Zeitschrift für Kristallographie, Bd. 117, S. 235–237 (1962)

Refinement of the α Al_2O_3, Ti_2O_3, V_2O_3 and Cr_2O_3 structures*

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With 1 figure

(Received February 27, 1962)

Auszug

Die Kristallstrukturen der Sesquioxyde α-Al_2O_3, Ti_2O_3, V_2O_3 und Cr_2O_3 wurden durch Anwendung der Methode der kleinsten Quadrate auf die an Einkristallen gewonnenen Röntgendaten verfeinert. Atomabstände und Bindungswinkel wurden errechnet und mit denen von α-Fe_2O_3 verglichen.

Abstract

The crystal structures of α Al_2O_3, Ti_2O_3, V_2O_3, and Cr_2O_3 have been refined using a least-squares analysis of single-crystal x-ray data. Interatomic distances and bond angles are calculated and compared with those of α Fe_2O_3.

The crystal structure of α Al_2O_3, Ti_2O_3, V_2O_3, and Cr_2O_3 have been refined using single crystals grown by the Verneuil (flame-fusion) method. All four sesqioxides are isomorphous with corundum, α Al_2O_3, in which the oxygen positions approximate hexagonal close packing, with trivalent cations occupying two thirds of the octahedral interstices. The corundum structure was analyzed by Pauling and Hendricks[1]; its space group is $R\bar{3}c$ with six formula units in the hexagonal unit cell. The metal ions are located in special positions along the threefold axis at $\pm$ $[0\,0\,z;\ 0\,0\,\frac{1}{2}+z]$ and the oxygens lie on diads at $\pm$ $[x\,0\,\frac{1}{4}\ ;\ 0\,x\,\frac{1}{4}\ ;\ \bar{x}\,\bar{x}\,\frac{1}{4}]$.

The atomic parameters z and x were deduced from zero-layer intensity data collected about [100] using a Weissenberg camera and Mo$K\alpha$ radiation. Each oxide gave approximately 120 intensities which were estimated visually

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* Sponsored by Air Force Cambridge Research Laboratories, Contract AF 19 (604)—6155.

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[1] L. Pauling and S. B. Hendricks, The crystal structures of hematite and corundum. J. Am. Chem. Soc. 47 (1925) 781—790.

by comparison with a calibrated scale. After preliminary trial-and-error adjustments of the scale factor and temperature parameters, a least-squares solution gave the values of z and x listed in Table 1. The R factors for the four structures ranged between 8 and $10\,^0/_0$, despite significant extinction errors observed for several of the intense small-angle reflections. Tabulations of the observed and calculated structure factors are available upon request. The standard deviations σ were estimated from the least-squares calculation; differences in bond lengths or angles greater than $2.3\,\sigma$ are significant. Graphical extrapolation of large-angle powder line data gave the lattice parameters listed in Table 1. These are in good agreement with the numerous values given in the literature[2,3], although there is evidence that the structural parameters of Ti_2O_3 and V_2O_3 are slightly dependent on stoichiometry[3].

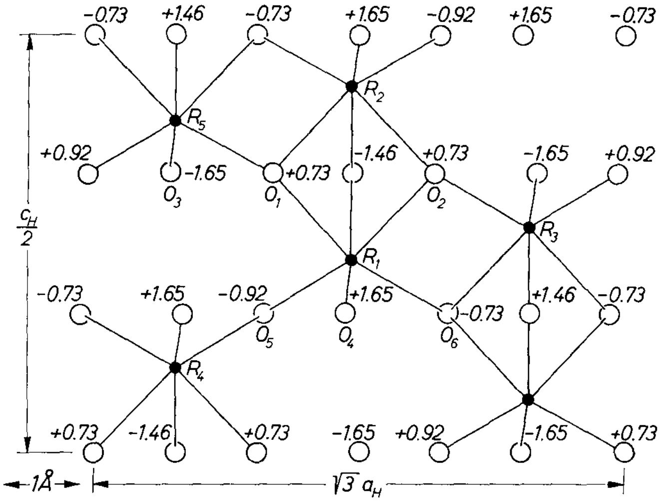

Fig. 1. Projection of $\alpha\,Al_2O_3$ on $(2\bar{1}\cdot 0)$. The vertical distances (in Å) from the oxygens to the plane of projection are given in parentheses. The metal ions lie at height zero

The interatomic distances and bond angles are given in Table 1; the corresponding values for $\alpha\,Fe_2O_3$[4,5] are listed for comparison. Figure 1 shows

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[2] H. E. Swanson, N. T. Gilfrich and M. I. Cook, Standard x-ray diffraction powder patterns. U. S. Department of Commerce, National Bureau of Standards, NBS Circular 539, Vol. 2, 1953, p. 20—23; Vol. 5, 1955, p. 22—23.

[3] C. Nordmark, Mixed oxides of titanium and vanadium. Acta Crystallogr. **13** (1960) 1023; Acta Chem. Scand., to be published.

[4] B. T. M. Willis and H. P. Rooksby, Crystal structure and antiferromagnetism in haematite. Proc. Physic. Soc. [London] B **65** (1952) 950—954.

[5] G. Shirane, S. J. Pickart, R. Nathans and Y. Ishikawa, Neutron diffraction study of antiferromagnetic $FeTiO_3$ and its solid solutions with αFe_2O_3. J. Physic. Chem. Solids **10** (1959) 35—43.

Table 1. *Crystallographic data for the corundum structures* (notation explained in Fig. 1)

		σ	α Al_2O_3	Ti_2O_3	V_2O_3	Cr_2O_3	α Fe_2O_3[4,5]
a_H		0.001 Å	4.7589	5.149	4.952	4.9607	5.0345
c_H		0.005 Å	12.991	13.642	14.002	13.599	13.749
z (R)		0.0003	0.3520	0.3450	0.3463	0.3475	0.355
x (O)		0.004	0.306	0.317	0.315	0.306	0.300
Interatomic distances in Å							
R_1—O_1	(3)	0.015	1.97	2.08	2.06	2.02	2.09
R_1—O_5	(3)	0.010	1.86	2.01	1.96	1.97	1.96
R_1—R_2	(1)	0.008	2.65	2.59	2.70	2.65	2.89
R_1—R_3	(3)	0.002	2.79	2.99	2.88	2.89	2.97
R_1—R_4	(3)	0.001	3.22	3.56	3.47	3.43	3.37
R_1—R_5	(6)	0.004	3.50	3.74	3.69	3.65	3.70
O_1—O_2	(2)	0.035	2.52	2.83	2.70	2.63	2.62
O_1—O_3	(4)	0.020	2.87	3.05	2.94	2.99	3.06
O_1—O_4	(2)	0.007	2.62	2.80	2.81	2.74	2.76
O_1—O_5	(4)	0.007	2.73	2.88	2.89	2.85	2.89
Bond angles in degrees							
R_1—O_1—R_2	(3)	0.7	84.6	76.9	81.7	82.3	87.4
R_1—O_2—R_3	(6)	0.5	93.6	93.7	91.4	93.1	94.1
R_1—O_5—R_4	(3)	0.4	120.3	124.2	124.4	121.4	118.2
R_1—O_1—R_5	(6)	0.5	132.3	132.0	132.9	133.1	132.1
O_1—R_1—O_2	(3)	1.4	79.7	85.4	81.9	81.4	77.5
O_1—R_1—O_5	(6)	0.6	86.4	86.3	88.6	86.9	85.9
O_5—R_1—O_6	(3)	1.0	101.1	98.4	97.0	99.0	102.7
O_1—R_1—O_6	(3)	0.7	164.3	170.5	169.1	167.0	161.5

a projection of the corundum structure along [100] on to the $(2\bar{1}\cdot 0)$ plane. The short R_1—R_2 distances in the Ti, V, and Cr sesquioxides lend credence to the cation-cation interactions proposed by MAGNÉLI[6] and GOODENOUGH[7].

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[7] J. B. GOODENOUGH, Direct cation-cation interaction in several oxides. Physic. Rev. **117** (1960) 1442—1451.