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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.

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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 4*c* octahedral site, leaving more room for Al at the 8*f* 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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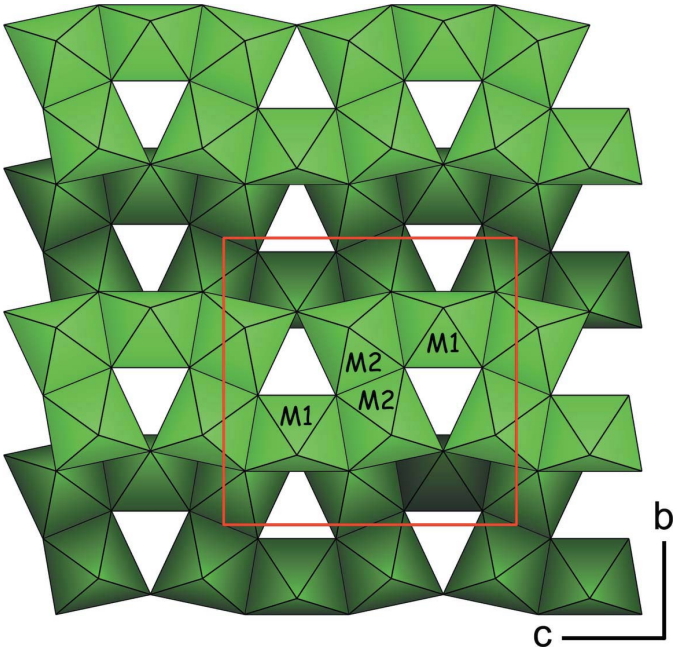

Figure 1
A polyhedral representation of the pseudobrookite-type β-Al_2TiO_5 structure, viewed along [100]. The unit cell is outlined.

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 4*c* site and 1.943 (2) Å at the 8*f* site], but the larger Ti^{4+} ion prefers the slightly more regular 4*c* 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,

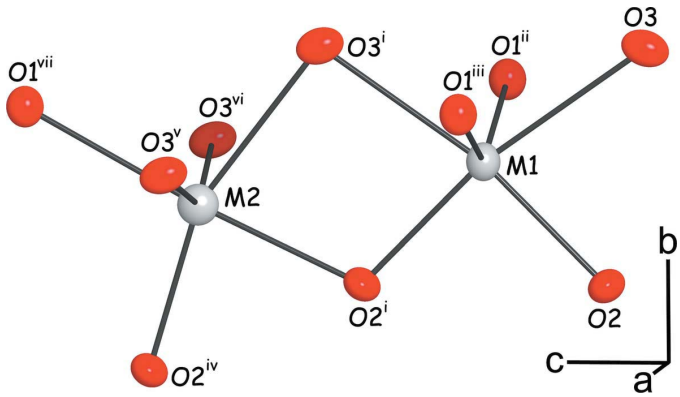

Figure 2
A plot of the β-Al_2TiO_5 structure. Displacement ellipsoids are drawn at the 80% probability level. All symmetry codes are as given in Table 1.

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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