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Low-temperature $Na_4Ti_5O_{12}$ from X-ray and neutron powder diffraction data

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The crystal structure of the low-temperature $Na_4Ti_5O_{12}$ (tetrasodium pentatitanium dodecaoxide) phase has been solved and refined from X-ray and neutron powder diffraction data at 295 K. The structure is trigonal, space group $P3$, with $Z = 1$, although it is pseudo-centrosymmetric. The O and Na atoms form a distorted close-packed structure, where Ti atoms occupy octahedral sites.

Comment

Recently, it was reported (Nalbandyan, 2000) that the low-temperature sodium titanate earlier described as $Na_2Ti_2O_5$ (Batygin, 1967), in fact corresponds to the formula $Na_4Ti_5O_{12}$. It was found that the compound is stable below *ca* 973 K. Above this temperature, the compound decomposes to $Na_8Ti_5O_{14}$ and $Na_2Ti_3O_7$, and does not undergo the phase transition to any high-temperature form, because it was shown that previously described $Na_4Ti_5O_{12}$ (Werthmann & Hoppe, 1984) does not exist in the Na_2O–TiO_2 system, and this structure type is actually stabilized by doping (Nalbandyan *et al.*, 1998). The X-ray powder pattern of low-temperature $Na_4Ti_5O_{12}$ was indexed and the parameters of hexagonal unit cell were found to be a = 5.319 Å and c = 9.556 Å. It was supposed that the structure is *ABAC* or *ABAB* close-packed with oxygen anions, and sodium and titanium occupy octahedral sites. However, neither that guess was checked nor the structure was solved *ab initio*. Therefore, we undertook the study of $Na_4Ti_5O_{12}$ structure, and the results are reported here. The structure is based on the distorted close-packed layers consisting of large ions (oxygen and sodium) and the titanium ions occupy octahedral voids.

Experimental

The title compound was prepared by solid-state method from TiO_2 (anatase form) and Na_2CO_3 at *ca* 923 K (Nalbandyan, 2000). A colourless crystalline powder resulted.

Crystal data

$Na_4Ti_5O_{12}$
M_r = 522.30
Trigonal, $P3$
a = 5.31997 (14) Å
c = 9.5567 (3) Å
V = 234.24 (1) Å^3
Z = 1
D_x = 3.710 Mg m^{-3}
Cu $K\alpha_1$ radiation
λ = 1.54056 Å
Cu $K\alpha_2$ radiation
λ = 1.54439 Å
Neutron radiation
T = 295 K
White
Specimen shape: flat sheet
Specimen shape: cylinder
18 × 20 × 0.5 mm
20 × 5 × 5 mm
Rigaku D/MAX–B diffractometer
Neutron powder diffractometer

Data collection

Θ-2Θ scans
Time-of-flight scans
IBR-2, Joint Institute for Nuclear Research, Dubna, Russia
Specimen mounting: drifted powder on off-cut glass
Specimen mounted in reflection mode
Specimen mounting: loaded powder to vanadium can
Specimen mounted in reflection mode
$2\theta_{\min}$ = 18.0, $2\theta_{\max}$ = 120.0°
Increment in 2θ = 0.02°

Refinement

R = missing
R_p = 6.85
R_{wp} = 9.44
R_{exp} = 4.07
Profile function: pseudo–Voigt
R_p = 6.27
R_{wp} = 5.07
R_{exp} = 2.13
Profile function: Gaussian
60 parameters
Weighting scheme based on measured s.u.'s
$(\Delta/\sigma)_{\max} < 0.01$
Preferred orientation correction: $G2 + (1 - G2)\exp(G1{*}a^{2*})$
Scattering factors from *FULLPROF* (Version of February 2000; Rodriguez-Carvajal, 1990)

Table 1
Selected geometric parameters (Å).

Ti1—O1^{i}	1.82 (5)	TI3—O4^{iii}	2.27 (8)
Ti1—O1^{ii}	1.82 (5)	TI3—O4	2.27 (8)
Ti1—O1	1.82 (5)	TI3—O4^{iv}	2.27 (8)
Ti1—O2^{i}	1.90 (7)	TI4—O3^{v}	1.78 (6)
Ti1—O2	1.90 (7)	TI4—O3^{vi}	1.78 (6)
Ti1—O2^{ii}	1.90 (7)	TI4—O3^{vii}	1.78 (6)
Ti2—O4	1.86 (5)	TI4—O1	2.18 (8)
Ti2—O4^{i}	1.86 (5)	TI4—O1^{viii}	2.18 (8)
Ti2—O4^{ii}	1.86 (5)	TI4—O1^{ix}	2.18 (8)
Ti2—O2^{i}	2.20 (8)	TI5—O4	1.97 (7)
Ti2—O2	2.20 (8)	TI5—O4^{iv}	1.97 (7)
Ti2—O2^{ii}	2.20 (8)	TI5—O4^{iii}	1.97 (7)
TI3—O2	2.02 (5)	TI5—O3^{x}	2.01 (5)
TI3—O2^{iii}	2.02 (5)	TI5—O3^{xi}	2.01 (5)
TI3—O2^{iv}	2.02 (5)	TI5—O3^{xii}	2.01 (5)

Symmetry codes: (i) $-x + y, 1 - x, z$; (ii) $1 - y, 1 + x - y, z$; (iii) $-1 - x + y, -x, z$; (iv) $-y, 1 + x - y, z$; (v) $-y, x - y - 1, z$; (vi) $1 - x + y, 1 - x, z$; (vii) $x - 1, y, z$; (viii) $-y, x - y, z$; (ix) $-x + y, -x, z$; (x) $-y, x - y, z - 1$; (xi) $x - 1, y, z - 1$; (xii) $-x + y, 1 - x, z - 1$.

The list of peak positions was obtained from the X-ray raw data using the *XFIT* program (Cheary & Coelho, 1997) and used for indexing by *CRYSFIRE* suite (Shirley, 1999). A hexagonal cell [a = 5.31997 (14) Å and c = 9.5567 (3) Å] having FOM = 103 was found, in agreement with a previous report (Nalbandyan, 2000). After that, the assumptions on close-packing *ABAC* or *ABAB* structure were checked. Since no systematical absence of reflections was observed, the space group $P3$ (No. 143) having the lowest possible symmetry within the system was chosen. In both cases, all the O atoms were placed at the special positions of close-packed structure, and all the cations were distributed over 12 octahedral voids uniformly. The occupancies of cation positions were considered as variables. However, no agreement of calculated and experimental profiles was obtained in both cases, and the refinement process was unstable, giving large negative occupancies of some cation sites. Therefore, *ab initio* structure determination has been performed. The structure-factor amplitudes were extracted by *FULLPROF* (Rodriguez-Carvajal, 1990) in profile matching mode with pseudo-Voight peak shape function (NPROF = 5). To prevent using the data from overlapping reflections, the reflection list was filtered by *OVERLAP* program (LeBail, 1999), and finally 68 F_o values were obtained. Patterson functions interpretation and Fourier syntheses were performed by *SHELXS*97 (Sheldrick, 1997). All the O atoms and cation sites were revealed and structural model obtained was used for Rietveld refinement with *FULLPROF* (pseudo-Voigt peak-shape function). The distribution of sodium and titanium over cation sites was refined using constraints occ(Na) + occ(Ti) = 1. The reasonable results were obtained: sodium allocated at distorted cubooctahedral voids, whereas titanium occupies octahedral ones.

The time-of-flight neutron data were collected using DN-2 diffractometer at IBR-2 source (Joint Institute for Nuclear Research, Dubna, Russia). The data were refined using MRIA program (Zlokazov *et al.*, 1992). Since the resolution in the neutron data is rather low and peak overlapping is strong, the simultaneous refinement of all the variables resulted in unstable and mostly divergent process. Therefore, the positional and thermal parameters obtained by X-ray data refinement were fixed, and only the distribution of cations over nine non-equivalent sites was checked by neutron diffraction data refinement. Since sodium and titanium have opposite sign of the amplitude of coherent scattering of neutrons, the atoms can be distinguished easily by neutron diffraction. The refinement converged to the same results: sodium occupies large distorted cubooctahedral voids, forming together with O atoms distorted close-packed structure, whereas titanium occupies octahedral sites (Gaussian peak-shape function, $R_p = 6.27$, $R_{\rm wp} = 5.07$, $\chi^2 = 5.67$).

The final coordinates are close to those obeying the $P\overline{3}$ space group, where there is a pseudocentre of symmetry at the Ti4 atom. A refinement of the structure based on the X-ray data using $P\overline{3}$ space group resulted in no improvement ($R_p = 9.26$, $R_{\rm wp} = 11.3$ and $\chi^2 = 7.62$).

Data collection: *D*/*MAX–B* (Rigaku, 1992); cell refinement: *FULLPROF* (Rodriguez-Carvajal, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); software used to prepare material for publication: *WINPLOTR* (Roisnel & Rodruguez-Carvajal, 1999).

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