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TRANSLATION

CRYSTALLINE STRUCTURE OF THE NEW
CLOSE-GRAINED MODIFICATION OF SILICA, SiO_2

By

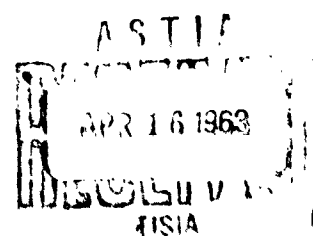
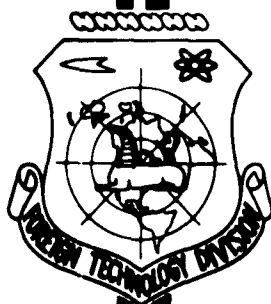
S. M. Stishov and N. V. Belov

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MODIFICATION OF SILICA, SiO_2

BY: S. M. Stishev and N. V. Belov

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CRYSTALLINE STRUCTURE OF THE NEW CLOSE-GRAINED MODIFICATION OF SILICA, SiO_2

by

S. M. Stishov and N. V. Belov

Not long ago a description was given of a new modification of SiO_2 with a density $\delta_{\text{exp}} = 4.35 \text{ g/cm}^3$ (1), obtained under conditions of high pressure (160 to 180 thousand atm)* and temperature (1,200—1,400°). For the time being we do not have at our disposal material which is suitable for X-ray analysis by the monocrystal method, but there has been obtained a powder pattern (filtered Cu emission, diameter of chamber 114 mm) of very satisfactory quality. In Table 1 there are presented for the new phase the angles of reflection, interplane distances, and intensities. The latter were evaluated in accordance with the marks of darkening. One was successful in accomplishing a faultless indexing of a Debye powder pattern (Table 1 on the basis of a primitive tetragonal nucleus with the parameters:

$$\begin{array}{c} \text{SiO}_2 \\ a = 4.176\text{\AA} \\ c = 2.666\text{\AA} \\ c/a = 0.638 \end{array} \left(\begin{array}{ccc} \text{MnO}_2 & \text{TiO}_2 & \text{SnO}_2 \\ a = 4.44\text{\AA} & a = 4.58\text{\AA} & a = 4.72\text{\AA} \\ c = 2.80\text{\AA} & c = 2.95\text{\AA} & c = 3.16\text{\AA} \\ c/a = 0.651 & c/a = 0.644 & c/a = 0.660 \end{array} \right) \quad (1)$$

In accordance with the indicated value δ_{exp} in such a nucleus there are contained precisely two units of SiO_2 . In the brackets beside the parameters of the new modification of SiO_2 there are shown the analogous data for MnO_2 , TiO_2 , and SnO_2 , and in Fig. 1 along with the Debye powder pattern of the new phase there is placed the X-ray picture of rutile TiO_2 . The great affinity (of the relationships) of the parameters and the diffraction patterns, as well as the conformity to rules of the known series, $\text{CO}_2\text{--SiO}_2\text{--TiO}_2\text{--GeO}_2\text{--(SnO}_2\text{)--CeO}_2\text{--ThO}_2$ warranted one's thinking that we have before

* On the scale of Kennedy and Lamore (2) the above-mentioned limits correspond to 120--140 thousand atm.

us the long awaited rutile-like modification of SiO_2 with Si in the sixfold coordination, which is well known for the fluoride compounds of silicon. In the list presented of indexed reflections there are lacking all those which would go against the spatial group of rutile (cassiterite) $D_{4h}^{14} = F4_2/mnm$ (the h0l are extinguished with the odd sum $h + l$). By writing the coordinates of the atoms of the rutile-like pseudocentered structure in the form $\text{Si}(000, \frac{1}{2}, \frac{1}{2})$; $\text{O}(xx0, \bar{x}\bar{x}0, \frac{1}{2} + x, \frac{1}{2} - x, \frac{1}{2}; \frac{1}{2} - x, \frac{1}{2} + x, \frac{1}{2})$ we reduce the structure-analytical problem to the finding of a single oxygen parameter x .

In (3) M. V. Belov and V. I. Mokeyeva gave numerous examples of the solution of not very complicated single-parameter structures with the use of all, without exception, lines of the Debye powder pattern with the aid of very simple diversity of the three-dimensional Patterson synthesis, namely, Harker piercing (linear synthesis). In the structural type of rutile the piercing is done along the diagonal of the tetragonal basis, which analytically is presented in the form, $x = y$; $z = 0$. The Patterson function for any point of the piercing will be

$$\bar{P}(xx0) = \frac{1}{V} \sum_{h,k,l} \sum_{h',k',l'} F_{hkl}^2 \cos 2\pi(h+h')x = \frac{1}{V} \sum_{n=-\infty}^{+\infty} C_n \cos 2\pi nx, \quad (2)$$

where $C_n = \sum_{h,k,l} \sum_{h',k',l'} F_{hkl}^2$ with the condition $|h + h'| = n$, with random l .

It is necessary to note that the intensities of the Debye lines $\{hkl\}$ presented in Table 1 represent the result of the adding of the intensities 16, 8, 4 and 2 of the separate reflexes. Into $\{hkl\}$, along with hkl with all positive indices, there enter $\bar{h}kl$, khl , $\bar{k}hl$, etc., which still have the same intensity. It is easy to see (3) that from each group $\{hkl\}$ the half F^2 gets into C_n , where $n = |h| + |k|$, and the other half into C_m , where $m = ||h| - |k||$. An exception is formed only by $\{h0l\}$, which go entirely into C_n where $n = |h|$.

The totalling of the F^2 series was accomplished with the aid of the

hkl	θ	$d, \text{\AA}$	I	hkl	F_{hkl}^2	F_{hkl}	ϕF_{hkl}	ψF_{hkl}
1	15°18'	2.95	100	110	3.766	1.943	27	29
2	20°18'	2.21	28	101	1.964	1.401	14	12
3	21°42'	2.09	1	200	0.083	0.284	4	6
4	22°58'	1.98	49	111	4.623	-2.150	-22	-20
5	24°24'	1.87	21	120	2.275	1.509	15	15
6	30°19'	1.53	68	121	12.056	4.910	25	24
7	31°31'	1.48	25	220	4.828	1.553	31	27
8	35°23'	1.312	13	002	3.202	0.805	38	33
9	35°45'	1.320	7	130	1.763	1.328	13	12
10	36°40'	1.202	2	221	0.529	-0.727	-7	-8
11	38°43'	1.233	28	301	8.163	2.858	29	31
12	39°27'	1.214	14	112	4.204	2.050	20	19
13	40°44'	1.181	4	131	1.262	1.588	8	8
14	43°22'	1.123	2	202	0.682	0.825	8	8
15	45°18'	1.085	3	122	1.068	1.462	7	9
16	46°37'	1.061	4	231	1.449	1.702	8	8
17	47°38'	1.044	4	400	1.460	0.854	17	14
18	49°37'	1.012	3	140	1.099	-1.048	-10	-10
19	51°13'	0.989	11	222	4.000	2.000	20	20
20	51°29'	0.986	7	330	2.536	1.126	22	25
21	54°34'	0.947	9	141	3.125	2.408	12	15
22	55°14'	0.940	6	132	2.055	2.028	10	10
23	55°40'	0.934	4	240	1.356	1.165	12	16
24	61°02'	0.882	3	421	0.867	1.316	7	7
25	62°35'	0.869	3	103	0.815	0.903	9	9
26	65°05'	0.851	2	113	0.490	-0.700	7	8
27	69°37'	0.823	7	402	1.356	1.168	12	11
28	70°05'	0.819 a_1	10	510	1.898	1.378	14	15
29	70°37'	0.819 a_2	5					
30	72°50'	0.8065 a_1	9	142	1.440	-1.696	-8	-8
31	73°14'	0.8065 a_2	4					
32	73°46'	0.8022 a_1	21	123	3.167	2.517	13	14
33	74°18'	0.8021 a_2	11					
34	75°05'	0.7971 a_1	21	501; 431	2.877	1.199; 1.695	4; 12	4; 11
35	75°38'	0.7971 a_2	11					
36	76°15'	0.7919 a_1	21	332	2.567	1.602	16	20
37	77°33'	0.7918 a_2	11					

Table 1*

*Experimental and computed structural amplitudes are presented on the general scale, and besides in the experimental structural amplitudes there is taken into consideration the factor of recurrence.

three-degree strips (for 120 points of the diagonal) and the results of the numerical synthesis (with relative values of F_{hkl}^2 and with the initial member discarded) are given in Table 2. Besides the trivial initial peak only one stands out very smoothly with the coordinate 38/120, i. e., $x = 0.317$. This number must be compared with the known x , equal for rutile 0.31 and cas-citerite 0.26.

By the determined parameter x one can compute the signs of the structural amplitudes for all 37 reflexes of the powder X-ray picture and further accomplish the diagonal piercing through the three-dimensional

Table 2

Harker Piercing through Paterson's Three-Dimensional Synthesis

along the Diagonal of the Base

0	1	2...	14	15	16...	28	27	26	25	24...	12	11
331	327	312...	84	84	84...	19	23	23	23	22...	83	83

distribution of the electron plane. The formula for this piercing remains the same, but into the sums C_n instead of F_{hkl}^2 the enter the F_{hkl} provided by the computed signs. Wishing to construct the synthesis on the same basis as with F_{hkl}^2 , i. e., considering the table F_{hkl} as the sums of the respective 16, 8, 4, and 2 of the amplitudes we should multiply $\sqrt{F_{hkl}^2}$ by $\sqrt{2}$, 1, $1/\sqrt{2}$, $\frac{1}{2}$ [compare (3)]. Besides in the distribution of

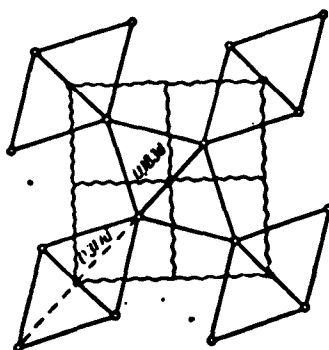


Fig. 2. Plan of rutile-type structure

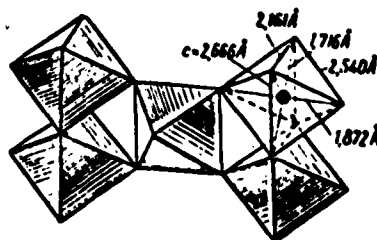


Fig. 3. Axometry of the structure of the new modification of SiO_2 in octahedrons

$\sum F_{hkl}$ according to $C_n = |h+k|$ and $C_n = ||h| - |k||$ it is necessary to keep in mind that in the group $P4_2/mnm$ the place of slipping n makes the equality $F_{hkl} = F_{hkl}$ valid only for $h + k + l = 2n$; if, however, $h + k + l = 2n + 1$ then $F_{hkl} = -F_{hkl}$.

In this way the second synthesis was by no means simply a recurrence of the first with change of scale; it lead, however, as Table 3 shows, to the identical value $x = 0.317$.

In comparing the experimental F_{hkl} with the computed value we obtained the coefficient of the dispersion $R = 0.10$ (for all 37 reflexes).

Cut across the Three-Dimensional Synthesis of the Electron Plane

along the Diagonal of the Base										
0	1	2...	14	15	16...	27	28	29...	50	60
150	147	139...	57	58	57...	35	36	33...	31	30

According to Fig. 2 the ratio $x : (1-x)$ determines how many times greater the diagonal of the SiO_6 octahedron is than the horizontal edge of the octahedron. The value 1.74 obtained is considerably greater than the same value for the correct octahedron (1.414) and shows that the SiO_6 octahedron is extended along the diagonal (as is the octahedron TiO_6 , but not the octahedron SnO_2), i. e., of the 6 atoms of oxygen around the Si 4 are considerably closer than the remaining 2. The precise computation of the distance Si—O gives for the first ones 1.716 Å and for the second ones 1.872 Å (Fig. 3). If one considers as standard for the tetrahedric coordination the distance Si—O = 1.63 Å, then for the first four distances we get the value by ~6%, i. e., just in agreement with what was shown by Goldschmidt already in 1928 for the ratio of the distances of the respective 6th and 4th coordinations. One can also consider that for the four lesser distances we have an ionic bond onto which there is put a covalent one, while in the two remaining ones there is only a single ionic one. Computation of the length of the horizontal edge of the Si Octahedron O—O gives 2.161 Å. This is considerable less than the sum of two oxygen radii, but the shortening corresponds well to that which should be for the general edge in the column from the octahedrons according to the 3rd and 4th rules of Pauling. The lengths of the vertical edges, apparently, represent nothing other than the parameters of the nucleus $c = 2.666$ Å, i. e., they are almost precisely equal to the diameter of the oxygen ion. The inclined edges of the coordination octahedron all equal 2.540 Å.

In conclusion the authors express their thanks to Member-Correspondent of the Academy of Sciences of the USSR L. F. Vereshchagin for giving his attention to and reviewing this present work.

Moscow State University

Entered

named for M. V. Lomonosov

January 19, 1962

Institute of the Physics of Higher Pressures
of the Academy of Sciences of the USSR.

L i t e r a t u r e C i t e d

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