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Structural Transformations of Silicates upon Prolonged Grinding

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Abstract — Structural changes in diopside, $CaMgSi_2O_6$, and wollastonite, $CaSiO_3$, upon prolonged (up to 84 h) grinding in a mechanic agate mortar under environmental conditions were studied. X-ray phase analysis and specific surface measurements were used to show that the stage of amorphization of the starting substances under mechanical treatment is followed by the formation of a partially ordered phase whose reflexes correspond to reflexes of α-quartz. Possible mechanisms of the structural transformations were discussed.
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Phase formation upon mechanical action on substances and their mixtures is the subject of active investigations. The processes of new phase formation upon mechanical treatment include mechanochemical synthesis, phase transitions, and decomposition of substances (for reviews, see [1–4]).

Mechanically stimulated reactions make possible synthesis of compounds with various types of chemical bonds: ionic, covalent, and metallic. Phase transitions under the action of mechanical forces are usually accompanied by formation of more compact phases, whereas thermally stimulated phase transitions most commonly provide less compact modifications [1]. There are many examples of transitions of unstable mineral phases into stable phases: TiO_2(anatase) → TiO_2(rutile), ZnS(wurtzite) → ZnS(sphalerite), β-PBO → α-PbO, etc. Transitions of stable into unstable phases upon fairly long mechanical treatment were also noted. Under such conditions, mechanochemical equilibrium may establish, when two phases interconvert and simultaneously coexist in a certain proportion, for example, $CaCO_3$(calcite) → $CaCO_3$(aragonite) [5].

The distinguishing feature of mechanically stimulated solid-phase processes is that they occur at temperatures substantially lower than the melting points of the starting substances and reaction products. Of certain importance are momentary high local pressures and temperatures developing when particles contacts with each other and grinding bodies [1]. Important is also the energy factor: Prevailing are processes accompanied by a maximum gain in the free energy [6]. In this connection one should take into account the energy of plastic deformations accumulated upon mechanical treatment, as well as the stance increases by ΔG [1].

$$\Delta G = (2\sigma V)/r + G_d. \quad (1)$$

The first term in Eq. (1) includes the particle size according to Thomson's formula (V is the volume of the substance, σ, surface tension, and r, particle size), and the second term relates to the accumulated elastoplastic energy. In other words, crystallization of a new phase is the more thermodynamically favorable, the smaller is the particle size of the starting substance (the surface is more developed) and the greater is the energy of plastic deformations accumulated in their volume. We emphasize that the mechanisms of such transformations are complicated and scarcely studied.

We previously found that prolonged grinding of diopside ($CaMgSi_2O_6$) in a mechanical mortar results, along with amorphization of the substance, in appearance of α-quartz reflexes in the X-ray diffraction patterns [7]. The aim of this work was to study in more detail the structural transformations of two silicates, diopside and wollastonite ($CaSiO_3$), upon prolonged grinding.

Figures 1 and 2 show the X-ray diffraction patterns of the starting and ground (maximum grinding time 84 h) samples of diopside (D-1) and wollastonite. As follows from the figures, the first stage involves gradual amorphization of the minerals. After 60-h treatment the samples are almost X-ray amorphous. On further grinding reflexes corresponding to α-quartz appear in the X-ray diffraction patterns. In view of the low intensity of the reflexes and their halfwidth,

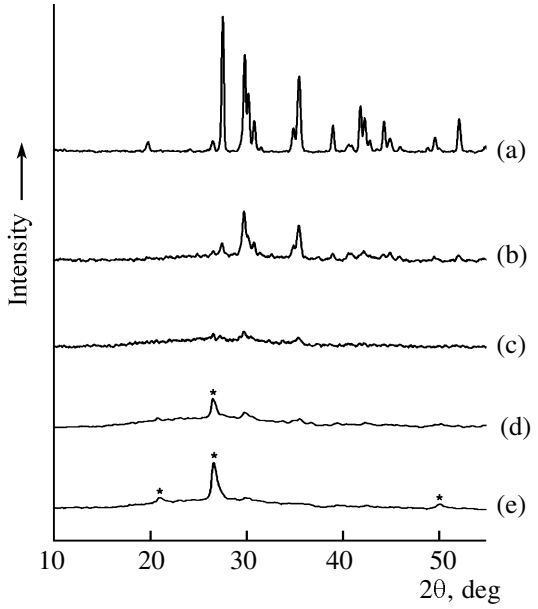

Fig. 1. X-ray diffraction patterns of diopside (sample D-1). (a) Starting sample and (b–e) after grinding for 36, 60, 72, and 84 h, respectively. Reflexes of α-quartz are shown by asterisks (the same for Figs. 2 and 3).

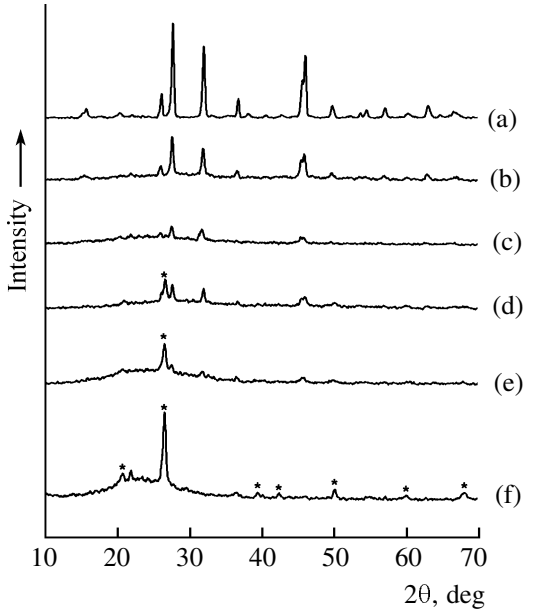

Fig. 2. X-ray diffraction patterns of wollastonite. (a) Starting sample, (b–e) after grinding for 40, 60, 70, and 84 h, respectively, and (f) sample (e) with after treatment with acid.

we cannot state that prolonged grinding of the silicates gives rise to crystalline quartz. Here, we have to do with nothing more than formation of a partially ordered phase whose structure corresponding to α-quartz.

One of the most important questions that arise when one discusses the resulting data is whether the quartz-like phase can appear as a result of milling, i.e. self-grinding of the agate pestle and mortar. Agate is known to be a cryptocrystalline (in the mineralogical sense) modification of quartz, and the X-ray diffraction patterns of these minerals are alike. The use of a mechanical mortar made of, for example, tungsten carbide would completely exclude the possibility of an artifact. Unfortunately, we had at hand an agate mechanical mortar only. Therefore, we carried out special experiments to estimate the amount of milling. To this end, we ground under the same conditions titanium dioxide of rutile modification, whose hardness by the Mohs scale is 6.0–6.5, i.e. it is harder than wollastonite (4.5–5.0) and diopside (5.5–5.0). For comparison sake, the hardness of quartz is 7.0. After mechanical treatment of titanium dioxide in an agate mortar for 80 h, the X-ray diffraction patters (not presented) shows broadened rutile reflexes, but no new phases were detected. Chemical analysis of the resulting titanium dioxide powder showed that the content of SiO_2 in it, as determined by the gravimetric method [8], does not exceed 4–5 wt%. Therefore, prolonged treatment does involve self-grinding of the agate pestle and mortar, but the milling is relatively small. Moreover, the milling seems to consist of either X-ray amorphous silica or very fine SiO_2 particles, since no reflexes of new crystal phases were found in the X-ray diffraction pattern of ground titanium dioxide.

After treatment of ground wollastonite with 0.5 M HCl (weight ratio of the solid and liquid phases 1 : 25), the intensity of reflexes increases (Fig. 2f). As we found earlier [9], the reaction of diopside subjected to prolonged mechanical treatment in a planetary mill until complete amorphization results in an almost 100% extraction of calcium and magnesium cations into the solution. The solid residue represents hydrated amorphous silica. After acid treatment of wollastonite, the solid residue seems to contain a mixture of hydrated amorphous SiO_2 and a neogenic quartz-like phase.

As follows from the X-ray diffraction patterns in Figs. 1 and 2, the new phase appears only after prolonged grinding (60 h) resulting in amorphization. If sample D-2 first rendered amorphous in a vibration mill (for 65 h) is taken as the starting sample and ground in a mechanical mortar, then the quartz-like phase appears much earlier, even in 24–36 h (Fig. 3).

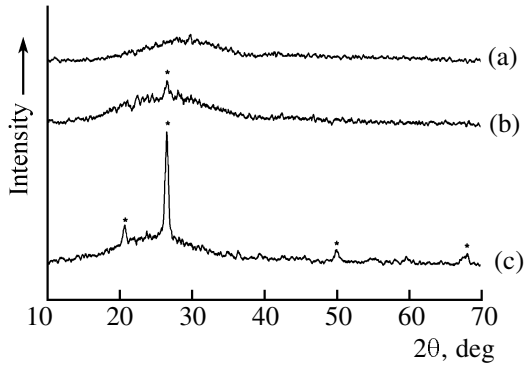

Fig. 3. X-ray diffraction patterns of preliminarily amorphized diopside (sample D-2). (a) Starting sample and (b, c) after grinding for 24 and 36 h, respectively.

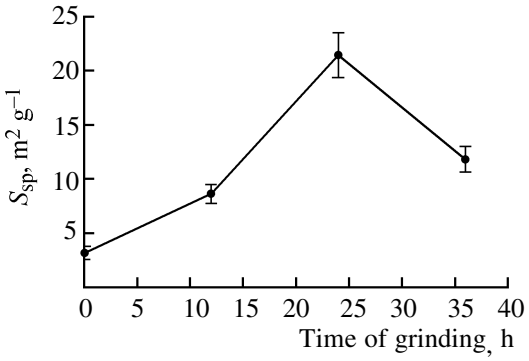

Fig. 4. Plot of the specific surface area of preliminarily amorphized diopside (sample D-2) vs. time of grinding in an agate mortar.

An important parameter of mechanical treatment is dependence of sample dispersity, measured by specific surface area, on treatment time. Figure 4 presents the dependences of the S_{sp} of diopside D-2 samples on grinding time. Comparison of Figs. 3 and 4 clearly shows that the specific surface area first increases, and then, as the quartz-like phase is formed, noticeably decreases, which can be attributed both to particle aggregation and to increasing size and relative density of particles in the new phase.

Diopside and wollastonite belong to the class of chain silicates [10]. Their structures involve endless chains of silicon–oxygen tetrahedra $(SiO_4)_n$ in two of the four oxygens being bridging atoms. The chains are linked to each other by Ca and Mg cations. Unlike diopside and wollastonite, amorphous silica contains only bridging oxygen atoms, and their silicon–oxygen tetrahedra form a regular structure of six-membered nonplanar rings. In amorphous silica, SiO_4 tetrahedra are incorporated into 4–8-membered rings that form no regular structure. It can be suggested that grinding in the presence of traces of moisture involves repolimerization [Eq. (2)], as a result of which silanol groups form siloxane bridges.

$$\rangle\!\!>\!\!\text{Si–OH} + \text{HO–Si}\!\!<\!\!\langle \longrightarrow \rangle\!\!>\!\!\text{Si–O–Si}\!\!<\!\!\langle + H_2O. \qquad (2)$$

Water acts here to catalyze cross-linking of silicon–oxygen tetrahedra into a framework. The capability of silicon–oxygen anions of recrystallizing by Eq. (2) has also been described for other processes. In solubility experiments on chain silicates, wollastonite treated with acids at pH 2 and 5 was found to dissolve incongruently and exchange calcium cations for protons, forming silanol groups. Therewith, the surface enriched with silicon compared to untreated mineral is reconstructed. Due to spontaneous repolymerization, silanol groups form a framework of four-membered silicate rings and areas of crystallization nucleation [11].

The transformation of the chain diopside structure into framework as a result of prolonged grinding was detected by ^{29}Si NMR high-resolution spectroscopy [7]. Our experiments (Figs. 1–3) testify that, along with repolymerization of SiO_4 tetrahedra, a short-range order of the atoms is formed, which corresponds to the α-quartz structure. According to Burger's classification, from the crystallographic point of view the observed changes belong to reconstructive transformations in the second coordination sphere [12]. The primary common structural element, silicon oxygen tetrahedron, is preserved, but a new coordination polyhedron is formed by transformation involving bond cleavage.

By the reference method [13], we estimated the quantity of the neogenic phase by measuring the integral intensity of the main reflex of α-quartz (101) in the X-ray diffraction patterns of ground silicates (Figs. 1–3). Pure crystalline quartz (main substance content 99.7%) was used as reference. According to our estimates, the content of the partially ordered quartz-like phase after grinding of 5 g of the starting silicate for ~80 h attains 5–10 vol%. We did not carry out further grinding, since after 80-h grinding the amount of the sample in the mortar decreased to 1 g and even smaller due to losses. It can be suggested that as the fraction of and particle size in the quartz-like phase increase, the reverse process occurs, namely, destruction of this phase on mechanical treatment. However, quartz cannot be rendered completely amorphous, i.e. converted into amorphous silica, by mechanical treatment [14]. Prolonged (300 h) treatment of quartz in a vibration mill only partially destroyed the nonplanar six-membered rings

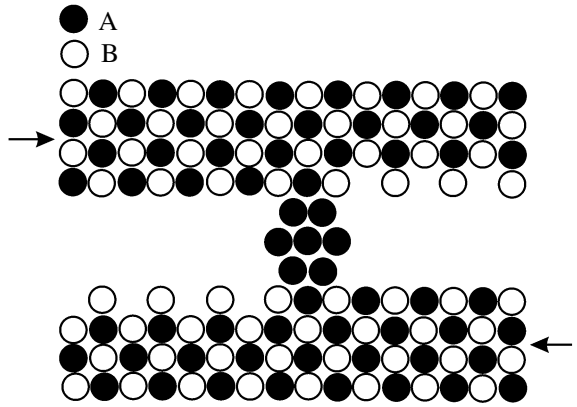

Fig. 5. Scheme of the growth of a crystalline nucleus of phase A on the decomposition of phase AB under conditions of plastic flow [19].

of SiO_4 tetrahedra, the short-range order of atoms being preserved.

In our experiments, as noted above, crystalline diopside and wollastonite are almost completely amorphized in the first, rather long stage of grinding, and α-quartz reflexes are only later detected in the X-ray diffraction patters of the powders. To reach the same effect on grinding of preliminarily amorphized $CaMgSi_2O_6$, a much shorter time is required. It is not inconceivable that preliminary amorphization creates thermodynamic prerequisites for new phase formation. The formation of quartz from diopside can be represented by reaction (3).

$$2CaMgSi_2O_6 \longrightarrow Ca_2MgSi_2O_7 + MgSiO_3 + SiO_2\ (\alpha\text{-quartz}). \quad (3)$$

Reaction (3) with crystalline diopside, ockermanite ($Ca_2MgSi_2O_7$), clinoenstatite ($MgSiO_3$), and quartz is thermodynamically impossible, since, according to the reference data [15], it is characterized by $\Delta_r G^0(298)$ 58.5 ± 7.1 and $\Delta_r H^0(298)$ (68.4 ± 7.1) kJ. The X-ray patterns of diopside upon prolonged grinding showed reflexes of quartz only (Figs. 1 and 3). This fact suggests that amorphous diopside decomposes to amorphous ockermanite and clinoenstatite and crystalline quartz. We failed to find in available reference literature the standard energies of formation of these silicates in the amorphous state. Handbook [15] gives the standard enthalpies of formation of amorphous (glass-like) diopside and ockermanite. On the basis of available reference data we calculated the standard enthalpy of the decomposition of amorphous diopside to amorphous ockermanite and crystalline clinoenstatite and quartz. In this case, the $\Delta_r H^0(298)$ of reaction (3) is –(80.4 ± 7.1) kJ, i.e. the process is exothermal, and its $\Delta_r G^0(298)$ should also be negative. This rather crude estimate shows that amorphization of substances can essentially affect the thermodynamic possibility of transformation.

When interpreting the mechanism of new phase formation on grinding of silicates, one of the key factors to be accounted for is the character of mechanical processes in the mortar. Many researchers admit that shear stresses and their induced plastic deformations play an important if not determining role in the mechanochemical synthesis. There is experimental evidence [1, 3, 16, 17] showing that the increase of the share component under high pressure substantially increases the yield of chemical reactions in powder mixtures. It is the shear deformation with its inherent mutual shifts of atoms and abrupt increase of the mobility of the structure as a whole that to the greatest extent favors formation of new phases [18]. In our experiments we just deal almost exclusively with shear effects.

A combination of pressure and shear deformation accelerates chemical reactions and decreases the temperature of a number of polymorphic transformations. A common feature of such processes is, on the one hand, thermodynamic possibility, and on the other hand, low reaction rate due to slow mass transfer [19]. In the case of simultaneous action of pressure and shear deformation, mass transfer essentially enhances, and kinetic constraints are lifted. The enhancement of mass transfer upon plastic deformation is possible owing both to diffusion (increasing number of point and linear defects and their transfer) and to plastic flow, the latter prevailing [1].

Dremin and Breusov [19] put forward a roller model of nucleation and growth of a new phase during chemical reaction under the action of plastic flows. Figure 5 shows the scheme of growth of a new phase A upon decomposition of compound AB. A nucleus of phase A, which is located between two layers of compound AB, shifting relative to each other, is considered as a roller. As the roller moves due to mutual motion of two layers, it contacts with atoms of both kinds (A and B). Since it is assumed that under these conditions A–A bonds are stronger than A–B bonds, and the time of atomic contact ($\sim 2 \times 10^{-12}$ s [19]) is noticeably longer than the time of electronic rearrangement (10^{-13}–10^{-14} s), atoms A have time to join to the roller in the course of plastic flow. The maximum size and total number of the resulting crystalline particles seem to depend on the dynamic strength of the obtained substance and on the possibility of the reverse or side reactions under mechanical action.

It is conceivable that the quartz-like phase is formed from silicates by the roller model. In this case, the thermodynamic possibility and, according to Eq. (1), a high dispersity of the powders play a certain role (Fig. 4). As mentioned above, we should also take into account the catalytic effect of water that is always present on the sample surface under the environmental conditions, on the formation of the framework of silicon–oxygen tetrahedra. One more circumstance should also be mentioned. According to the roller model (Fig. 5), the presence of a nucleus of the future roller is required for a new crystal phase to appear and grow. The nucleus of phase A can appear as the result of decomposition of phase AB under mechanical treatment. In our case, fine agate particles present as milling can also act as nuclei.

The discovered structural transformations are one more illustration to the general regular trends found earlier. A distinguishing feature of our data is that the starting compounds, silicates, are very stable high-melting substances. A combination of pressure and shear when applied to these substances under the environmental conditions makes it possible to obtain a quartz-like phase, using very simple instrumentation. It should be emphasized once more that we do not deal here with the mechanochemical synthesis of crystalline quartz in a rigorous sense. The described transformations of the silicate matrix can furnish a deeper insight into the the nature of new phase formation and the role mechanical action plays in this process.

EXPERIMENTAL

X-Ray diffraction analysis was performed on a DRON-2 diffractometer (CuK_α radiation) equipped with a unit that allows X-ray patterns to be obtained in the digital form. The specific surface areas were measured by the nitrogen heat desorption technique on a FlowSorb II-2300 (Micromeritics) device.

A monomineral fraction (–0.250 + 0.125 mm) of natural diopside from the Kovdor deposit (Kola Peninsula) was used in the experiments. The contents of admixture minerals (carbonates and micas) in the diopside did not exceed 1%. According to chemical and atomic absorption analysis, the starting diopside contained (wt%): SiO_2 49.70 ± 0.08, CaO 24.50 ± 0.05, MgO 16.10 ± 0.05, Al_2O_3 1.34 ± 0.05, FeO 2.88 ± 0.05, TiO_2 0.48 ± 0.05, Na_2O 0.43 ± 0.05, K_2O 0.19 ± 0.02, and MnO 0.08 ± 0.02. This sample was denoted as D-1. Additionally, an X-ray amorphous $CaMgSi_2O_6$ (sample D-2) was used, obtained by prolonged treatment (65 h) of a crystalline sample D-1 in a 75T-DRM vibration mill.

$CaSiO_3$ (high-temperature pseudowollastonite) was synthesized by sintering stoichiometric amounts of analytical grade $CaCO_3$ and analytical grade amorphous SiO_2 (calcined at 1000°C for 12 h to remove water) at 1200°C for 10 h. Before sintering the mixture was thoroughly ground and pressed it into pellets. For complete reaction, the grinding–pelleting–sintering cycle was repeated three times.

The grinding experiments were carried out in a Fritsch mechanical agate mortar (Model 2) at room temperature and relative air humidity of 30–40%. The weight of the starting sample was 5 g. It was ground step by step (10–14 h each) with intervals of the same duration. Prolonged grinding gave such a finely dispersed powder that a fraction of it deposited as an air suspension on the mortar walls and even under the protective cover on the apparatus lid at a distance of 5–10 cm from the mortar. During intervals between grinding , the substance was gathered with a little brash and put back into the mortar. The grinding apparatus comprises a mortar and a pestle. The mortar is evenly rotated with the help of an electromechanical drive. A horizontal lever with a movable counterbalance attached to the vertical rod of the pestle makes it possible to increase or decrease the pressure of the pestle on the mortar by moving the counterbalance along the lever. In our experiments, the counterbalance was at the extreme position providing a maximal pressure and, consequently, the most efficient grinding.

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