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Sc_2TiO_5, an entropy-stabilized pseudobrookite-type compound

Uwe Kolitsch* and Ekkehart Tillmanns

Universität Wien, Institut für Mineralogie und Kristallographie, Geozentrum, Althanstr. 14, A-1090 Wien, Austria

Correspondence e-mail:
uwe.kolitsch@univie.ac.at

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Sc–O) = 0.001 Å
Disorder in main residue
R factor = 0.016
wR factor = 0.048
Data-to-parameter ratio = 15.5

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

Discandium(III) titanate(IV), Sc_2TiO_5, prepared by the flux method, has a pseudobrookite-type structure. The Sc and Ti atoms are partially disordered on the two octahedrally coordinated metal (M) sites (Wyckoff designations 8f and 4c in space group $Cmcm$). The most probable cation distribution suggests the approximate structural formula $^{[8f]}(Sc_{0.6},Ti_{0.4})_2{}^{[4c]}(Sc_{0.8}Ti_{0.2})O_5$, in agreement with earlier observations of a preference of Ti for the more distorted 8f site in isotypic $A^{III}{}_2B^{IV}O_5$ compounds. The average M—O bond lengths for the 8f and 4c sites are 2.059 and 2.095 Å, respectively. The strongly distorted octahedra share edges to form trioctahedral units, which are linked into infinite double chains along c. Further sharing of octahedral edges results in a three-dimensional framework. All atoms are on special positions. An Al-bearing variety of Sc_2TiO_5 has Al preferentially incorporated on the 4c site.

Comment

Knowledge of the quaternary, ternary and even some binary phase equilibria in the system Sc_2O_3–Al_2O_3–TiO_2–SiO_2 is poor or lacking, although the physicochemical properties of the

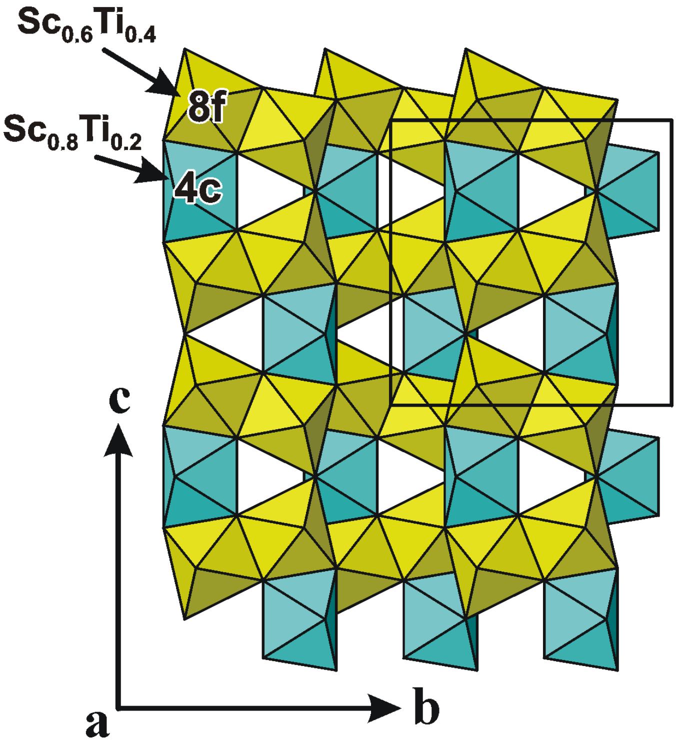

Figure 1
View along the a axis of the crystal structure of pseudobrookite-type Sc_2TiO_5. Note the trioctahedral units extending approximately parallel to [001]. The suggested occupancies of the two metal sites 8f and 4c are indicated (see text).

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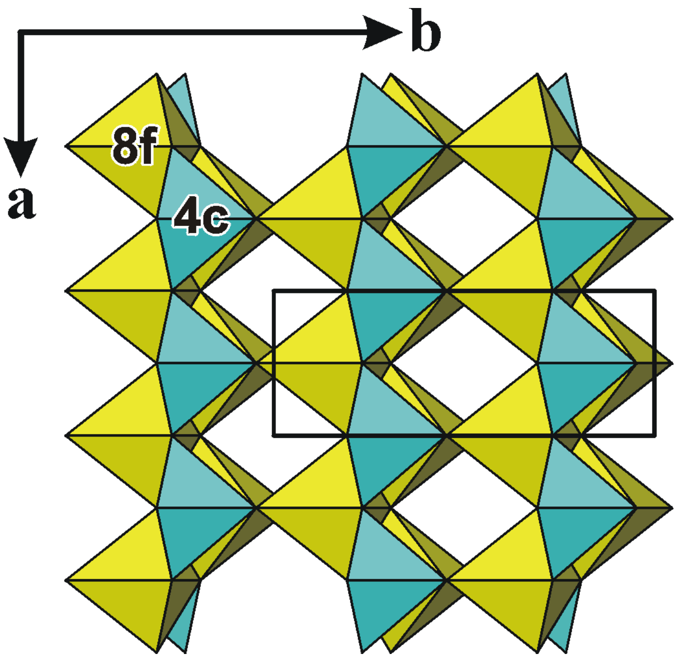

Figure 2
View along the *c* axis of the crystal structure of Sc_2TiO_5.

known compounds in this system suggest various applications, mainly in the field of high-performance ceramics. Only the component oxides, mullite and Al_2TiO_5, are well characterized, and data on Sc substitution for Al or Ti are either lacking or contradictory.

As part of a detailed study of the crystal chemistry and phase equilibria of compounds in this system, Sc_2TiO_5, a compound suggested by Ito (1971) to have a pseudobrookite [Fe_2TiO_5]-type structure (*cf.* Pauling, 1930; Navrotsky, 1975; Tiedemann & Müller-Buschbaum, 1982; Teller *et al.*, 1990*a*,*b*; Guo *et al.*, 1999), has been synthesized by the flux method, and its previously unknown crystal structure has been characterized.

The structure has been solved and refined in space group *Cmcm*. The results confirm the pseudobrookite structure type of Sc_2TiO_5. Refined single-crystal unit-cell parameters are close to values given by Ito (1971) for synthetic Sc_2TiO_5 crystals containing 0.17 wt% Fe_2O_3 [a = 3.8509 (5), b = 10.127 (1), c = 10.274 (1) Å and V = 400.66 Å^3], and values given by Pokrovskii *et al.* (1970) (a = 3.843, b = 10.105, c = 10.272 Å and V = 398.90 Å^3).

Sc_2TiO_5 contains two octahedrally coordinated metal (M) sites, with Wyckoff designations 8*f* and 4*c* (Fig. 3). The strongly distorted octahedra share edges to form trioctahedral units, which are further linked into infinite double chains along *c* (Figs. 1 and 2). Further sharing of octahedral edges results in a three-dimensional framework.

The average M—O bond lengths for the 8*f* (Sc1,Ti1) and 4*c* (Sc2,Ti2) sites are 2.059 and 2.095 Å, respectively. A detailed bond-valence analysis, using parameters from Brown (1996) and Brese & O'Keeffe (1991), clearly suggests that the cation distribution is more or less random on the 8*f* site, but that Sc has a distinct preference for the 4*c* site. The most probable cation distribution suggests the approximate structural formula $^{[8f]}(Sc_{0.6},Ti_{0.4})_2{}^{[4c]}(Sc_{0.8}Ti_{0.2})O_5$. It is noteworthy that a model with freely refined occupancies of both 8*f* and 4*c* sites gave the formula $^{[8f]}(Sc_{0.57},Ti_{0.43})_2{}^{[4c]}(Sc_{0.89}Ti_{0.11})O_5$, *i.e.* reasonably close to the suggested formula, albeit not completely charge-balanced (9.97 positive charges and 10 negative charges).

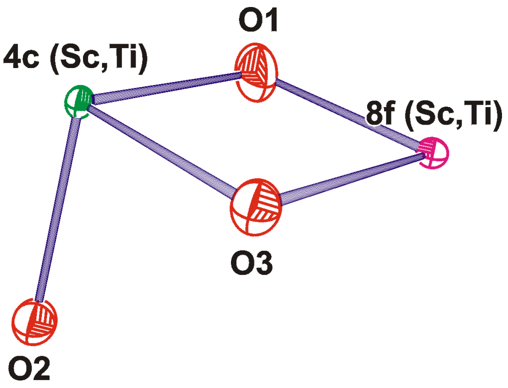

Figure 3
Displacement ellipsoids (probability 75%) of the atoms in the asymmetric unit of Sc_2TiO_5. Note that no effects of the substitutional disorder are recognizable.

These conclusions also agree with several facts: (i) the commonly observed average Sc—O distance, 2.105 Å, is slightly larger than the corresponding Ti^{IV}—O distance, 1.97 Å (Baur, 1981); (ii) in both $A^{III}{}_2B^{IV}O_5$ and $A^{II}B^{IV}{}_2O_5$ pseudobrookite compounds, Ti seemingly prefers the (somewhat more distorted) 8*f* site (Navrotsky, 1975); (iii) similarly random cation distributions (albeit not identical and also depending on temperature) were observed for isotypic Al_2TiO_5 (Morosin & Lynch, 1972; Epicier *et al.*, 1991) and Ga_2TiO_5 (Müller-Buschbaum & Freund, 1974); (iv) preparations of $A^{III}{}_2B^{IV}O_5$ pseudobrookite-type compounds at high temperatures favor cation disordering (Navrotsky, 1975).

The substitutional disorder results in a substantial positive entropy of formation, and thus makes Sc_2TiO_5 a typical example of an entropy-stabilized pseudobrookite-type compound.

Al_2TiO_5, aluminium(III) titanate(IV), is a very important ceramic due to its unusual mechanical properties. However, it is thermodynamically unstable below approximately 1473–1573 K and exothermically decomposes into the component oxides, if it is not quenched into a metastable state (*e.g.* Goldberg, 1968; Bayer, 1971; Kameyama & Yamaguchi, 1976; Kato *et al.*, 1980; Hauck, 1981; Hennicke & Lingenberg, 1985, 1986; Thomas & Stevens, 1989*a*,*b*,*c*; Buscaglia, 1998; Segadaes *et al.*, 1998). A very similar behavior is shown by other $A^{III}{}_2B^{IV}O_5$ compounds, such as Ga_2TiO_5 (decomposition temperature *ca* 1253 K; Bayer, 1971). However, a chemical–structural stabilization of Al_2TiO_5 can be achieved by additions of Mg^{2+}, Fe^{3+} and other cations (*e.g.* Goldberg, 1968; Kato *et al.*, 1984; Ishitsuka *et al.*, 1987; Thomas & Stevens, 1989*b*; Buscaglia *et al.*, 1997). Substituting Sc for Al in Al_2TiO_5 may result in a similar chemical–structural stabilization, but has never been investigated so far.

In order to study the influence of Al incorporation, Al-bearing Sc_2TiO_5 crystals have been grown from a $PbF_2-PbO-MoO_3$ flux containing additional Al_2O_3 and SiO_2. As expected, the unit-cell parameters, $a = 3.833$ (1), $b = 10.086$ (2), $c = 10.248$ (2) Å and $V = 396.18$ (15) Å^3, are smaller than those of pure Sc_2TiO_5. Structure refinement and bond-valence analysis clearly suggest that the incorporated Al prefers the 4*c* site: (Sc,Ti)$_2$(Sc,Ti,Al)O$_5$. This preference is in accordance with the conclusions presented above. A solid-solution member even richer in Al was grown from an $LiF-MoO_3$ flux; it has the unit-cell parameters $a = 3.782$ (1), $b = 9.889$ (2), $c = 10.091$ (2) Å and $V = 377.41$ (15) Å^3, and the refinement shows that the 4*c* site is predominantly occupied by Al. More detailed investigations of the solid solubility ranges along the series $Sc_2TiO_5-Al_2TiO_5$ are underway. For the comparable system $Sc_2TiO_5-Fe_2TiO_5$, the existence of a complete solid solution has been suggested on the basis of X-ray powder diffraction data for samples prepared by heating precursor gels at 1423 K (Ito, 1971). In $FeAlTiO_5$, prepared at 1973 K, complete disorder between Fe, Al and Ti was assumed by Tiedemann & Müller-Buschbaum (1982). For Ga_2TiO_5 prepared at 1803 K and cooled at 20 K h^{-1}, the formula $^{[8f]}(Ga_{0.75},Ti_{0.25})_2{}^{[4c]}(Ga_{0.5}Ti_{0.5})O_5$ was reported (Müller-Buschbaum & Freund, 1974), which, however, would contradict the observed trend that Ti prefers the 8*f* site. Ga_2TiO_5–Al_2TiO_5 solid solutions have not been studied yet.

Experimental

Sc_2TiO_5 has been synthesized in air from a $PbF_2-PbO-MoO_3$ flux containing dissolved Sc_2O_3 and TiO_2 (experimental parameters: 0.88 g PbF_2, 0.88 g PbO, 0.70 g MoO_3, 0.1583 g Sc_2O_3, 0.0917 g TiO_2; Pt crucible covered with lid, T_{max} = 1423 K, holding time 12 h, cooling rate 1.5 K min^{-1}, T_{min} = 1123 K, slow cooling to room temperature after switching off furnace). The small colorless tabular {010} crystals of Sc_2TiO_5 were accompanied by $PbTiO_3$ (dark brown cubic grains), $PbMoO_4$ (synthetic wulfenite; pale yellow tabular crystals and very small flakes) and Pb_2MoO_5 (pale brown, idiomorphic glassy prisms). Chemical analyses of the title compound with SEM–EDS showed the presence of Sc and Ti as the only metals.

Crystal data

Sc_2TiO_5
$M_r = 217.82$
Orthorhombic, *Cmcm*
$a = 3.851$ (1) Å
$b = 10.131$ (2) Å
$c = 10.287$ (2) Å
$V = 401.34$ (15) Å^3
$Z = 4$
$D_x = 3.605$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 454 reflections
$\theta = 2.0$–$32.6°$
$\mu = 5.13$ mm^{-1}
$T = 293$ (2) K
Plate, colorless
0.10 × 0.10 × 0.03 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{min} = 0.628$, $T_{max} = 0.883$
728 measured reflections

435 independent reflections
416 reflections with $I > 2\sigma(I)$
$R_{int} = 0.008$
$\theta_{max} = 32.5°$
$h = -5 \rightarrow 5$
$k = -15 \rightarrow 15$
$l = -15 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.016$
$wR(F^2) = 0.048$
$S = 1.20$
435 reflections
28 parameters

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.83P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.85$ e Å^{-3}
$\Delta\rho_{min} = -0.85$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0143 (12)

Table 1
Selected geometric parameters (Å).

Ti1—O1^{i}	1.9215 (15)	Ti1—O3	2.2164 (14)
Ti1—O3^{ii}	2.0117 (6)	Sc2—O1^{iii}	2.0333 (14)
Ti1—O1	2.0269 (16)	Sc2—O2	2.0711 (9)
Ti1—O2^{ii}	2.1655 (10)	Sc2—O3	2.1807 (14)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $-\frac{1}{2}-x, \frac{1}{2}-y, 1-z$; (iii) $x, y, \frac{3}{2}-z$.

Occupancies of the two metal sites were fixed in the final refinement (see text for details).

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999) and *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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