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Redetermination of β-Al_2TiO_5 obtained by melt casting

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Key indicators

Single-crystal X-ray study
T = 297 K
Mean σ() = 0.000 Å
Disorder in main residue
R factor = 0.028
wR factor = 0.028
Data-to-parameter ratio = 10.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

β-Al_2TiO_5 (dialuminium titanium pentaoxide), grown by rapid cooling of a melt of equimolar amounts of Al_2O_3 and TiO_2, adopts the same overall structure as that crystallized by more conventional methods, such as sintering. Nevertheless, re-investigation of this structure has resulted in an improved structure model with previously unknown site preferences determined. Ti prefers the slightly more regular 4c octahedral site, leaving more room for Al at the 8f octahedral site. The formula has been determined as $^{[4c]}[Al_{0.626\,(7)}Ti_{0.374\,(7)}]^{[8f]}$-$[Al_{0.687\,(3)}Ti_{0.313\,(3)}]_2O_5$.

Comment

The conventional method of fabricating ceramic workpieces is by high-temperature sintering of fine-grain powders. Even though this method is well known and has been thoroughly investigated, it is still a challenge to produce fully dense ceramics with complex shapes. Additionally, sintered ceramics have a tendency to be brittle, and so finding alternative means of obtaining bulk ceramics with a defined microstructure is important. We have therefore recently focused on the use of oxide melts, which can be moulded to a specific shape. In order to investigate such melts on a laboratory scale, we employ an image furnace (Laszlo, 1965), with a xenon lamp as radiation source. With such a furnace, high-melting oxides such as hafnia (HfO_2, m.p. 3076 K) can be easily melted within a few seconds (Yamada *et al.*, 1986).

The recent discovery of negative thermal expansion in ZrW_2O_8 over the temperature range 0.3–1050 K (Mary *et al.*, 1996) has increased interest in the unusual phenomenon of low and negative thermal expansion materials, leading us to investigate the Al_2O_3–TiO_2–ZrO_2 pseudo-ternary system (Berezhnoi & Gulko, 1955; Pena & DeAza, 1980) with respect to phase formation and glass formation. Ceramic composites containing the low thermal expanding compound β-Al_2TiO_5 are candidates for applications requiring good thermal-shock resistant materials, such as in metallurgical industries (Thomas & Stevens, 1989). Difficulties in interpreting powder diffraction patterns that showed reflections of an unknown crystalline phase prompted us to re-investigate the pseudo-binary system Al_2O_3–TiO_2 (Goldberg, 1968). Results so far include the recently determined $Al_6Ti_2O_{13}$ phase (Norberg *et al.*, 2005), as well as complex intergrowth products, such as $Al_{16}Ti_5O_{34}$ (Hoffmann *et al.*, 2005). Like β-Al_2TiO_5 (Goldberg, 1968), these materials are thermodynamically unstable and can only be prepared in a narrow temperature range of around 2073–2123 K, decomposing to their respective precursors unless rapidly cooled into a metastable state.

In the course of studying the Al_2O_3–TiO_2 system, the structure of β-Al_2TiO_5 was re-investigated, not only to confirm

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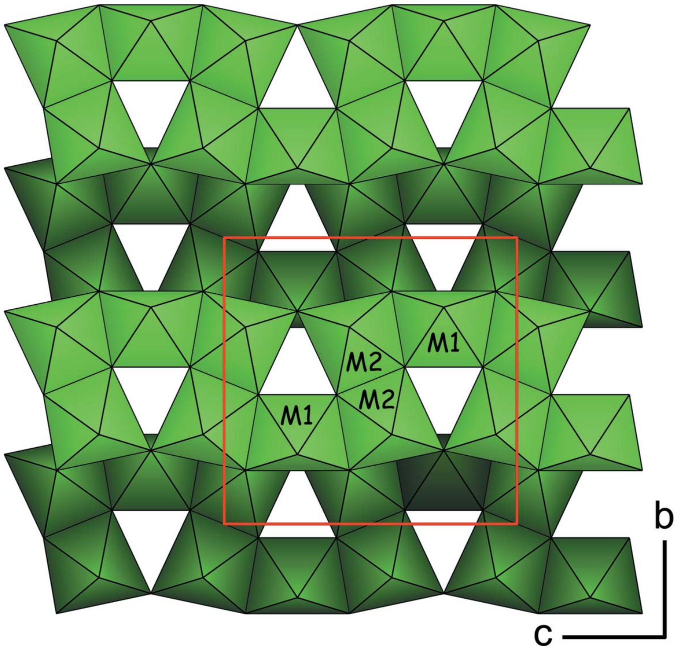

Figure 1
A polyhedral representation of the pseudobrookite-type β-Al_2TiO_5 structure, viewed along [100]. The unit cell is outlined.

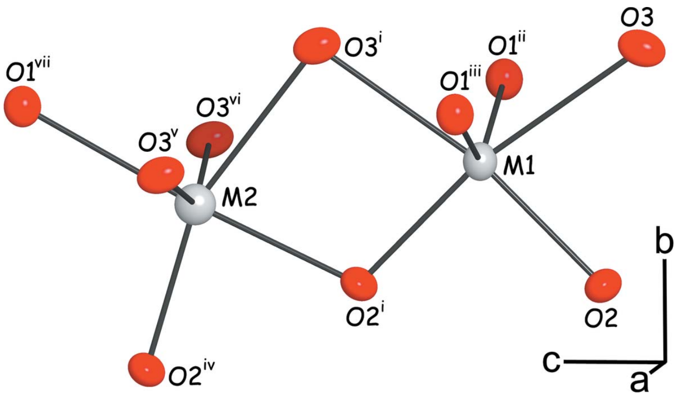

Figure 2
A plot of the β-Al_2TiO_5 structure. Displacement ellipsoids are drawn at the 80% probability level. All symmetry codes are as given in Table 1.

that it corresponds to that previously determined, but also to obtain more precise positions and Al/Ti distributions of the two metal sites. It should be noted that the β-Al_2TiO_5 crystals resulting from our experiments have a blueish tint, which likely indicates some Ti^{3+} inclusion. However, any such inclusion was below detectable levels during all X-ray diffraction measurements.

As shown in Fig. 1, β-Al_2TiO_5 (Austin & Schwartz, 1953) crystallizes in the well known pseudobrookite structure (Pauling, 1930). An earlier structure determination, with an R value of approximately 0.06 (Morosin & Lynch, 1972), and a high-resolution electron micrsocopy study (Epicier *et al.*, 1991), both indicated complete Al/Ti disorder at the metal sites. Our re-determination reveals preferential occupation of Al and Ti in their octahedral sites. The mean M—O bond lengths of both sites are quite similar [1.948 (2) Å at the 4c site and 1.943 (2) Å at the 8f site], but the larger Ti^{4+} ion prefers the slightly more regular 4c octahedral site to some extent, resulting in the formula $^{[4c]}[Al_{0.626\,(7)}Ti_{0.374\,(7)}]^{[8f]}$-$[Al_{0.687\,(3)}Ti_{0.313\,(3)}]_2O_5$. The low standard uncertainties make the determined site preference reliable and the final R value of 0.028 is significantly lower that that of the previously determined structure. We conclude that β-Al_2TiO_5 grown by quick cooling of a melt containing equimolar quantities of Al_2O_3 and TiO_2 has the same structure as that prepared by conventional sintering methods. Table 1 shows bond lengths compared with those of Morosin & Lynch (1972) and Fig. 2 shows a plot of the displacement ellipsoids.

This improved determination of β-Al_2TiO_5 will be useful for theoretical considerations where a good structural model is needed. For example, in order to understand new complex Al_2O_3–TiO_2 phases with an Al:Ti ratio greater than 1, β-Al_2TiO_5 has been found to be a basic building block in their structures (Norberg *et al.*, 2005; Hoffmann *et al.*, 2005).

Experimental

An equimolar mixture of α-Al_2O_3 (Sumitomo Chemicals, type AKP-30, high purity) and TiO_2 (High Purity Chemicals Köjundo Kagaku Kenkyü, 99.99%) was melted in an arc-imaging furnace. A 15 min soaking period followed immediately below the solidification point, which was indicated by a deformation of the sample surface as well as by a change in reflectivity. It should be noted that the solidification point temperature was not determined directly, but it is known from the literature (Lang *et al.*, 1952, and references therein) that equimolar melts of alumina and titania solidify between 2073 and 2133 K.

Crystal data

Al_2TiO_5
M_r = 181.84
Orthorhombic, $Cmcm$
a = 3.605 (2) Å
b = 9.445 (4) Å
c = 9.653 (4) Å
V = 328.7 (3) Å^3
Z = 4
D_x = 3.675 Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 8632 reflections
θ = 3.0–30.5°
μ = 3.02 mm^{-1}
T = 297 (1) K
Block, blue
0.09 × 0.07 × 0.06 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: Gaussian (*RAPID-AUTO*; Rigaku, 2003)
T_{min} = 0.827, T_{max} = 0.880
1774 measured reflections

304 independent reflections
288 reflections with $F > 2\sigma(F)$
R_{int} = 0.025
θ_{max} = 30.5°
$h = -5 \rightarrow 5$
$k = -13 \rightarrow 13$
$l = -13 \rightarrow 13$

Refinement

Refinement on F
$R[F^2 > 2\sigma(F^2)]$ = 0.028
$wR(F^2)$ = 0.028
S = 1.09
288 reflections

28 parameters
$w = 1/[\sigma^2(F) + 0.015(F)]$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.91 e Å^{-3}
$\Delta\rho_{min}$ = −0.73 e Å^{-3}

Table 1
Comparison of M—O bond lengths (Å) from this work with those determined by Morosin & Lynch (1972).

Bond	This work	Morosin & Lynch (1972)
$M1—O2^{i}$	1.826 (2) × 2	1.823 (4) × 2
$M1—O1^{ii, iii}$	1.9253 (14) × 2	1.920 (2) × 2
$M1—O3^{i}$	2.093 (2) × 2	2.087 (4) × 2
$M2—O2^{iv}$	1.816 (2)	1.814 (4)
$M2—O3^{v, vi}$	1.8708 (11) × 2	1.864 (1) × 2
$M2—O2^{i}$	1.907 (2)	1.900 (4)
$M2—O1^{vii}$	2.0799 (17)	2.076 (3)
$M2—O3^{i}$	2.115 (2)	2.114 (4)

Symmetry codes: (i) $-x, y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (iv) $-x, -y, \frac{1}{2} + z$; (v) $\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (vi) $-\frac{1}{2} - x, \frac{1}{2} - y, \frac{1}{2} + z$; (vii) $-x, 1 - y, \frac{1}{2} + z$.

Refining Al and Ti without the constraint of them being situated at the same x, y, and z coordinates was possible but did not improve the overall refined structure. The calculated Al1—Ti1 separation for such a refinement converged to 0.06 (5) Å, while the calculated Al2—Ti2 separation converged to 0.07 (4) Å.

Data collection: *RAPID-AUTO* (Rigaku, 2003); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*, and *DIFDAT*, *SORTRF* and *ADDREF* in *Xtal3.7* (Hall *et al.*, 2000); method used to solve structure: atomic positions from Morosin & Lynch (1972); program(s) used to refine structure: *CRYLSQ* in *Xtal3.7*; molecular graphics: *DIAMOND* (Brandenburg, 2001), and *FOURR*, *SLANT* and *CONTRS* in *Xtal3.7*; software used to prepare material for publication: *BONDLA*, *ATABLE* and *CIFIO* in *Xtal3.7*.

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