂O_{3-0.03}, for example, do not exhibit the monoclinic to rhombohedral phase change found in pure V₂O₃ upon warming through 155°K.

The change in dimensions of the V₂O₃ unit cell over the temperature range 23-600°C is close to that observed when the chromium-doped system, Cr-V₂O₃, undergoes the transition from the low-temperature, α , form to the high-temperature, β , form (Table 1). Our observations agree very well with those reported by Chandrashekhar & Sinha (1974) for powder specimens of the same sample. The linear increase with heating of the unit-cell dimensions of unannealed β Cr-V₂O₃ are identical with those observed by these workers. This increase also parallels that observed in (Cr_{0.038}V_{0.962})₂O₃ (McWhan & Remeika, 1970) although the cell dimensions differ slightly. It is apparent

from the data in Table 1 that the unit-cell dimensions of the pure and doped systems converge at elevated temperatures. The behavior of the unit-cell volumes parallels that of the *a* axes in these systems.

The *c/a* ratios of pure V₂O₃ and α Cr-V₂O₃ are significantly larger than those of 2.63–2.78 observed in isomorphous oxides (Prewitt, Shannon, Rogers & Sleight, 1969). However, upon heating, this ratio is reduced from 2.83 to 2.78 in both systems.

The coordinates of the metal and oxygen atoms in V₂O₃ and β Cr-V₂O₃ converge at high temperature. The changes are primarily in the atomic positions in V₂O₃. The metal atom at 0,0,*z* in V₂O₃ changes its position by about 40 estimated standard deviations while that in β Cr-V₂O₃ changes by about 10 e.s.d.'s.

Table 4. *R.m.s. thermal displacements (Å) and orientation (°) along crystallographic axes*

Temperature	Metal*		Oxygen		
	R.m.s. displacements	R.m.s. displacements	<i>a</i>	<i>b</i>	<i>c</i>
V₂O₃					
23 °C	0.0438 (82)	0.056 (10)	90	120 (6)	35 (8)
	0.0726 (39)	0.062 (10)	180	60	90
	0.0726 (39)	0.095 (7)	90	45 (5)	55 (8)
115 °C	0.0583 (57)	0.066 (8)	90	117 (6)	31 (7)
	0.0785 (32)	0.068 (8)	180	60	90
	0.0785 (32)	0.103 (6)	90	42 (5)	59 (7)
212 °C	0.0670 (49)	0.070 (8)	90	123 (5)	39 (6)
	0.0879 (31)	0.087 (7)	180	60	90
	0.0879 (31)	0.109 (6)	90	48 (5)	51 (6)
300 °C	0.0801 (42)	0.084 (7)	90	126 (6)	42 (8)
	0.0916 (30)	0.087 (7)	180	60	90
	0.0916 (30)	0.115 (6)	90	50 (6)	47 (8)
400 °C	0.0839 (36)	0.088 (6)	90	129 (6)	46 (7)
	0.0973 (27)	0.098 (6)	180	60	90
	0.0973 (27)	0.118 (5)	90	53 (6)	44 (7)
600 °C	0.0983 (29)	0.099 (6)	90	124 (4)	40 (5)
	0.1069 (24)	0.104 (5)	180	60	90
	0.1069 (24)	0.135 (5)	90	49 (4)	50 (5)
α Cr-V₂O₃					
23 °C	0.0539 (37)	0.055 (7)	90	118 (4)	33 (5)
	0.0670 (23)	0.071 (6)	180	60	90
	0.0670 (23)	0.098 (5)	90	44 (3)	57 (5)
β Cr-V₂O₃					
23 °C	0.0534 (39)	0.066 (5)	90	125 (7)	41 (9)
	0.0672 (25)	0.067 (5)	180	60	90
	0.0672 (25)	0.087 (4)	90	49 (7)	49 (9)
113 °C	0.0623 (35)	0.070 (5)	90	128 (6)	46 (8)
	0.0734 (25)	0.075 (5)	180	60	90
	0.0734 (25)	0.093 (4)	90	53 (6)	44 (8)
310 °C	0.0776 (28)	0.079 (5)	90	121 (4)	37 (5)
	0.0870 (24)	0.088 (4)	180	60	90
	0.0870 (24)	0.110 (4)	90	46 (4)	53 (5)

* The table of angles with *a*, *b*, and *c* for all metal r.m.s. displacements is

90	90	0
120	0	90
30	90	90

The changes in the oxygen positions (*x*,0, $\frac{1}{4}$) are 7 and 2 e.s.d.'s, respectively.

The temperature factors (Tables 1 and 2) resulting from anisotropic refinement are well behaved. The β_{ij} 's of V₂O₃ and Cr-V₂O₃ at 23 °C are identical within two standard deviations. The root-mean-square vibrational amplitudes of the atoms in V₂O₃ (Table 4) increase most rapidly in the temperature range 23–300 °C in which the unit-cell volume increases most rapidly. The rate of increase is less at higher temperatures.

The structures of α Cr-V₂O₃ and V₂O₃ at room temperature are identical with that reported by Dernier (1970) and Newnham & de Haan (1962) for V₂O₃ while the structure of β Cr-V₂O₃ at 23 °C is identical with that of (Cr_{0.038}V_{0.962})₂O₃ (Dernier, 1970). Since the details of these structures have been fully discussed by these authors, we shall concentrate on the changes induced by temperature.

The effect of the changes in atomic positions and cell dimensions on the metal-metal distances is indicated in Table 3 and Fig. 2. The distance between the mean positions of the metal atoms sharing octahedral edges of their coordination polyhedra, M(1)–M(3), increases with temperature as would be expected from the increasing *a* dimension in both V₂O₃ and β Cr-V₂O₃. The nonlinear change is significant in V₂O₃, from 2.880 (1) at 23 °C to 2.924 (1) Å at 600 °C, while the linear change in β Cr-V₂O₃ is small, from 2.917 (1) Å at 23 °C to 2.920 (1) Å at 310 °C. The behavior of the metal-metal distance across the shared octahedral face

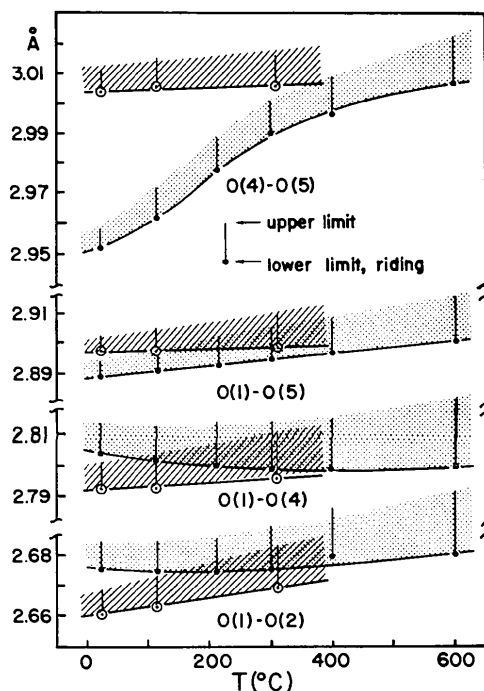


Fig. 3. Variation of uncorrected oxygen-oxygen distances and ranges of thermal corrections for V₂O₃ and β Cr-V₂O₃. The symbols are the same as in Fig. 2.

is more unexpected. As the c dimension of V_2O_3 decreases with temperature, the vector between the mean positions of M(1) and M(2), which is parallel to c , increases from 2.697 (1) Å at 23°C to 2.738 (1) Å at 600°C in a nonlinear manner. A plot of c against this M(1)–M(2) distance is linear with a negative slope in the 23–400°C temperature range. The change in the separation of the mean M(1)–M(2) positions in β Cr– V_2O_3 is small but significant. A linear decrease from 2.747 (1) Å at 23°C to 2.739 (1) Å at 310°C is observed although the c axis is increasing over this temperature range. The behavior of the distances between mean metal atom positions in α and β Cr– V_2O_3 parallels that in V_2O_3 between 23 and 600°C.

Changes in the distances between the mean positions of the metal and oxygen atoms in V_2O_3 at 23 and 600°C and in α and β Cr– V_2O_3 are not large, but are statistically significant (Table 3 and Fig. 2). The changes in these distances in β Cr– V_2O_3 over the temperature range 23–310°C are not statistically significant with a maximum change of 0.003 Å.

As may be seen in Table 3 and Fig. 3, the largest change in the distances between the mean positions of the oxygen atoms is the distance between oxygens of the unshared octahedral face parallel to the shared octahedral face, O(4)–O(5). The difference in this distance in V_2O_3 at 23 and 600°C and in α and β Cr– V_2O_3 is an increase of somewhat more than 0.05 Å from about 2.955 to about 3.005 Å. This change accompanies the motion of the metal atoms toward the center of this face. Most of the other changes in oxygen–oxygen distances are small increases which just border on statistical significance.

The variations in bond distances considered above reflect changes in distances between the mean positions of the atoms rather than mean interatomic distances. To calculate the mean distances one needs to know the correlations between the thermal displacements of the atoms. Since these correlations are not known, only the upper and lower bounds of the thermally corrected interatomic distances can be determined. These are reported in Table 3. Figs. 2 and 3 show the ranges of interatomic distances encompassed by the upper and lower bounds and how these ranges vary with temperature. The lower bounds are equal to the uncorrected bond lengths and to interatomic distances calculated using the riding approximation (Busing & Levy, 1962).

Even allowing for thermal corrections, the structures of V_2O_3 at 23°C and α Cr– V_2O_3 differ from that of β Cr– V_2O_3 at 23°C. As may be seen in Table 3 and Figs. 2 and 3, with the exception of the metal–oxygen distances, the various interatomic distances at 23°C are different using any combination of thermal corrections. Equal metal–oxygen distances would require a large thermal correction in V_2O_3 and α Cr– V_2O_3 and no thermal correction in β Cr– V_2O_3 . It is likely that V_2O_3 and β Cr– V_2O_3 become isostructural at elevated temperatures in spite of the uncertainty in the precise

interatomic distances. Both the unit-cell dimensions and atomic positions of V_2O_3 and β Cr– V_2O_3 converge at elevated temperatures, and the anisotropic temperature parameters are not statistically different. Since both materials are of the same symmetry with atoms of essentially the same mass, it is unlikely that the thermal corrections to the interatomic distances would vary to any appreciable degree.

The variation in thermal corrections as the sample changes temperature is difficult to judge. An increasing thermal correction to the metal–oxygen distances in V_2O_3 could double the increase in these distances over the 23–600°C range. On the other hand, a correction whose magnitude decreases with temperature could imply that there is no change or even a decrease in the mean metal–oxygen distances. It is apparent, however, that increases in the metal–metal distances and in the O(4)–O(5) distance are real since the changes in these distances are four to five times greater than the possible thermal corrections.

Discussion

The unusual thermal expansion of V_2O_3 in the 23–500°C range is a reflection of two effects: (1) a change in the band structure or chemical bonding in the material and (2) the anharmonicity of the atomic vibrations. The gradual changes in the unit-cell parameters upon heating occur over the same temperature range as the change in electrical conductivity of this material (McWhan & Remeika, 1970). These changes are accompanied by smooth changes in the mean atomic positions and real increases of about 0.04 Å in the metal–metal distances. The effects of changes in band structure and of the anharmonicity of atomic vibration can be observed separately in the 1% chromium-doped V_2O_3 system. The difference in structure between α and β Cr– V_2O_3 at room temperature is a consequence of differing band structures in the two systems while the thermal expansion of β Cr– V_2O_3 probably reflects anharmonic vibrational effects. The close correspondence between the structures of α Cr– V_2O_3 and V_2O_3 at room temperature and of β Cr– V_2O_3 and V_2O_3 at elevated temperatures suggests that the structural change in V_2O_3 upon heating is a combination of an electronically induced change in structure of about the same magnitude as that occurring during the α to β rhombohedral Cr– V_2O_3 transition coupled with thermal expansion of the same magnitude as that of β Cr– V_2O_3 .

From a comparison of the changes associated with the α to β transition in Cr– V_2O_3 and those associated with the thermal expansion of β Cr– V_2O_3 it is apparent that the larger structural changes are associated with the change in electronic properties. In view of the relatively small changes in the metal–oxygen distances, it seems likely that both the distortions of the structure of Cr– V_2O_3 with the α to β transition and the predominant changes in the structure of V_2O_3 between

23 and 600°C result from the increased metal-metal distances. In order to maintain approximately constant metal-oxygen distances, the oxygens of the unshared octahedral face move farther apart while those of the shared face move together. At the same time the distance between the parallel shared and unshared faces decreases. This distortion of the filled octahedra allows both the M(1)-M(2) and M(1)-M(3) distances to increase while keeping the metal-oxygen distances essentially constant. This is consistent with the band structure proposed by Goodenough (1971) for V₂O₃. The metal-oxygen bands in this scheme lie some 4 eV below the Fermi level while metal-metal bands lie at or near this level. Temperature-induced changes in bonding in such a system would primarily effect the metal-metal interactions and, consequently, the metal-metal distances and would have little effect on the metal-oxygen interactions.

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The Crystal and Molecular Structure of Potassium Monoaquamono(nitritotriacetato)cobaltate(II) Dihydrate, K[Co(C₆H₆NO₆)(OH₂)]·2H₂O

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Crystals of potassium monoaquamono(nitritotriacetato)cobaltate(II) dihydrate, K[Co(C₆H₆NO₆)(OH₂)]·2H₂O, are monoclinic, space group *P2₁/n* with *a* = 16.36 (1), *b* = 9.99 (1), *c* = 7.13 (1) Å, β = 91.6 (1)° and *Z* = 4. The X-ray analysis was carried out by three-dimensional Patterson, Fourier and least-squares methods (final *R* = 3.4%). Coordination around Co^{II} is octahedral and involves the nitrogen and three carboxylic oxygens from the same nitritotriacetate ion, one water molecule and one carboxylic oxygen from an adjacent anion. The packing is determined by the K⁺···O interactions and by the water-water and water-carboxylic oxygen hydrogen bonds.

Introduction

Nitritotriacetic acid is a tetradentate ligand which can form 1:1 metal complexes. In the present paper the

results of the crystal structure analysis of potassium monoaquamono(nitritotriacetato)cobaltate(II) dihydrate are given. This study was carried out as part of a research programme on metal-aminoacid interactions.