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SiO_2

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SYNTHESIS OF THE ORTHORHOMBIC PHASE OF SILICA IN DYNAMIC COMPRESSION*

The crystalline structure of silica (silicon dioxide) is investigated after the samples are compressed by shock waves with finite pressures of 350, 500, 700 and 900 kbar. The maximum pressures in 700 and 900 kbar were obtained by placing the sample (in protective sleeve having known explosive properties) between strips of heavy metals. The qualitative character of the sample loading in these arrangements, is given. The results of the X-ray structural and electron-graphical analysis of the shock-compressed samples are presented. Using these results, one can register a new high-density phase of silica with ρ = 4.435 gm/cm³. The possibility of formation of the orthorhombic modification of silica in an expansion wave from an unknown high-density phase (unstable in normal conditions) forming after repeated compressions is suggested.

Interest in investigations on the behavior of silica under the action of high pressures arises mainly from geophysical considerations, particularly from the decisive role of silica in the composition of the Earth's mantle. In this sense the study of both the known high-density phases of SiO_2 (coesite and stishovite) and of the attempts at an experimental detection of still higher density phases of quartz, is of special significance.

The majority of the ten different crystalline structures of silica known at the present time, is stable only in certain rigorous conditions. The basic crystalline form in this structural modification series is α-quartz, which is a stable phase of silica in normal conditions (pressure and temperature), whose hexagonal lattice belongs to the space group $P3_121$ and contains 3 molecules in the elementary cell. Its parameters are: a = 4.914 Å, c = 5.405 Å, crystal density, ρ = 2.648 gm/cm³ [1]. The α-quartz structure is characterized by a fourfold anionic coordination: the closest neighbors of the silicon atom are the four atoms of oxygen.

In static loading conditions, two new denser phases of silica, which were unknown earlier, were synthesized. The first is coesite [2] characterized by a monoclinic structure with a crystal density,** ρ = 2.911 gm/cm³. The coesite lattice belongs to the space group B2/b with sixteen molecules in the elementary cell and having the following parameters: a = 7.152, b = 12.379, c = 7.152Å and β = 120.001°. The anionic coordination number of coesite is about 4.

In [3], the results were published of a synthesis of the rutile-like modification of silica with a tetragonal lattice, belonging to the space group P4/mnm, containing two molecules in the elementary cell and having the parameters a = 4.179 and c = 2.665 Å. The crystal density of this phase (called stishovite) is 4.287 gm/cm³. Silica in both these forms was subsequently discovered in the crater of the Diablo canyon in Arizona (USA). It is surmised that they formed under the action of the shock wave at the time of impact of a gigantic meteorite on the Earth's surface.

However, attempts to obtain fairly large quantities of coesite and stishovite from silica samples, subjected to shock compression in laboratory conditions, did not produce appreciable results. Thus, in the first work of this kind, namely in [4], where the structure of α-quartz samples, preserved after the shock-wave induced compression, was analyzed, their transition to the nonstructural amorphous form (the maximum value of the shock-wave pressures was 500 kbar) was fixed. The effect of the pressure P = 250 kbar on the sample, in fact, did not in any way alter their primary structure.

In [5] the authors could discover (as also in the preserved samples) traces of coesite. A detailed analysis of the quartz samples after they were subjected to the action of shock waves was carried out in [6]. In this work, the authors could separate out (after dissolving the amorphous phase in fluoric acid) a small quantity of stishovite. They concluded that the short-range order in the amorphous silica samples has, as in the case of stishovite, a six-fold anionic coordination. In a recent scientific communication [7] a synthesis of the new phase of SiO_2, similar to the orthorhombic high-pressure phase of TiO_2 [8], was reported. In the present article we describe the technique and the experiments relating the shock-wave synthesis of this phase of silica.

For purposes of investigation the samples were prepared in the form of discs of diameter 16 mm and thickness 0.8 to 1 mm, from natural quartzite, monocrystals of α-quartz and from fused quartz glass. In the first two cases, the initial density of the samples was ρ = 2.65 gm/cm³ and the density of fused quartz crystals was 2.2 gm/cm³. The size of the natural quartz crystals was $\sim 10^{-3}$ cm. These crystals were oriented arbitrarily in relation to the geometrical dimensions of the sample and hence also to the direction of propagation of the shock wave in the sample. The monocrystalline α-quartz samples were cut in such a way that the direction of propagation of the shock wave in the sample coincided with the direction [001] in the crystalline lattice.

The samples were loaded with the aid of explosive devices, described in [9]. The block design of these devices is given in Fig. 1. The pressures in the container, containing the sample under inspection, were built up by means of a shock of the brass platinum, compressed by the explosion products of a plane detonation wave. The explosive devices were calibrated by measuring the mass velocity U in the shields covered by the samples. These velocities, measured by the method of the fly-off indicator [10], were 0.84 and 1.13 km/sec, depending on the weight of the charge of the explosive material. The transition to the pressures in the sample, was made by the construction of a P-U diagram [10], making use of the dynamic adiabats of iron, tungsten (materials of the shield and the strips) and quartz, taken from [11-14]. The pressures thus obtained were equal to 350 and 500 kbar respectively for the two velocity values considered.

In a series of experiments with a protective sleeve of the explosive device [9] and with a mass velocity in

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**The crystal parameters given in [2] and [3] were refined many times later; in the present articles, they are given as taken from [1].
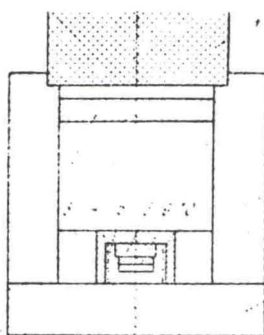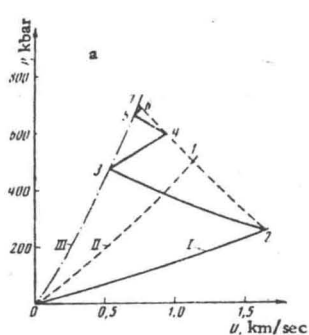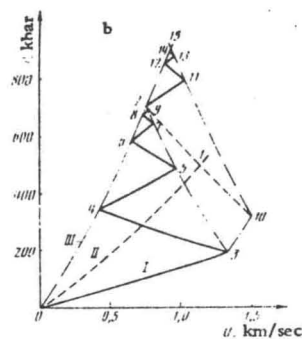
Fig. 1   Fig. 2

Fig. 1. Block diagram of the explosive device: 1) generator of the plane detonation wave;
2) dispersal plate; 3) brass ring; 4) the outer case of the container; 5) the inner case of
the container; 6) shield, covering the sample; 7) steel socket; 8) brass strip; 9) sample
under investigation; 10) heavy-metal strip.

Fig. 2. P–U-diagram of the sample compression: a) device with a maximum pressure of
700 kbar (one tungsten strip); b) device with a maximum pressure of 900 kbar (two tungsten
strips). I - shock adiabat of silica, according to [14]; II - shock adiabat of iron, according
to [13]; III - shock adiabat of tungsten, according to [11 and 12]. 1) State of the shock
wave in the container material; 2-9, 11-15) states of the shock waves in the sample; 10)
state on the tungsten-iron interface.

an iron shield, $U = 1.13$ km/sec one or two strips of heavy
metals (mainly tungsten) were introduced. These strips
were in contact with the surface of the samples under
study. On account of the change in the character of the
sample loading, the above-mentioned method enables one
to obtain in the samples higher amplitude characteristics
of the pressures ($P \sim 700$ to 900 kbar).

The character of the sample loading in the devices
with a single tungsten strip is shown in Fig. 2a. The
shock wave, emerging from the iron shield (state 1) into
the sample under inspection, stresses it to the state 2
(pressure amplitude P_2 and mass velocity U_2). At the
time of its emergence into the lower surface of the sam-
ple, the tungsten strip of the sample, which is already
compressed by the pressure due to the first passing
wave, is additionally loaded up to the state 3 (P_3, U_3) by
the shock wave, reflected from this strip. The subse-
quent magnification of the sample compression takes
place due to the new reflection of the shock wave from
the upper sample-shield boundary, and so on. Thus, by
means of a series of circulating shock waves the sample
is stressed from the state 2 (state of the first shock wave
in the sample) up to the state 7.

A further magnification of pressures was obtained by
placing the sample under study between two tungsten
plates. In this the pressure in the sample changed in
conformity with the states 3 to 9 (Fig. 2b) corresponding
to the passage of the shock waves reflected from the tung-
sten plates. The additional magnification of pressure
(states 9 to 15) was due to the approach of the wave re-
flected from the tungsten-iron interface to the SiO_2 sam-
ple (state 10). Assuming that the sample loading, after
the first shock wave has passed through it, is almost
isentropic, we estimated its temperature. In both cases
it was of the order of 800°K.

The pattern of pressure change with time in the sam-
ple can be traced in P–τ diagrams (Fig. 3). The time
of action of the shock wave on the sample is 4.5 msec
according to the estimates and is determined by the dur-
ation of the passage of the waves in the striking plate.
In this instance, the time of action of the shock wave
with the maximum pressure amplitude is 0.5 msec. The
dimensions of the container and the brass strip were

chosen in such a way that the maximum breaking points
were concentrated outside the container with the sample.
In this way, the sample was also preserved after the
experiment.

We may note here that we always employed the curve
relating to the compression of silica, obtained in condi-
tions of single compression [14]. Such an approxima-
tion does not affect the final states in the sample, but
the pattern of pressure variation in time, at the initial
stage, is only qualitative.

An analysis of the crystalline structures of the shock-
compressed samples was carried out with an X-ray dif-
fractometer of type URS-50-IM. We used an X-ray tube
with a copper anode as the source of radiation. For fil-
tering the radiation, we used a nickel filter. The com-
pressed samples were scanned either from the surface
of the sample (which is located at the immediate contact
with the material of the container or the support) or
from the surface of a specially prepared specimen. In
this case the silica sample, as preserved in the experi-
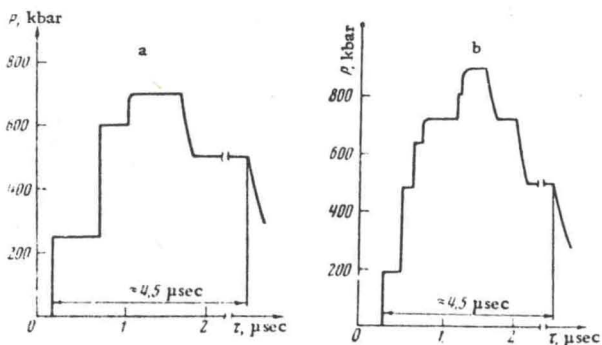ments, was ground up and from the power so obtained

Fig. 3. P–τ (time) diagram of the sample loading: a)
in the device with maximum pressure of 700 kbar, b) in
the device with maximum pressure of 900 kbar.

Table 1

Values of the Interplanar Distances d_{obs} of the Orthorhombic
Phase of Silica, Synthesized in Shock Waves and Also the Values
of d_{cal} Calculated from the Parameters Given in [7].

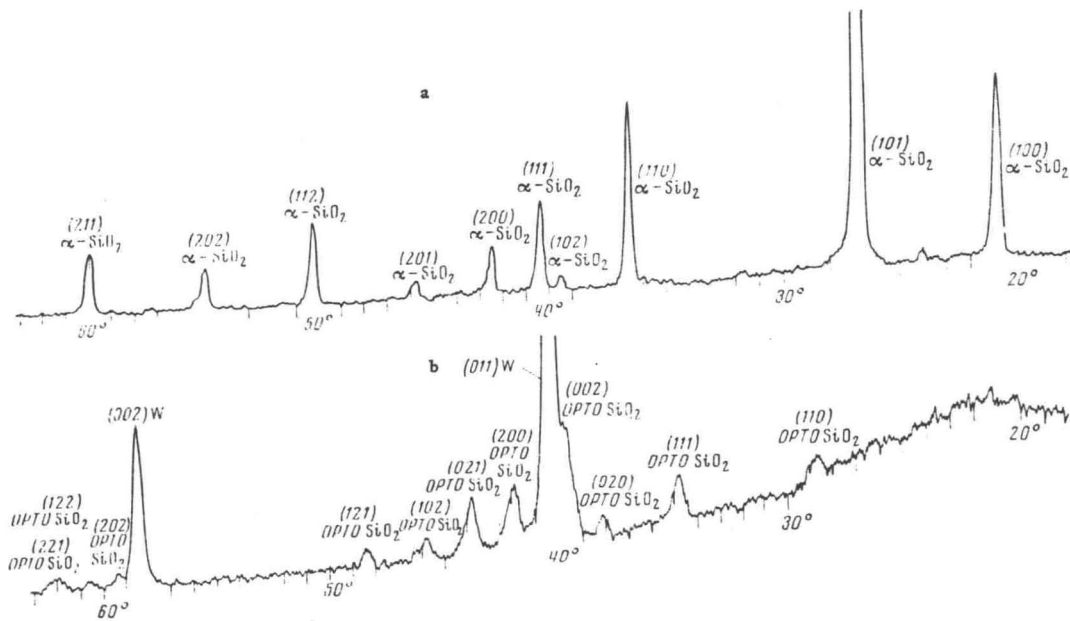| d_{obs}	Intensity	hkl	d_{cal}	d_{obs}	Intensity	hkl	d_{cal}
3.15	Weak	110	3,175	–	–	022	1.626
2,59	Strong	111	2,594	1.58	Weak	220	1.588
2,35	Moderate	020	2,351	1,55	»	202	1.555
2.25	»	002	2,250	–	–	122	1.521
2.15	»	200	2,152	1,49	Moderate	221	1.497
2.08	Strong	021	2.084	1.35	Very weak	113	1,357
1.99	Weak	102	1.994	1,31	»	311	1,312
1.88	Very weak	121	1.875	–	–	222	1,297
–	–	112	1,836	1,24	Very weak	132	1,232

Fig. 4. Diffractogram of the silica sample: a) initial; b) after compression by a shock wave of am-
plitude P = 900 kbar.

special pellets were prepared for investigations with the diffractometer.

The results of the X-ray-structural measurements are set out in Table 1, where besides the observed values of the interplanar distances, we have given the corresponding values calculated from the lattice parameters of the orthorhombic phase of silica [7] a = 4.30, b = 4.70, c = 4.50 Å. Some typical diffraction patterns are displayed in Fig. 4. As in [4], the compression of the samples with the maximum pressures of 350 kbar did not appreciably alter the diffraction pattern: in place of the α-quartz lines one could observe a certain magnification of the diffuse background. The state of the samples after compression with pressures of 500 kbar was characterized by the absence of diffraction maxima and by well diffused backgrounds (especially in the region of small angles). These results were obtained irrespective of whether the scanning was done from the surface of the compressed sample or from the surface of the specially prepared pellet. In large pressures (700 to 900 kbar), one could observe, besides the background, a number of maxima which correspond to the orthorhombic lattice (with a sixfold anionic coordination) on the diffractograms

obtained from both sample surfaces (front and rear) immediately in contact with the material of the container or the strip. The scanning of the powder pellets revealed that a large part of the substance is in a nonstructural amorphous state (perhaps in the form of the so-called short-range-order phase [6]). One could not identify the stishovite lines in any of the experiments.

Thus, the orthorhombic phase of silica is synthesized only in the surface layer of the sample, at its contact with the strip material. We should note here that this layer is intensely polluted by tungsten (strip material): on the diffractograms one could also identify the lines of this metal besides the lines of the orthorhombic phase. To verify the fact that the new lines are not the lines of the chemical compounds of tungsten with SiO_2, formed as a result of the shock, we laid out, between the samples and the tungsten discs, a tatalic foil of thickness 0.2 mm in some experiments which hardly changes the character of the silica loading. In this case also we could identify the lines of the orthorhombic phase of silica on the diffractograms. The probable cause for the formation of the orthorhombic phase of silica in the surface layer of the samples only should

obviously be sought in the large displacements which take place during the transition of the shock wave from a medium with a given dynamic rigidity to another and which stimulate the process of phase transformation.

The crystalline structure of some samples was also analyzed with an electron microscope of the type UEMV-100, equipped with an electronograph. The results of these investigations are in full agreement with the x-ray measurements.

The interpretation of the diffractograms could be made on the basis of an orthorhombic lattice, which is more or less close to the one described in [8] where a new crystalline modification of TiO_2 was synthesized in static conditions; the orthorhombic lattice of this modification belongs to the space group Pbcn, while the elementary cell contains in itself four molecules of TiO_2. The new phase of silica has the following parameters: $a = 4.30$, $b = 4.70$, $c = 4.50$ Å. The values of the interplanar distances are d_{cal}, calculated from these parameters, satisfactorily coincide (see Table 1) with the observed values d_{obs}.

In the above-mentioned work, there is no detailed calculation of the intensities of the new-phase lines of SiO_2, but a comparative evaluation of the relative value of the diffraction maxima of the diffractograms and the relative intensities of the new phase of TiO_2 reveals a

satisfactory agreement between the two. The crystal density, calculated from the lattice parameters, is equal to 4.435 gm/cm^3. We may note here that, due to the fairly strong broadening of the diffraction maxima and also due to the absence of diffraction maxima with large values of hkl, the accuracy of determination of the lattice parameters, did not exceed 0.01Å.

In conclusion, we must remark that the complex shock-wave process of sample loading and the subsequent removal of pressures from it, naturally, does not justify the assertion that the formation of the orthorhombic modification of silica takes place at the top of application of shock pressures to the SiO_2 sample. As was already observed, especially in [15], one cannot rule out the possibility that the orthorhombic phase is a consequence of the transformation of silica from an unknown high-density phase (possibly from a fluorite type of structure), which forms after repeated compressions and which seems to be unstable in normal conditions.

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