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Abstract

Full Text

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CRYSTAL STRUCTURE OF SYNTHETIC SODIUM TITANOSILICATE $Na_2(TiO)[SiO_4]$

Analysis of the products of hydrothermal crystallization in the system $Na_2O-ZnO-SiO_2-H_2O$ showed that increasing the concentration of NaOH in the solution to 25-30% leads to appreciable dissolution of Ti-containing inserts and, ultimately, to the formation of titanium-containing phases. At an alkali concentration of about 25% and a temperature of 350° (autoclave filling coefficient 85%), the formation of a mixed (Zn, Ti)-silicate of composition $Na_2O \cdot 2ZnO \cdot TiO_2 \cdot SiO_2$ (phase T) is observed. With a further increase in the NaOH concentration to 30% and at temperatures up to 550° (filling coefficient 75%), in the upper zone of the autoclave—the crystallization zone—a "pure" titanosilicate phase E containing no ZnO is formed, of composition $Na_2O \cdot TiO_2 \cdot SiO_2$.

Inhomogeneous crystals of phase E, often with inclusions of the nutrient material, are characterized by a tabular habit with principal forms {001}, {100}, and {201} (Figs. 1 and 2). Transparent samples without impurities are colorless, while crystals of phase E activated with manganese are colored pale yellow and luminesce in the yellow part of the spectrum ($\lambda = 560\,\mathrm{m}\mu$) under UV excitation. X-ray irradiation produces a bright blue glow in the samples.

Fig. 1. Crystals of phase E, 15×

Fig. 2. Principal crystallographic forms of phase E

Optically, crystals of phase E are uniaxial, negative:
$n_g = 1.745 \pm 0.003$; $n_p = 1.722 \pm 0.003$.

Other properties: cleavage perfect along (001), hardness 4.0, density (X-ray) 3.16 g/cm^3. Interplanar spacings for phase E are given in Table 1.

For the structural study of this Na-titanosilicate, single-crystal samples without internal stresses were selected in the form of plates $\sim 0.3 \times 0.3\,\text{mm}^2$ with a thickness of 0.1 mm. At the first stage, the ···

Laue symmetry $\frac{4}{m}mm$. The parameters of the tetragonal cell, measured initially from rotation radiographs and subsequently refined from Weissenberg photographs, are: $a = 6.47$ Å, $c = 5.08$ Å. The cell contains two formula units of the composition indicated above. We used only zero-layer nets: $hk0$ and $0kl$ (MoK_α radiation). Analysis of the systematic extinctions leads unambiguously to the Fedorov group

$$D_{4h}^7 = P\frac{4}{n}mm.$$

In the corresponding unit cell the general positions are sixteenfold, and therefore all atoms occupy special positions.

Table 1

Interplanar spacings for crystals of phase E
Radiation Cu K, unfiltered, camera diameter 57.3 mm

d/n	I	d/n	I	d/n	I
5.08	9	2.51	2	1.63	8
3.99	3	2.37	7	1.501	4
3.25	5	2.28	3	1.464	4
2.73	10	1.70	6	1.407	6
2.54	4	1.64	4	1.393	5

Table 2

Coordinates of the basis atoms in the structure
$Na_2(TiO)[SiO_4]$
(origin of coordinates at the special point of an inversion axis)

Atoms	x/a	y/b	z/c
Ti	0.500	0	0.932
Si	0	0	0
Na	0.250	0.250	0.500
O_1	0.206	0	0.826
O_2	0.500	0	0.742

Fig. 3. Plot of the dependence $R_{0kl} = f(z_{\mathrm{Ti}})$

Figure 3: Fig. 3. Plot of the dependence $R_{0kl} = f(z_{\mathrm{Ti}})$

positions. There are three kinds of twofold positions in this group: on rotation axes ($2c$) with one parameter and at special points of inversion axes $\bar{4}$ ($2a, 2b$). Proceeding from the symmetry of the usual environment of Si and Ti, it is natural to place the silicon atoms in positions $2a$ (or $2b$), and the titanium atoms in $2c$; then the four Na atoms can be located only at the centers of symmetry $\frac{1}{4}\frac{1}{4}0(4d)$ or $\frac{1}{4}\frac{1}{4}\frac{1}{2}(4e)$. For 10 O atoms there remain the positions $(8i)$–$0xz$ and–$2c$ $(0\frac{1}{2}z)$.

The proposed model was confirmed by construction of electron-density maps. Refinement of the initial coordinates and introduction of a correction for thermal motion ($B = 0.3$ Å^2) made it possible to reduce the R-factor in the $hk0$ zone from 24.1 to 13.4% at

$$\left(\frac{\sin\theta}{\lambda}\right)_{\max} = 1.33\ \text{Å}^{-1};$$

the z-coordinates of the oxygen atoms were obtained from the Patterson projection $p(xz)$ and refined by $\sigma(xz)$. In view of the overlap of the Ti, Si, and two O atoms in the xz projection, to localize the one-parameter Ti atom a plot of the dependence $R_{0kl} = f(z_{\mathrm{Ti}})$ was constructed with the coordinates of the remaining atoms unchanged (Fig. 3).

Fig. 3. Plot of the dependence $R_{0kl} = f(z_{\mathrm{Ti}})$

The best agreement of the calculated structural amplitudes with the experimental ones was recorded at $z_{\mathrm{Ti}} = 0.568$. An analogous value ($z_{\mathrm{Ti}} = 0.566$) was obtained independently from the difference Fourier series with coefficients $F_{\mathrm{exp}} - F_{\mathrm{calc}}(\mathrm{Si} + 2\mathrm{Na} + \Sigma\mathrm{O})$.

Introducing into F_{calc} an isotropic temperature correction $B = 0.83$ Å^2 reduced the value of R_{0kl} from 16.5 to 9.7%

$$\left(\text{at }\max\frac{\sin\theta}{\lambda} = 0.92\ \text{Å}^{-1}\right)$$

over all 50 independent nonzero reflections. The coordinates of the basis atoms for these values of R are given in Table 2.

The structural motif is very clearly delineated in the xy projection (Fig. 4

Somewhat distorted Na octahedra create a pattern of squares with a side half the length of the unit-cell edge. At the centers of these small squares there alternate inversion axes $\bar{4}$ (through the origin of the cell) and fourfold rotation axes (through the midpoints of the sides). At the special points of the former

Fig. 4. Projection of the structure of phase E onto the xy plane (in polyhedra)

Figure 4: Fig. 4. Projection of the structure of phase E onto the xy plane (in polyhedra)

are located Si tetrahedra; on the fourfold rotation axes are Ti atoms with a quite unexpected environment: five oxygen atoms in the form of a tetragonal pyramid. The distances from the Ti located at the center of this pyramid to the O atoms at the base do not exceed the already known values (1.98 Å). But the fifth Ti–O distance, to the O atom at the apex of the pyramid, is sharply shortened (1.67 Å). If the pyramid is completed to the usual Ti octahedron, then the sixth Ti–O distance, equal to $5.08 - 1.67 = 3.41$ Å, is much greater than the standard 1.90-2.10 Å. The sharp displacement of the Ti atom toward one of the vertices of the octahedron and the shortening of the Ti–O distance make it possible to suppose that in the structure of Na_2TiSiO_5 we are dealing with the complex titanyl ion $[Ti = O]^{2+}$, well known to chemists, and therefore the formula Na_2TiSiO_5 may be represented as $Na_2(TiO)[SiO_4]$. There is no doubt that in aqueous solutions the multicharged Ti ion is strongly hydrolyzed (2,3) and that the degree of hydrolysis increases upon heating and with increasing pH of the medium; therefore it seems very probable that, at $T = 550^\circ$ and NaOH concentrations of about 30%, the titanyl ion enters the solid phase as an independent "building unit" (Baustein), just as occurs for osmium in the structure of $K_2OsO_2Cl_4$ (4) (two Os–O distances are 1.75 Å, with the sum of the ionic radii equal to 1.98 Å). Turning to interatomic distances in previously determined structures of titanates and titanoniobates, we can also note substantially differing distances within a "single" Ti octahedron: the shortest Nb, Ti–O distance is 1.73 Å, while the greatest is 2.40 Å (5,6). In the structure of sphene $CaTiSiO_5$ (7) the Ti–O distances vary from 1.85 to 2.04 Å. The structures of other salts of the titanyl group, $TiOF_2$ (8) or $TiO \cdot SO_4 \cdot H_2O$ (9), still require refinement (in the latter, for example, $R_{hol} = 29.5\%$), but in them too there is an analogous shortening of one or two Ti–O distances to 1.80-1.85 Å.

Fig. 4. Projection of the structure of phase *E* onto the *xy* plane (in polyhedra)

In a structure with such an unusual Ti polyhedron, one must approach the valence balance with considerable caution. The formal sum of the valence strengths converging on the O atom from the titanyl group $[Ti = O]^{2+}$ is 17/15, whereas on the O atoms at the base of the pyramid it is $2^2/15$. If the bond in the titanyl group is regarded as double (10), then the sums of the valence strengths on the oxygen atoms of both types become equal to 2. The structure of phase *E* explains the cleavage of the crystal along (001).

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Note: Figure translations are in progress. See original paper for figures.