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γ-Alumina: a single-crystal X-ray diffraction study

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The structure of γ-alumina ($Al_{21+1/3}\square_{2+2/3}O_{32}$) crystals obtained as a product of a corrosion reaction between β-sialon and steel was refined in the space group $Fd\bar{3}m$. The oxygen sublattice is fully occupied. The refined occupancy parameters are 0.83 (3), 0.818 (13), 0.066 (14) and 0.044 (18) for Al ions in 8*a*, 16*d*, 16*c* and 48*f* positions, respectively. The Al ions are distributed over octahedral and tetrahedral sites in a 63:37 ratio, with 6% of all Al ions occupying non-spinel positions.

Comment

Aluminium oxide, Al_2O_3, is a technologically important ceramic material with a large variety of applications. Its great usefulness rests especially on its high thermal stability, extreme hardness and low electrical conductivity. Al_2O_3 is known to form several polymorphs, of which the best crystallographically defined is the α-form, *i.e.* corundum. Besides this well defined form, there exist several so-called 'transition aluminas' (γ, κ, θ), whose structures are not yet well understood because they do not yield single crystals suitable for a standard structure analysis (Lippens & de Boer, 1964; Ollivier *et al.*, 1997; Zhou & Snyder, 1991; Smrčok *et al.*, 2001; Paglia *et al.*, 2003). Inasmuch as γ-alumina is widely used in catalysis, its structure and properties have been the subject of numerous studies. A review (Sohlberg *et al.*, 2000) provides a good survey of experimental and computational approaches used to study both bulk and surface structures of γ-alumina.

Since the early study of Verwey (1935), the structure of γ-alumina has been conventionally described as a defect spinel ($Fd\bar{3}m$) with the idealized formula $Al_{21+1/3}\square_{2+2/3}O_{32}$, where $\square$ denotes a vacancy. By accepting this formula, we implicitly assume that the oxygen sublattice (32*e* positions) is fully occupied, while Al ions and vacancies are distributed over octahedral (16*d*) and tetrahedral (8*a*) positions of the ideal spinel structure.

With the advent of more powerful computers, γ-alumina has become a subject of several computational studies. Among others, Gutiérrez *et al.* (2002) and Wolverton & Haas (2000) found that vacancies are preferably located in octahedral positions. Similarly, the lowest energy configuration found in a density functional theory (DFT) study of electronic and optic properties of γ-alumina (Ahuja *et al.*, 2004) also contained vacancies on octahedral sites. Similar results, although obtained at a lower level of theory (empirical potentials), were reported by Watson & Willock (2001). Vacancies residing at octahedral sites were also found in a solid-state DFT study of γ-aluminium oxynitride (Fang *et al.*, 2001). In contrast, Pecharromán *et al.* (1999) provided evidence of vacancies located in tetrahedral positions through NMR and IR experiments. In addition, they identified a small number of pentahedrally coordinated Al atoms appearing at the external surface of alumina. Enumerating all the approaches used to study vacancy distribution in 'transition' aluminas is beyond the scope of this paper and the reader is referred to the critical review by Wolverton & Haas (2000).

A standard route to γ-alumina is the thermal decomposition of boehmite, yielding a fine powder whose diffraction pattern is, as a rule, influenced by disorder, size/strain effects, *etc.* These factors normally preclude a reliable structure solution and/or refinement (Paglia, 2004; Paglia *et al.*, 2003, 2005, and references therein). In our case, γ-alumina whiskers appeared as an unexpected product of a corrosion reaction between β-sialon and steel. Refined occupancy parameters indicate that, in addition to the ideal spinel positions, the Al ions also occupy 'non-spinel' 48*f* (tetrahedral) and 16*c* (octahedral) positions. Such a cation distribution is in accord with the results of a recent computational study (Paglia *et al.*, 2005). The Al—O distances are 6 × 1.9326 (8) Å, 6 × 2.0394 (8) Å, 4 × 1.8112 (14) Å, and 2 × 1.700 (12) Å and 2 × 1.743 (10) Å for Al atoms in special positions 16*d*, 16*c*, 8*a* and 48*f*, respectively. These values are in reasonable agreement with the reference values of 1.785 Å for Al^{IV}—O and 1.910 Å for Al^{VI}—O (*International Tables for X-ray Crystallography*, 1962, Vol. III). An attempt was also made to refine the occupancy parameter of the oxygen site but the final value was not statistically different from unity.

Of all Al ions, approximately 37% reside in tetrahedral positions. A review of the reported distributions of Al ions in tetrahedral positions (Sohlberg *et al.*, 1999) shows that the closest is 30% found in an ^{27}Al MAS NMR study (Lee *et al.*, 1997). The difference can be probably attributed to the different methods of preparation. Approximately 6% of Al ions reside in non-spinel positions.

Experimental

A mixture of β-sialon and steel was prepared by homogenization of β-sialon powder and 20 wt% of steel sawdust in a planetary ball mill. Heating to 1973 K initiated solid-state reactions leading to the formation of several iron silicides and whiskers of γ-alumina (Křesťan *et al.*, 2006).

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Crystal data

$Al_{2.67}O_4$	D_x = 3.610 Mg m^{-3}
M_r = 135.94	Mo $K\alpha$ radiation
Cubic, $Fd\bar{3}m$	μ = 1.18 mm^{-1}
a = 7.9382 (1) Å	T = 173 (2) K
V = 500.23 (1) Å^3	Needle, colourless
Z = 8	0.58 × 0.06 × 0.06 mm

Data collection

Bruker SMART CCD area-detector diffractometer	4211 measured reflections 129 independent reflections
ω scans	119 reflections with $I > 2\sigma(I)$
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	R_{int} = 0.021 θ_{max} = 45.2°
T_{min} = 0.547, T_{max} = 0.932	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0726P)^2 + 1.4303P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.027	$(\Delta/\sigma)_{max}$ = 0.012
$wR(F^2)$ = 0.100	$\Delta\rho_{max}$ = 0.42 e Å^{-3}
S = 0.98	$\Delta\rho_{min}$ = −0.58 e Å^{-3}
129 reflections	
17 parameters	

An initial refinement with Al and O in ideal spinel positions converged smoothly; however, there was residual electron density in octahedral 16*d* and 'tetrahedral' 48*f* positions. An unconstrained refinement with Al atoms present in these positions gave a unit-cell content of 21.4 Al atoms per 32 O atoms, breaking electroneutrality. A final refinement with constrained total Al occupancies of 21.3 was then carried out.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* and *SADABS* (Sheldrick, 2003); program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; software used to prepare material for publication: *PLATON* (Spek, 2003).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BC3006). Services for accessing these data are described at the back of the journal.

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