

Refinement of the structure of scandium sesquioxide

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Auszug

Mit photographischen Röntgen-Einkristalldaten wurde die Struktur des Sc_2O_3 , welche isotyp ist mit Bixbyit, $(\text{Fe},\text{Mn})_2\text{O}_3$, verfeinert. Der durchschnittliche Abstand $\text{Sc}^{3+}-\text{O}^{2-}$ ist 2,11 Å, und das Verhältnis dieses Wertes zur Gitterkonstante ($9,810 \pm 0,002$) ist gleich 0,215. Letzterer Wert ist gleich dem analogen Verhältnis für In_2O_3 , dessen Struktur kürzlich mit Einkristall-Zählrohrdaten verfeinert wurde. Die Resultate werden mit denen des Y_2O_3 und anderer Sesquioxyde vom Bixbyit-Typ verglichen. Fünf andere Sesquioxyde, einschließlich Y_2O_3 haben das Verhältnis: durchschnittlicher M—O-Abstand/Gitterkonstante = 0,215. Wahrscheinlich ist dieser Wert für alle Sesquioxyde mit Bixbyit-Struktur charakteristisch.

Abstract

Single crystal x-ray photographic data have been used to refine the structure of Sc_2O_3 which is isostructural with bixbyite $(\text{Fe},\text{Mn})_2\text{O}_3$. The average $\text{Sc}^{3+}-\text{O}^{2-}$ distance is 2.11 Å, and the ratio of this value to the lattice constant 9.810 (± 0.002) Å is 0.215 equal to the analogous ratio for In_2O_3 , the structure of which has recently been refined from single-crystal counter data. The results are compared with those on Y_2O_3 based on single-crystal x-ray photographic data and those obtained in the last decade by neutron and x-ray powder techniques on other sesquioxides with the bixbyite structure. Five other sesquioxides, including Y_2O_3 , have an average M—O distance to lattice constant ratio equal to 0.215. It is probable that this is the value for all sesquioxides with this structure.

Introduction

Of all the sesquioxides which crystallize with the bixbyite structure, Sc_2O_3 is the best candidate for structure refinement by means of photographic techniques: scandium has the lowest atomic number of those cations which form these sesquioxide structures. In 1961, one of

us (J. P. R.) grew some small crystals of Sc_2O_3 ; we have used one of these for the refinement. The accuracy of the refinement is comparable with that of the In_2O_3 structure recently carried out by MAREZIO¹.

Crystal data

Scandium sesquioxide, Sc_2O_3 , has F. W. = 137.912; $\rho_x = 3.880$ g/cm³. The crystal is cubic with $a = 9.810 \pm 0.002$ Å and contains sixteen formula units per unit cell. Reflections hkl are present only when $h + k + l = 2n$ and $0kl$ only when $k, l = 2n$; the most probable space group is uniquely $Ia\bar{3}-T_h$ ⁷. The scandium ions are in positions 8(*b*) and 24(*d*), the oxygen ions in the general positions 48(*e*).

The absorption coefficient for $\text{MoK}\alpha$ radiation is 55.4 cm⁻¹ and for $\text{CuK}\alpha$, 485.2 cm⁻¹.

Experimental

Crystals of size suitable for this investigation were obtained as follows: 3.00 g of Sc_2O_3 , 4.00 g of B_2O_3 and 50.00 g of PbO were weighed into a 100 cm³ platinum crucible. The crucible was covered with a platinum lid and placed in a horizontally loaded, electrical resistance furnace which was at 1300 °C. This temperature was maintained for four hours after which controlled cooling at a rate of 50 °C per hour was initiated. Cooling was continued until the temperature was about 600 °C. The crucible was then removed from the furnace, allowed to cool to room temperature, and immersed in hot $\text{HNO}_3\text{-H}_2\text{O}$ in approximately 1:4 ratio by volume. This dissolved the flux, freeing the crystals. (A slower cooling rate and optimization of the concentration of the nutrient to flux ratio for the solution temperature used would probably produce larger crystals.)

Four layers (0–3) of data were obtained with the Buerger precession camera and $\text{MoK}\alpha$ radiation; precession axis was the a axis of the crystal of dimensions $0.25 \times 0.25 \times 0.40$ mm ($\parallel a_1 \times a_2 \times a_3$, respectively). Nine layers (0–8) of data about the crystal a axis were obtained with the integrating equi-inclination Weissenberg technique and $\text{CuK}\alpha$ radiation. Intensities were estimated by comparison with a carefully prepared intensity scale.

Because of the very large absorption of $\text{CuK}\alpha$ radiation, the precession camera data were used mainly. However, after the first two cycles of refinement, it became apparent that a number of reflections must be suffering from overlap by double reflections. This was con-

¹ M. MAREZIO, The effect of wavelength on the refinement of the crystal structure of In_2O_3 . *Acta Crystallogr.* **20** (1966) 723–728.

firmed by examination of the Weissenberg photographs. Since it was usually only one of a pair of reflections hkl , khl which was affected, corrections were made by estimating the pair of intensities on the Weissenberg photographs and applying the square root of the ratio of these to the apparently correct F_{hkl} to obtain the other. In some cases the reflections affected were outside the $\text{CuK}\alpha$ sphere of reflection; these were, therefore, excluded from the refinement.

Relative $|F_{hkl}|^2$ were obtained by applying the Lorentz-polarization corrections as obtained from WASER² and GRENVILLE-WELLS and ABRAHAMS³ charts. Since the absorption corrections for $\text{MoK}\alpha$ radiation would be low, they were not made. The observed $|F_{hkl}|^2$ were put on the same scale by the method of cross comparison of values common to more than one layer.

The lattice constant was determined from measurements of a powder photograph taken with a 114.6 mm camera and $\text{CuK}\alpha$ radiation.

Refinement of the structure

Structure refinement was carried out using the Busing-Martin-Levy least-squares computer program⁴. Atomic scattering factors of Sc^{3+} were those of CROMER and WABER⁵ corrected for the real part of the anomalous dispersion. The scattering factors of O^{2-} were those of BERGHUIS *et al.* for O arbitrarily modified such that $f_{\text{O}^{2-}} = 10.00$ at $(\sin \theta)/\lambda = 0$ and $f_{\text{O}^{2-}} = f_{\text{O}}$ at $(\sin \theta)/\lambda \geq 0.20$. All observed F 's were weighted equally at 1.00, while those too weak to be observed were weighted 0.10. Initially, isotropic thermal parameters, 0.2 \AA^2 for each Sc^{3+} and 0.3 \AA^2 for O^{2-} , were held constant. Convergence was very rapid, a value of $R = 0.07$ being obtained for the data shown in Table 1. (This is the value calculated by the Busing-Martin-Levy program; that is, multiplicity is neglected.) After convergence of the four positional parameters and scale factor was attained, all parameters were permitted to vary. No significant change in positional parameters occurred, but the oxygen thermal parameter became negative in the

² J. WASER, Lorentz and polarization correction for the Buerger precession method. *Rev. Sci. Instrum.* **22** (1951) 567--568; J. WASER, Erratum. *Rev. Sci. Instrum.* **23** (1952) 420.

³ H. J. GRENVILLE-WELLS and S. C. ABRAHAMS, Upper level precession photography and the Lorentz polarization correction. Part II. *Rev. Sci. Instrum.* **23** (1952) 328--331.

⁴ W. R. BUSING, K. O. MARTIN and A. A. LEVY, ORFLS, A FORTRAN crystallographic least-squares program. ORNL-TM-305 (1962).

⁵ D. T. CROMER and J. T. WABER, Scattering factors computed from relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18** (1965) 104--109.

Table 1. Observed and calculated structure amplitudes

hkl	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c	h k l	F _o	F _c
200	30.7	-20.4	8 0 0	272.9	308.1	6 8 2	132.1	131.9	8 9 1	87.2	87.6
211	78.3	77.9	8 1 1	93.5	92.7	9 4 3	49.4	45.7	12 2 0	133.7	-118.2
220	< 5.6	-9.2	7 4 1	57.9	-52.8	4 9 3	79.6	-76.8	2 12 0	119.6	115.4
222	*	-170.2	4 7 1	65.6	64.7	10 2 2	164.5	-148.9	11 5 2	52.2	44.5
321	32.4	25.4	8 2 0	105.2	-102.1	10 3 1	58.8	56.8	5 11 2	64.7	-65.7
231	< 6.2	-8.1	2 8 0	70.0	76.5	5 10 1	61.8	-56.6	10 7 1	57.9	52.4
400	171.7	207.0	6 5 3	80.3	-73.5	5 9 2	61.5	56.3	7 10 1	65.2	-57.3
411	65.6	73.9	5 6 3	79.6	72.6	9 5 2	65.6	65.5	12 2 2	121.8	111.2
420	51.2	-50.2	8 2 2	94.9	89.1	8 7 1	68.3	58.8	12 3 1	28.0	23.2
240	45.2	40.2	6 6 0	31.6	-24.3	7 8 1	71.7	-71.5	3 12 1	34.8	-32.9
332	133.2	-138.8	8 3 1	71.3	76.6	10 4 0	73.1	-79.2	9 8 3	57.5	67.2
422	33.7	47.0	3 8 1	68.3	-60.9	4 10 0	133.1	-133.7	8 9 3	22.4	-24.1
431	98.2	85.5	7 4 3	66.4	-60.5	10 3 3	64.4	-55.1	11 6 1	95.2	-91.5
341	99.9	-103.3	4 7 3	59.7	-59.4	9 6 1	83.8	74.3	6 11 1	88.1	73.0
521	71.0	65.4	6 6 2	199.3	-186.1	6 9 1	92.5	88.9	10 7 3	36.9	-40.5
251	72.8	71.0	7 5 2	10.2	7.6	10 4 2	122.2	126.4	7 10 3	22.9	-35.5
440	*	494.3	5 7 2	12.5	11.2	4 10 2	71.7	-62.8	12 4 0	125.0	112.7
433	77.0	-74.6	8 4 0	124.5	122.8	7 8 3	61.8	-63.8	4 12 0	115.4	111.9
600	73.5	-72.3	4 8 0	127.3	123.0	8 7 3	65.2	-64.3	12 3 3	33.2	-31.7
442	17.7	-15.4	8 3 3	74.2	-72.6	11 2 1	28.0	26.7	12 4 2	63.0	70.6
611	100.9	101.0	8 4 2	67.9	62.0	11 1 2	< 8.8	1.3	4 12 2	98.2	-89.7
532	62.3	-64.5	4 8 2	71.3	-65.9	10 5 1	78.0	75.5	8 10 0	141.5	-149.6
352	60.6	57.2	9 2 1	16.2	14.8	5 10 1	73.1	68.2	6 11 3	40.3	-41.0
620	59.4	-50.3	2 9 1	< 7.5	3.1	9 6 3	61.0	60.1	9 9 2	< 9.3	-5.3
260	75.2	76.7	7 6 1	36.9	-30.7	6 9 3	52.2	-52.3	10 8 2	136.4	143.8
341	84.1	77.1	6 7 1	54.2	46.5	8 8 0	131.0	125.3	12 5 1	45.2	46.0
451	104.9	99.9	8 5 1	46.3	42.9	8 8 2	12.5	-10.5	13 2 1	33.2	30.6
622	256.7	-283.8	5 8 1	62.7	66.1	11 3 2	52.7	-47.6	2 13 1	41.6	41.8
631	112.1	109.4	9 3 2	34.0	-31.3	3 11 2	83.2	-75.9	11 7 2	12.5	-10.2
613	117.0	-115.5	3 9 2	31.6	29.6	10 5 3	32.6	-37.9	7 11 2	< 9.4	6.8
343	71.3	74.1	7 6 3	119.0	-107.4	5 10 3	39.0	43.7	12 5 3	< 13.5	-6.9
453	52.2	-41.4	6 7 3	95.2	-85.1	9 7 2	47.5	-44.2	5 12 3	26.1	32.2
640	41.6	-45.1	9 4 1	53.7	58.2	7 9 2	39.0	34.5	12 6 0	112.7	-136.6
460	97.4	-99.8	4 9 1	59.7	50.6	10 6 0	28.7	-29.3	13 3 2	22.9	-19.3
721	111.2	-111.6	8 5 3	86.9	-96.0	6 10 0	71.7	70.4	3 13 2	20.5	21.4
271	95.5	82.6	5 8 3	71.3	61.3	11 4 1	54.7	-49.3	9 10 1	32.4	34.7
633	48.6	-46.7	10 0 0	105.9	-101.0	4 11 1	46.9	46.2	6 12 2	131.9	131.8
552	< 7.2	-5.0	8 6 0	132.3	-136.1	10 6 2	104.2	-88.6	4 13 1	54.7	59.2
642	74.6	77.4	6 8 0	66.6	50.2	6 10 2	91.9	-88.6	11 8 1	58.8	-51.2
462	40.3	-36.5	10 1 1	35.5	37.6	12 0 0	117.0	108.1	8 11 1	60.2	54.1
732	25.0	16.1	7 7 2	76.6	-70.2	12 1 1	19.2	21.2	10 9 3	57.5	-57.3
372	41.0	36.7	10 2 0	117.9	-110.6	11 4 3	33.7	-47.1	9 10 3	46.9	44.4
651	34.2	33.8	2 10 0	103.9	92.0	4 11 3	40.3	-43.2			
561	59.3	61.0	8 6 2	33.6	43.5	9 8 1	53.0	51.8			

* Not estimated, nor included in least-squares calculation.

first cycle. Standard deviations of the thermal parameters indicated that the values were not very meaningful. All correlations⁸ of positional parameters were less than 0.15; correlations between thermal and positional parameters were all less than 0.11, most being much smaller.

The final positional parameters obtained are for Sc³⁺ in 24(d): $x = 0.4649$, $\sigma_x = 0.0002$; for O²⁻ in 48(e): $x = 0.3928$, $y = 0.1528$, $z = 0.3802$, and $\sigma_x = \sigma_y = \sigma_z = 0.0007$.

Interatomic distances and angles

Distances and angles are given in Table 2. The standard deviation in a Sc³⁺(b)—O²⁻ distance is 0.012 Å; in a Sc³⁺(d)—O²⁻ distance, 0.013 Å; in an O²⁻—O²⁻ distance, ~ 0.01 Å; and in an O²⁻—Sc³⁺—O²⁻ angle, $\sim 0.4^\circ$. Thus the limits of error are, respectively: ± 0.036 Å, ± 0.039 Å, $\sim \pm 0.03$ Å, and $\sim 1.2^\circ$.

⁶ D. T. CROMER, Anomalous dispersion corrections computed from self-consistent field relativistic Dirac-Slater wave functions. *Acta Crystallogr.* **18** (1965) 17—23.

⁷ J. BERGHUIS, IJ. M. HAANAPPEL, M. POTTERS, B. O. LOOPSTRA, C. H. MACGILLAVRY and A. L. VEENENDAAL, New calculations of atomic scattering factors. *Acta Crystallogr.* **8** (1955) 478—483.

⁸ S. GELLER, Parameter interaction in least-squares structure refinement. *Acta Crystallogr.* **14** (1961) 1026—1035.

Table 2. *Interatomic distances and angles*

Polyhedron about Sc ³⁺ in 8(<i>b</i>)		Subtended O—Sc—O angles
Sc—O (6)	2.12 Å	
O—O (6)	2.73 Å	80.2°
O—O (6)	3.25 Å (diagonal)	99.8°
Polyhedron about Sc ³⁺ in 24(<i>d</i>)		
Sc—O (2)	2.16 Å	
Sc—O (2)	2.09 Å	
Sc—O (2)	2.08 Å	
O—O (4)	2.71 Å	79.4°
O—O (2)	2.73 Å	79.8°
O—O (2)	3.40 Å (diagonal)	109.2°
O—O (2)	3.18 Å (diagonal)	99.3°
O—O	2.84 Å (diagonal)	86.1°
O—O	3.66 Å (diagonal)	115.6°
O—O	3.94 Å (diagonal)	140.7°

Discussion

Adequate description of the structure has been given by others^{1,9-11}.

To date there appear to be three refinements of bixbyite-type structures which have been based exclusively on single-crystal data, namely those of Y₂O₃¹¹, In₂O₃¹ and of Sc₂O₃ (present work). Several others have been carried out by neutron or x-ray diffraction studies of powders, the most recent being those of HASE¹². In Table 3, we list the cation—oxygen distances, obtained during the past ten years for isostructural compounds, and their averages. This comparison shows that FERT's¹³ results for Mn₂O₃ are incompatible with the others. It is unlikely that the average Mn³⁺—O²⁻ distance is larger than that of the average Sc³⁺—O²⁻ distance. In the case of this structure, there is little doubt that the lattice constant will be directly proportional to the cation—oxygen distance. The lattice constant of Mn₂O₃ is 0.40 Å smaller than that of Sc₂O₃; thus, HASE's results are far more consistent with those obtained for Sc₂O₃ and In₂O₃ than those of FERT¹³.

⁹ L. PAULING and M. D. SHAPPELL, The crystal structure of bixbyite and the *C* modification of the sesquioxides. *Z. Kristallogr.* **75** (1930) 128—142.

¹⁰ C. HERMANN, O. LOHRMANN and H. PHILIPP, *Strukturbericht II* (1928—1932) p. 38—40. Akademische Verlagsgesellschaft M. B. H., Leipzig.

¹¹ M. G. PATON and E. N. MASLEN, A refinement of the crystal structure of yttria. *Acta Crystallogr.* **19** (1965) 307—310.

¹² W. HASE, Neutronographische Bestimmung der Kristallstrukturparameter von Dy₂O₃, Tm₂O₃, und α-Mn₂O₃. *Physica Status Solidi III* (1963) K 446—K 449.

¹³ A. FERT, Structure de quelques oxydes de terres rares. *Bull. Soc. Franç. Mineral. Cristallogr.* **85** (1962) 267—270.

There is experimental evidence¹⁴ consistent with crystal field theory¹⁵ that the Mn^{3+} ion is very slightly smaller than that of the Fe^{3+} ion. There is also experimental evidence that if an Fe_2O_3 with bixbyite structure existed, it would have the same lattice constant as that of Mn_2O_3 ¹⁶. Thus the average cation—oxygen distance in bixbyite should be very nearly the same as that in Mn_2O_3 . The results of DACHS¹⁷ and HASE¹² are, therefore, consistent with each other.

Listed also in Table 3 are the ratios of average cation—oxygen distance to lattice constant, which for the three structures refined from single crystal data are all equal to 0.215. Five others also have this ratio, and in fact, the over-all average excluding that for FERT's Mn_2O_3 is 0.215. This ratio value, then, is probably the ideal one for all the sesquioxides with the bixbyite structure. (The difference from the value 0.2144 calculated by TEMPLETON and DAUBEN¹⁸ based on the results of PAULING and SHAPPELL⁹ may not be significant.)

The plot of lattice constant vs cation atomic number for the rare-earth sesquioxides¹⁹ is very similar to that for the rare-earth iron garnets²⁰, i.e., with a cusp at Gd and an indication of a crystal field effect on size. In both cases, a decrease in the size of the rare-earth ion with increase in atomic number is indicated. Further, the lattice con-

¹⁴ S. GELLER, Crystallographic studies of perovskite-like compounds. V. Relative ionic sizes. *Acta Crystallogr.* **10** (1957) 248–251.

¹⁵ J. H. VAN SANTEN and J. S. VAN WIERINGEN, Some remarks on the ionic radii of iron-group elements. The influence of crystalline field. *Rec. Trav. Pays Bas* **71** (1952) 420–430; A. D. LIEHR, "Ionic radii," spin-orbit coupling and the geometric stability of inorganic complexes. *Bell System Tech. J.* **39** (1960) 1617–1626.

¹⁶ P. E. WRETBLAD, X-ray investigation of the systems $\text{Fe}_2\text{O}_3\text{—Cr}_2\text{O}_3$ and $\text{Fe}_2\text{O}_3\text{—Mn}_2\text{O}_3$. *Z. anorg. allg. Chem.* **189** (1930) 329–336; B. MASON, Mineralogical aspects of the system $\text{FeO—Fe}_2\text{O}_3\text{—MnO—Mn}_2\text{O}_3$. *Geol. Fören. Stockh. Förh.* **65** (1943) 95–180; V. MONTORO, Miscibilità fra i sesquiossidi di ferro e di manganese. *Gazz. Chim. Ital.* **70** (1940) 145–149; S. GELLER, H. J. WILLIAMS and R. C. SHERWOOD, Substitution of Fe^{3+} ion in Sc_2O_3 and In_2O_3 . *J. Chem. Phys.* **35** (1961) 1908–1909; S. GELLER and G. P. ESPINOSA, unpublished work.

¹⁷ H. DACHS, Die Kristallstruktur des Bixbyits $(\text{Fe,Mn})_2\text{O}_3$. *Z. Kristallogr.* **107** (1956) 370–395.

¹⁸ D. H. TEMPLETON and C. H. DAUBEN, Lattice parameters of some rare earth compounds and a set of crystal radii. *J. Amer. Chem. Soc.* **76** (1954) 5237–5239.

¹⁹ H. R. HOEKSTRA and K. A. GINGERICH, High pressure *B*-type polymorphs of some rare-earth sesquioxides. *Science* **146** (1964) 1163–1164.

²⁰ G. P. ESPINOSA, Crystal chemical study of the rare-earth iron garnets. *J. Chem. Physics* **37** (1962) 2344–2347.

Table 3. Cation—oxygen distances (Å) and ratios of average distance to lattice constant in M_2O_3 structures

M	Reference	M_1-O		M_2-O		Average	$\frac{\text{Average}}{a}$	0.215 a
Mn	12	2.02	2.26	1.87	2.01	2.04	0.217	2.02
Mn	13	2.11	2.18	2.02	2.21	2.13	0.226	2.02
(Mn, Fe)	17	2.01	2.24	1.90	1.92	2.02	0.215	2.02
Sc	Present work	2.12	2.16	2.08	2.09	2.11	0.215	2.11
In	1	2.18	2.19	2.23	2.13	2.18	0.215	2.18
Y	11	2.25	2.26	2.35	2.28	2.28	0.215	2.28
Y	13	2.25	2.25	2.34	2.27	2.28	0.215	2.28
Yb	13	2.25	2.31	2.23	2.21	2.25	0.216	2.24
Tm	12	2.24	2.23	2.34	2.27	2.27	0.217	2.25
Er	13	2.28	2.33	2.23	2.20	2.26	0.214	2.27
Ho	13	2.27	2.33	2.20	2.31	2.28	0.215	2.28
Dy	12	2.28	2.28	2.34	2.28	2.30	0.215	2.30
Pr	*	2.47	2.46	2.28	2.40	2.40	0.215	2.40
Lu								2.24
Tb								2.30
Gd								2.33
Eu								2.34
Sm								2.35
Nd								2.38
La								2.46

* Calculated in Ref. ¹ from data reported in Ref. ²¹.

stants of Y_2O_3 and Ho_2O_3 are very nearly the same as are those of the garnets $Y_3Fe_2Fe_3O_{12}$ and $Ho_3Fe_2Fe_3O_{12}$. One should, therefore, expect the cation—oxygen distances of Y—O and Ho—O to be very nearly the same. Application of the ratio 0.215 (see Table 3) to the M_2O_3 lattice constants gives plausible results.

Acknowledgments

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²¹ L. EYRING and N. C. BAENZIGER, On the structure and related properties of the oxides of praseodymium. *J. Appl. Physics* **33** (1962) 428—433.