The Yttria–Zirconia δ Phase

By H. G. Scott

CSIRO Division of Tribophysics, Box 4331, GPO Melbourne, Victoria 3001, Australia

Abstract. $Zr_3Y_4O_{12}$, rhombohedral, $R\bar{3}$ (No. 148), $a = 9.7345$ (5), $c = 9.1092$ (6) Å at 26 °C, $Z = 3$ (hexagonal representation), $D_c = 5.473$ g cm^{-3}. The structure is derived from the MO_{2-x} defect-fluorite type by ordering of the anion vacancies. The stability of the phase relative to that of the pyrochlore type is considered.

Introduction. The compound was prepared by the solid-state reaction of the component oxides, $3ZrO_2 + 2Y_2O_3$, at 1300 °C for three months. Lattice parameters at 26 °C were calculated by a least-squares method from Guinier photographs, with thoria ($a = 5.5972$ Å) used as an internal standard.

X-ray powder intensity data were collected on a diffractometer in the continuous scan mode with Ni-filtered Cu $K\alpha$ radiation. Referred to hexagonal axes, there were systematic absences only for $-h + k + l \neq 3n$, *i.e.* those characteristic of a rhombohedral cell. The region of reciprocal space scanned, from 12 to 107° in 2θ, contained 199 independent reflexions but the number of independent intensity observations, *i.e.* groups of coincident or unresolved reflexions, was only 88, of which six were below the limit of detection.

The structure was refined directly from the intensity data with *POWDER*, a full-matrix least-squares program which minimizes $\Sigma w(I_o - I_c)^2$, where $w = (I_o + I_{min})^{-1}$ and I_{min} is set approximately equal to the weakest measured intensity but is not in practice critical. The weighted residual R_w is defined as $\frac{1}{2}[\Sigma w(I_o - I_c)^2/\Sigma w I_o^2]^{-1/2}$, where the multiplier $\frac{1}{2}$ is not merely cos-

metic but provides numerical comparability with the more common residuals based on F values (Rossell & Scott, 1975). Unobserved reflexions were arbitrarily assigned intensities equal to about one quarter of the weakest measured, and included in the refinement. Scattering factors for neutral atoms (Cromer & Waber, 1965) with corrections for anomalous dispersion (Cromer, 1965) were used. The trial structure assumed ideal fluorite-derived atomic coordinates with disordered cations and ordered anions: the vacant anion sites were determined by the symmetry. After refinement of scale, overall temperature factor and atomic coordinates the residual R_w was 0.032; the parameters obtained are given in Table 1.* The relative paucity of high-angle intensity data precluded the meaningful inclusion of individual temperature factors; even the overall temperature factor may be partly an angle-dependent correction to the scale factor, arising from roughness of the specimen surface, rather than a true structure parameter.

When the occupancies of the cation sites were allowed to vary there were small changes which were consistent with the special site at the origin being occupied preferentially by Zr, but because of the similar scattering powers of the two cations these changes were not statistically significant. Refining the atomic coordinates in the non-centrosymmetric space group $R3$, by using two groups of sites to avoid degeneracy, resulted in only trivial changes and justified the choice of the centrosymmetric space group $R\bar{3}$. Other rhombohedral space groups permitted by the reflexion conditions were rejected as inconsistent with the fluorite-related nature of the structure.

Discussion. $Zr_3Y_4O_{12}$ has the δ-phase structure. This designation was given by Lefèvre (1963) to a rhombohedral phase appearing at about 52 mol % $ScO_{1.5}$ in the zirconia–scandia system and the ideal stoichiometry, $Zr_3Sc_4O_{12}$, was suggested by Collongues, Queyroux, Perez y Jorba & Gilles (1965). The structure

Table 1. *Fractional atomic coordinates (hexagonal axes), and temperature factor*

Standard deviations of the last digits are in parentheses. Overall temperature factor $B = 0.50$ (6) Å^2. M = $(3Zr + 4Y)/7$. Figures in italics are the ideal coordinates for the undistorted fluorite structure.

	x	y	z
M(1)	0.0	0.0	0.0
	0.0	*0.0*	*0.0*
M(2)	0.4109 (4)	0.2905 (4)	−0.0174 (3)
	0.4286	*0.2857*	*0.0*
O(1)	0.1544 (31)	0.4522 (25)	0.2734 (18)
	0.1429	*0.4286*	*0.250*
O(2)	0.4599 (25)	0.2965 (30)	0.2281 (18)
	0.4286	*0.2857*	*0.250*

Table 2. *Metal–oxygen distances* (Å) *in coordination polyhedra*

Estimated standard deviations are about 0·025 Å.

M(1)–O(2^i)	2·09	M(2)–O(1^i)	2·36
M(2)–O(2)	2·28	M(2)–O(1^{ii})	2·18
M(2)–O(2^i)	2·53	M(2)–O(1^{iii})	2·19
M(2)–O(2^{ii})	2·21	M(2)–O(1^{iv})	2·27

was determined by Thornber, Bevan & Graham (1968) who showed it to be essentially that of UY_6O_{12} (Bartram, 1966). The δ-phase structure is derived from the defect-fluorite type by ordering the anion vacancies to give a rhombohedral cell, the axes of which are related to those of the distorted fluorite subcell by the matrix $(1, -\frac{1}{2}, \frac{1}{2}/\frac{1}{2}, 1, -\frac{1}{2}/-\frac{1}{2}, \frac{1}{2}, 1)$. There are two types of cation sites: a single site at the origin which is octahedrally coordinated by anions, and six equivalent sites which are coordinated by anions on seven of the eight vertices of a slightly distorted cube.

The cation ordering in $Zr_3Y_4O_{12}$ cannot be determined directly from the X-ray data because of the similar scattering factors of the two cations, but it can be inferred from the interatomic distances. Shannon & Prewitt (1969, 1970) give the following ionic radii, $^{VI}Zr^{4+} = 0·72$, $^{VII}Zr^{4+} = 0·78$, $^{VI}Y^{3+} = 0·900$, $^{VIII}Y^{3+} = 1·015$ Å (whence $^{VII}Y^{3+} \doteqdot 0·96$ Å by interpolation) and $^{IV}O^{2-} = 1·38$ Å. Table 2 lists the non-equivalent metal–oxygen distances in the anion polyhedra coordinating the two distinct metal atoms. From these distances it can be deduced that M(1) has a radius of 0·71 Å which suggests that this site is occupied by Zr. M(2) has a mean radius of 0·91 Å, which agrees well with $(^{VII}Zr^{4+} + 2\ ^{VII}Y^{3+})/3 = 0·90$ Å from Shannon & Prewitt's figures. Thus interatomic distances indicate a structure in which the octahedrally coordinated cation site is occupied solely by Zr, and the remaining cation sites are occupied at random by Zr and Y in the ratio of one to two, as is required by the stoichiometry.

At least 20 δ phases are now known, mostly in binary oxide systems: Rossell (1976) has described the structure of several new examples and reviewed some of the earlier accounts. The common features of the structure are the relationship of the axes to those of the fluorite subcell, and the arrangement of the formal anion vacancies; there are, however, considerable variations in the cation ordering. The detailed conditions determining the formation of the phase and the nature of the cation ordering are not clear and further structural studies are needed. There is some evidence that in A_2O_3–BO_2 systems the δ phase forms in preference to the $A_2B_2O_7$ pyrochlore if the radius ratio of the cations, $r(A^{3+})/r(B^{4+})$, falls below about 1·19 (Brisse & Knop, 1967) based on the Ahrens (1952) radii for octahedral coordination. The overall metal–oxygen ratio for the two phases is similar, and both structures are fluorite-related.

The cation radius ratio in the Y_2O_3–ZrO_2 system is 1·16 based on the Ahrens radii, close to the lower limit for the pyrochlore structure. There is no satisfactory evidence for a pyrochlore in the system: the claim by Fan, Kuznetsov & Keler (1962) to have prepared $Y_2Zr_2O_7$ has never been confirmed, and has indeed been comprehensively rebutted by Smith (1966). The formation of a δ phase in this system is consistent with the hypothesis that the phase appears in systems for which the cation radius ratio is too small to stabilize the pyrochlore.

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