Physical chemical properties of geomaterials

Kolpakova T.G., Kotelnikov A.R., Suk N.I. Processing of borosilicate glass wasteforms into stable mineral phases.

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Abstract. The purpose of our work was processing of borosilicate glasses, containing elements of radioactive waste, in a stable mineral matrix. We have proposed and experimentally verified 2 methods of processing a borosilicate glass wasteform: a method of salting and phase separation method. During the experiments, we synthesized minerals-concentrators of radioactive waste elements such as loparite, euxenite and Cs-containing silicate.

Keywords: loparite, experiment, borosilicate system, crystallization.

According to the principle of phase and chemical conformity (Kotelnikov et al., 1994), matrix with elements of the radioactive waste must be stable in the earth's crust, that is, to be in a state of thermodynamic equilibrium with the surrounding rocks. However, modern glass matrix doesn't satisfy this condition, glasses are unstable in the earth's crust. Therefore, it is necessary to process existing glasses. The purpose of this work was the development of possible methods for processing borosilicate glass. We have proposed and tested 2 methods of processing borosilicate glass matrix: a method of salting out and a liquation method. Sr, Cs, La and Ce was selected as elements-imitators of radionuclides (RN) in the composition of the borosilicate glass, as the most significant elements of the radioactive waste. The compositions of products were determined on a digital electron scanning microscope Tescan Vega II XMU with an energy dispersive spectrometer INCA Energy 450 with the Si(Li) semiconductor detector with an INCA XSight with wave spectrometer INCA Wave 500 (I = 400пA).

The method of salting out lies in adding another substance(as a rule, soluble in the given solvent) into the solution.

We applied this method in our experiments. Here borosilicate melt acted in the role of solution, and we added to it aluminium oxide, as according to the literature, this component leads to an increase of the susceptibility of glass to devitrification (Plodinec and Wiley, 1979). Oxides of Ti and Nb were used as reagents for better crystallization of titanium niobate (such as loparite). Also natural loparite was used as a seed. In works (Suk et al., 2008, 2013) experimentally investigated the formation of loparite in complex silicate-salt systems. Based on these works, the following parameters of experiments was chosen: 2 kbar and 1100°C. The experiments were carried out under dry conditions and in the presence of water.

In the experiments (No. 6858 - 6860) 3 phases were obtained: niobium rutile, euxenite and glass (Fig. 1). The ratio of Ti/Nb in rutile changes within 1.13-5.62. The composition of rutile corresponds to the formula: $(Ti_{(0.73-0.9)}, Nb_{(0.13-0.8)})_{(0.86-0.98)}O_2$. Its amount is 15% of the sample volume. The size of the rutile crystals does not exceed 10 microns. Euxenite corresponds to the formula $(Ca_{0.18}La_{0.14}Ce_{0.64})_{0.96}(Ti_{0.81}Nb_{1.18})_{1.99}O_6$. Its amount is 2% of the volume of the sample. Replacement of elements in isomorphous series euxenite ($YNbTiO_6$) – fersmite ($CaNb_2O_6$) occurs according to the scheme: $Y^{3+}+Ti^{4+}=Ca^{2+}+Nb^{5+}$. Thus, if the substance is euxenite, its formula composition should respond to this scheme of isomorphism. As you can see on the chart (Fig. 2), the experimental data are in good agreement with the specified type of isomorphism. Analysis of the glass showed significant concentrations of elements-imitators RN (Table 1), such as Sr and Cs.

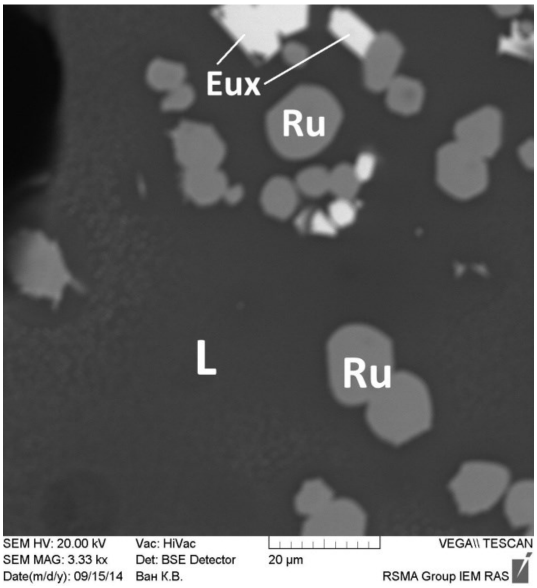

Fig. 1. BSE image of sample № 6860. Lop – loparite, Ru – niobium rutile, Eux – euxenite, L –glass.

Thus, it is shown that using the method of salting out is possible to achieve crystallization of the melt, adding aluminium oxide.

Liquation method lies in the fact that the melt, depleted in silica and enriched in components of loparite, is formed as a result of phase separation (Galakhov and others, 1968; Galakhov and Alekseeva, 1976). Production recommendations for the melting of borosilicate glass (Plodinec and Wiley, 1979) indicated that addition of aluminium leads to increase probability of occurrence of glass heterogeneity. Therefore, in our experiments we added Al_2O_3 and decreased temperature to reach a field of liquation. The experiments were carried out at atmospheric pressure. At first ampoules were heated up to 1300°C for melting and homogenizing the melt and then the temperature was reduced to 850° to reach a field of liquation.

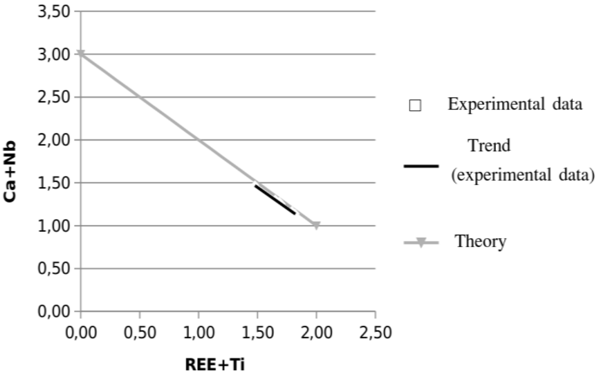

Fig. 2. Function of changes in the composition of the solid solution of theoretical and experimentally obtained euxenite.

Table 1. The contents of elements-imitators RN in glasses obtained in the experiments No. 6858 – 6860 (wt. %)

Experiment	La_2O_3	Ce_2O_3	SrO	Cs_2O
6858	0.16	0.24	1.20	1.54
6859	0.31	0.79	0.96	1.33
6860	2.18	0.60	1.25	1.02

In the experiments (No. 6897, 6934) 3 phases were obtained: two immiscible melt and loparite (Fig. 3, 4). One melt is enriched with boron and loparite components (Ti, Nb, REE, Sr, Ca, Na), the second has f aluminosilicate composition and is enriched with Mg. The contents of elements-imitators RN is 5 times less than in the first experiments (Table 2). However, cesium enriches melt. Loparite in these experiments is the only crystalline phase and its average composition corresponds to the formula $(Na_{1,19}Ca_{0,41}Sr_{0,12}Ce_{0,2}La_{0,07})_2\ (Ti_{1,22}Nb_{0,72})_{1,94}\ O_6$.

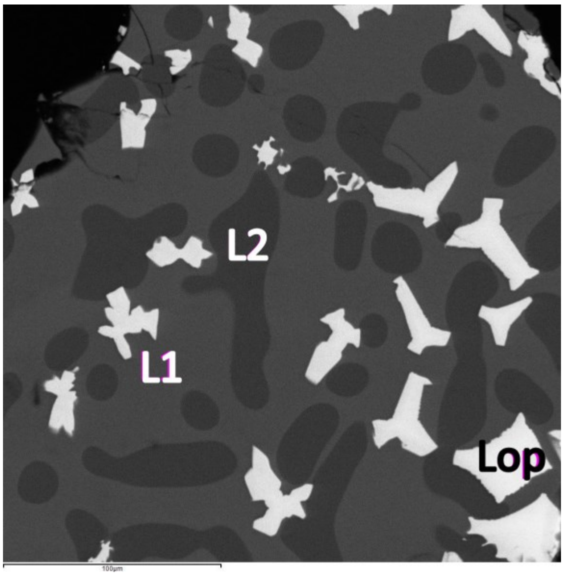

Fig. 3. BSE image of sample № 6934. Lop – loparite, L1, L2 – glasses of immiscible melts.

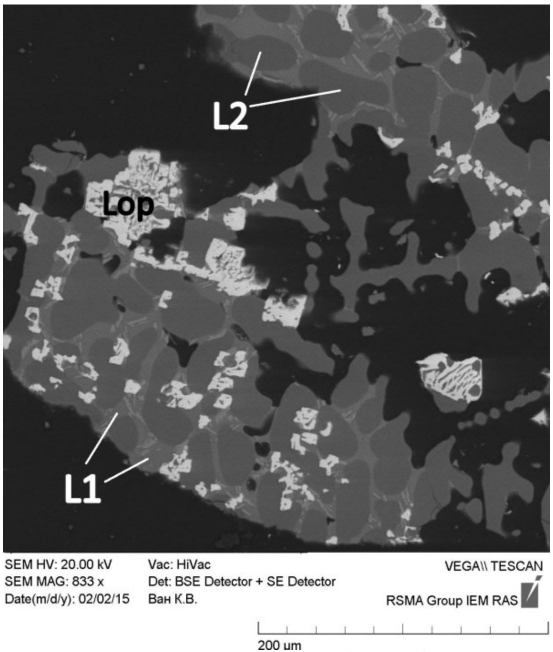

Fig. 4. BSE image of sample № 6897. Lop – loparite, L1, L2 – glasses of immiscible melts.

Table 2. The average compositions of glasses from experiment № 6897 and 6934, wt. %

Number run	Phase	SiO_2	TiO_2	Al_2O_3	Nb_2O_5	MgO	CaO	Na_2O	B_2O_3	SrO	La_2O_3	Ce_2O_3	Cs_2O	Total
6897	L2	29.51	0.93	32.10	0.00	1.36	0.08	26.82	8.63	0.45	0.00	0.07	0.06	100
6897	L1	16.59	17.61	8.61	5.41	0.22	0.17	30.27	18.20	0.51	0.38	0.35	1.70	100
6934	L2	37.82	0.71	28.47	0.04	2.98	0.03	28.10	0.00	1.46	0.20	0.18	0.00	100
6934	L1	28.32	16.04	12.50	2.52	0.48	0.27	33.82	4.44	0.88	0.21	0.24	0.28	100

Table 3. The average compositions of glasses from experiment No. 6974, wt %.

Phase	SiO_2	TiO_2	Al_2O_3	CaO	MgO	Na_2O	K_2O	Nb_2O_5	La_2O_3	Ce_2O_3	SrO	Cs_2O	Total
L2	7.02	55.08	1.35	0.13	0.20	22.27	0.03	0.87	0.21	0.32	0.21	0.05	87.75
L1	35.10	0.70	25.66	0.07	1.83	26.12	0.06	0.09	0.20	0.15	0.34	0.08	90.39

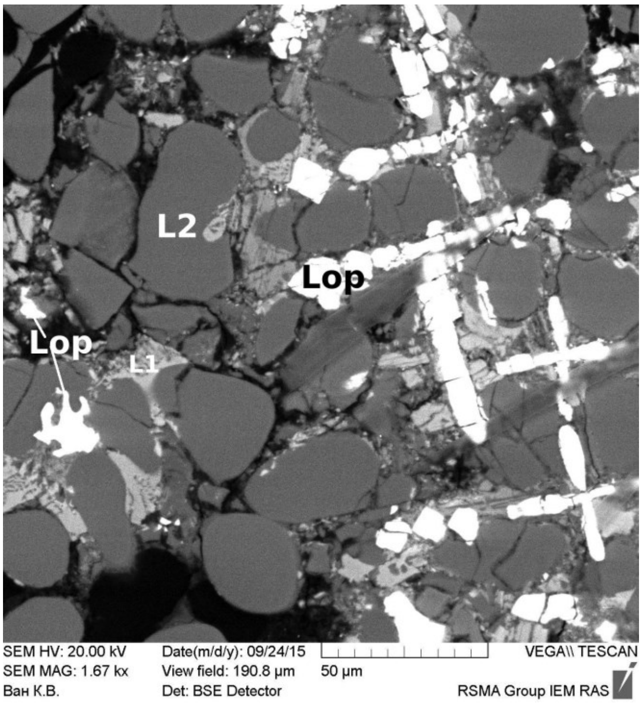

Fig. 5. BSE image of sample № 6974. Lop – loparite, L1, L2 – glasses of immiscible melts.

Residual borosilicate melt has elements such as Na, Al and Si in significant quantities. We assumed that at lower temperatures (600°C), the cesium will form its own crystalline phase. To test this, we carried out an experiment (No. 6974), which differs from the previous only in mode of cooling. From 850°C to 600°C the ampoules were stepwise cooled in steps of 25 ° C every 30 minutes.

In the experiment (No. 6974) 5 phases were obtained (Fig. 5). As in the previous experiments liquation was observed here. The distribution of elements between 2 melts is the same that observed in the previous experiments. Among the crystalline phases, sodium titanate and Cs-aluminosilicate were synthesized , in addition to loparite. The contents of elements-imitators RN in the glass are below the detection limit (Table 3). We assumed that Cs-aluminosilicate is nepheline, whose composition corresponds to the formula $(Na_{0,58}Cs_{0,08})_{0,66}(B_{1,34}Si_{0,45}Al_{0,31})_{2,1}O_4$.

Conclusions. The two methods (method of salting out and liquation method) of possible processing of borosilicate glass were checked. It is proved that both of them are effective methods that lead to crystallization of minerals that are resistant to natural processes. Borosilicate melt, depleted in SiO_2, were formed as a result of liquation. Loparite, sodium titanate and Cs-aluminosilicate crystallized from borosilicate melt.

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Yakushev D.A.[1], Kuzmina N.A.[2], Eremin N.N.[1], Svetlov I. L.[2], Marchenko E.I.[1] Features of niobium silicides crystal structures containing carbon and boron impurities by supercomputer calculations.

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Abstract. Geometric analysis of voids in the Nb_5Si_3 polymorphous modifications structures were studied. The most energetically favorable crystallographic positions in the structures of α-, β- and γ –modifications of Nb_5Si_3 for entry of the impurity of boron and carbon atoms were revealed, considered their final geometric characteristics after energy optimization. Calculations were carried out using by atomistic simulation methods.

Keyword: atomistic calculations (GULP program), Nb_5Si3 modifications, aircraft materials, impurities of C and B in Nb_5Si_3

One of the most important tasks of modern material science is the development of a super-heat-resistant material with a low density (7.2-7.5 g/cm^3) and operable at high temperatures (up to 1350 ° C). A high-temperature natural niobium-based composite is considered as an alternative heat-resistant material of the future, which, perhaps, can replace single-crystal nickel heat-resistant alloys in the manufacture of blades for perspective gas-turbine engines. The niobium silicide Nb_5Si_3 is the reinforcing phase in this composite. The objectives of this study were the estimation the energies of the entry of impurity atoms B and C into the voids of crystal structures under investigation, the study of the defect areas geometry, the most energetically favorable positions for the entry of impurity atoms identification and the semi quantitative estimation of the maximum B and C impurity concentrtion in the niobium silicide polymorphic modifications. At the moment, there are three known Nb_5Si_3 polymorphic modifications (see Table 1): tetragonal α and β modifications that crystallize in the same symmetry group *I*4/*mcm*, but in different structural types (Cr_5B_3 and Mo_5Si_3, respectively) and hexagonal γ- Nb_5Si_3 (space symmetry group *P*6$_3$/*mcm*), whose structure is an analog of the structure of the mineral mavlyanovite Mn_5Si_3 [Yusupov et al., 2009].

α - and β - modification structures have a solid frames, with no apparent channels and voids, while in γ - Nb_5Si_3 single pseudochannel along *c* parameter of structure is observed.

In our previous study [Marchenko et al., 2017] the geometric analysis of all available voids for three polymorphous modifications of Nb_5Si_3 for the entry of impurity atoms C, B, N and O into them was described. As a result of calculations, it was shown that for γ- Nb_5Si_3 there is one-dimensional channel for the migration of C, N, and O atoms along the pseudo-channel located along the *c* parameter of structure, while in the α- and β-modifications C, B, N, and O can exist only as isolated impurity. Given the theoretically possible positions for the impurities atoms [Marchenko, etc., 2017] provided theoretical modeling using semiempirical methods. The calculations were performed using GULP code [Gale, 2006] with the help of interatomic potentials of the Morse type for Nb-Si, Nb-Nb, Si-Si, C-Nb, C-Si, C-C pairs from [Marchenko et al., 2017] and self-developed interatomic potentials of the Morse type for B-Nb, B-B, B-Si interactions. Because of the significant impact of the bonds covalence in the investigated structures and small electronegativity difference between of Nb (1.6 eV) and Si (1.9 eV), the atomic charges were taken as zero values and Slater's atomic radii system was used. The calculations were carried both by Mott-Littleton method and supercells modeling with different dimensions (4×4×3 (768) supercells for the modification of α- Nb_5Si_3, 3×3×5 (720 atoms) for the modifications of β- Nb_5Si_3 and γ- Nb_5Si_3).

As a result the most energetically favorable positions for the entry of boron and carbon atoms into the studied structures were identified. Thus entering into γ- Nb_5Si_3 carbon atom placed in correct octahedral coordination from Nb atoms with Nb-C bond lengths of 2.31 Å and a volume of 16.42 Å^3, whereas in α- and β-modifications of Nb_5Si_3, impurity carbon atom is surrounded by 4 Nb atoms in the form of distorted tetrahedron with volumes of 3.97 and 4.02 Å^3, respectively. The relative energies are 0 eV, 0.25 eV, 0.04 eV (Fig. 1 (a)). The most energy preferable position for boron atoms in γ-Nb_5Si_3 structure is also an octahedron, but with larger volume (16.56 Å^3); In α-Nb_5Si_3 structure boron coordination is 4 Nb atoms and 3 Si atoms, who forms a distorted seven-vertex three-dimensional polyhedron with a volume of 16.02 Å^3, but the energy of such defect impurity is 2.41 eV greater than the boron entry into the Nb-octahedron in γ-Nb_5Si_3 structure. For the β-modification, the energetically favorable polyhedron for the entry of

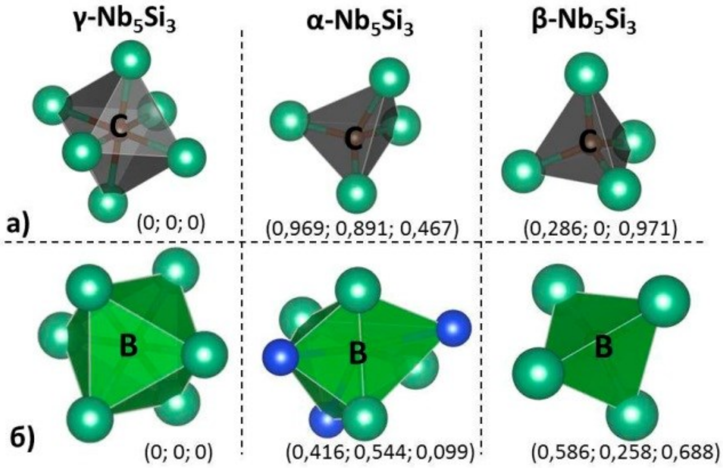

Fig1. Energetically favorable positions for carbon atoms (a) boron atoms (b) entrance in different polymorphic modifications of Nb_5Si_3

Table 1. Polymorphic modifications of Nb_5Si_3.

Modification, space group	Unit cell parameters, Å	Structural type
α, *I*4/mcm [*Aronsson*; 1955]	*a*=6.570 *c*=11.884	Cr_5B_3
β, *I*4/mcm [*Kocherzhinsky et al.,* 1980]	*a*=10.0180 *c*=5.0720	W_5Si_3
γ, *P*6$_3$/mcm [*Schachner et al.;* 1954]	*a*=7.5360 *c*=5.2490	Mn_5Si_3

boron atoms is the Nb tetrahedron (as in the case of carbon) with a volume of 4.36 Å^3 and energy by 0.85 eV larger than the entry of B into the Nb-octahedron of the γ-modification (Fig. 1 (b)). Thus, the energy optimization of defect areas in some cases leads to a change in the starting geometry of the defect area. Only for γ- Nb_5Si_3, the initial octahedral coordination of Nb atoms remains, only the bond lengths and the polyhedron volume vary depending on the size of the impurity atom. It should be noted that, due to the limited application of the models of interatomic interaction potentials, it is possible to compare the values of the carbon and boron input energies separately with respect to different modifications.

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Bublikova T.M., Balitsky V.S., Setkova T.V. Features of morphology of synthetic malachite. UDC 549.743.12

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Abstract. Two methods for obtaining a complete synthetic analogue of natural malachite are known at present: 1- crystallization in closed (recirculation) system and 2 – crystallization in open (flow) system. Both methods make it possible to synthesize almost all textural varieties typical for natural malachite. The appearance of different textural varieties is mainly determined by chosen synthesis method, composition of the solution, TP-conditions of crystallization and shape of the surface substrate.

Keywords: synthesis, malachite, morphology, ammonium solution

Two methods for obtaining synthetic analogs of malachite were developed as a result of experimental and theoretical studies of the conditions for the formation of basic copper carbonates. The composition and physico-chemical properties of the synthesized malachite are similar to those of the natural mineral. The best samples obtained are not inferior to natural jewelry and ornamental malachite according to pattern and color gamma.

For the first time, synthetic malachite was obtained in the 1980s at the Leningrad State University, under the direction of Professor T.G. Petrov. The synthesis was carried out in closed-type crystallizers. Since the development of the laboratory method has been constantly improved, and is now introduced into production in the company Etalon-Jenavi (Petrov et al, 1983). At the same time, investigations on the synthesis of malachite were begun in VNIISIMS (Alexandrov city, Vladimir region). The experiments were carried out in an open flow system at atmospheric pressure, at a temperature of 45-90°C, using copper-ammonium solutions of 1.5-2*M* NH_4OH (Timokhina et al, 1983). Dense, well-polished aggregates of malachite with a variety of textures and alternating layers of light green to dark green (almost black) were synthesized. However, this method had serious drawbacks: the high labor intensity of the process, associated with the constant preparation of new portions of the solution, low plant productivity and the need to neutralize large volumes of waste solution. Later in the IEM RAS experiments on the search for new methods of synthesis of basic copper carbonate were continued. The authors developed a laboratory method for producing malachite in a closed recirculation system (Balitsky et al, 1987). The experiments were carried out in hermetically sealed crystallizers of a recirculation type at a temperature of 65 - 80° C and a saturated vapor pressure. To obtain a variety of textures, we used both low-concentration solutions (of the order of 0.5 *M* NH_4OH) and highly concentrated solutions up to 2 *M* NH_4OH (Bublikova et al., 2012). The developed methods for synthesizing malachite allow one to obtain analogues of practically all of its most popular textural varieties. In the closed-type recirculating crystallizer, malachite of a diverse texture is synthesized in both low- and high-concentration ammoniac solutions: silky, banded and spherolitic, with fine-grained concentric-zonal structure of the aggregates. In solutions with a low concentration of ammonia 0.5 - 1.0 *M* NH_4OH, at a constant temperature in most cases a silky malachite of radial-radiant structure is formed (Fig. 1a). The synthesized malachite is uniformly colored and has a silky gloss on the break. The individuals composing the aggregate of the silky malachite reach a size of a few fractions of a millimeter, which mainly determines the dark tones of the green color. A periodic change in the degree of supersaturation of the solution makes it possible to obtain banded or ribbon-like malachite (Fig. 1b). Banding in it is manifested due to the alternation of contrast zones, differing in color: from pale to dark green, almost black. The thickness of the zones varies according to the specified thermobaric conditions. The boundaries between the zones can be rectilinear, slightly wavy, or intricately curved. In general, malachite is composed of a set of tightly adjoining aggregates consisting of acicular or plate-shaped crystals (Fig. 2a). For spherolites, the phenomena of geometric selection, which lead to their enlargement, are characteristic. Banded synthetic malachite is visually close to Zaire's jewelry-ornamental malachite.

The best samples of synthetic malachite, the closest in the figure to the famous turquoise Ural malachite, were obtained by us in a recirculating crystallizer using highly concentrated ammonia solutions. Malachite has a bud-like texture (Fig. 2b). The sizes of individual buds range from 2-5 to 10-15 mm in diameter. The buds are formed by the growth of individual spherolites and can have radial-radiant and concentric-zonal structure. In the first case, the crystals composing the bud are located radially with respect to the center of nucleation of the spherolites. In sections, such buds are characterized by a smooth color change - from almost black in the center to light green around the periphery. This is due mainly to the relationship between the orientation of the elongation of the crystals and the plane of the cut. In the second case, the buds are composed of concentric zones with different colors: from light green, with a turquoise hue, to dark green. Each zone has a spherolite structure. Dimensions of spherolites 0.01 - 3 mm in diameter. The zones composed of small spherolites have a lighter coloration than the zones composed of large spherolites. Each new zone is usually accompanied by the nucleation of new generation spherolites, although there are cases of crystallographic inheritance of early spherolites later. The alternation of spherolites of different diameters and zones of various shades of green create a whimsical geometric pattern, making this stone unique and inimitable.

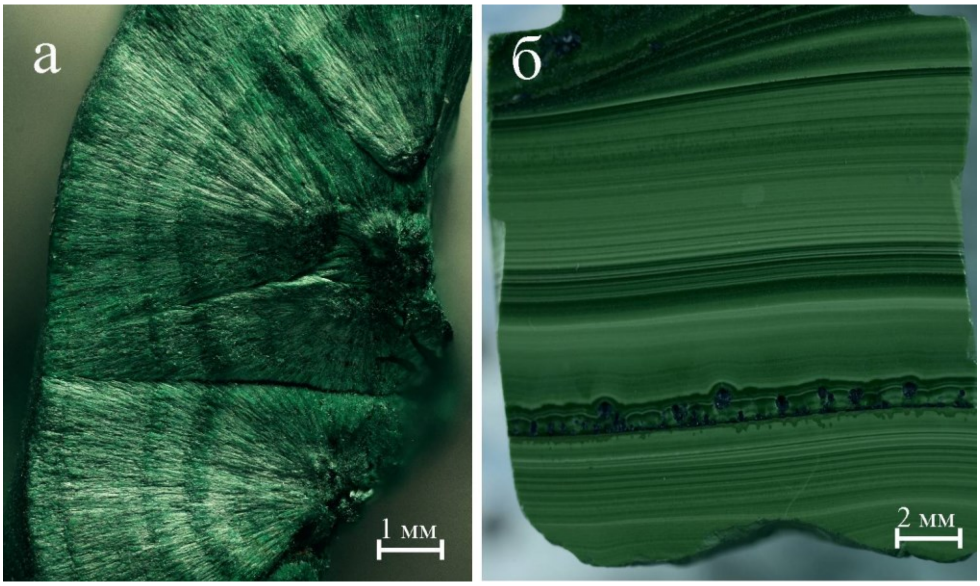

Fig. 1. Synthetic malachite obtained in a closed system a - silky malachite; b - banded malachite.

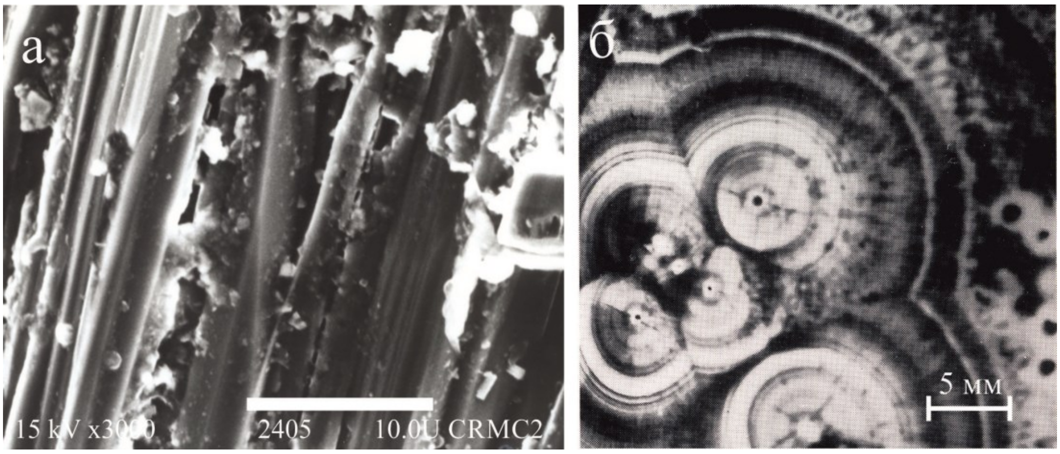

Fig. 2. a - the finest parallel-piecemeal crystals composing synthetic banded malachite; b – bud-like malachite, transverse section.

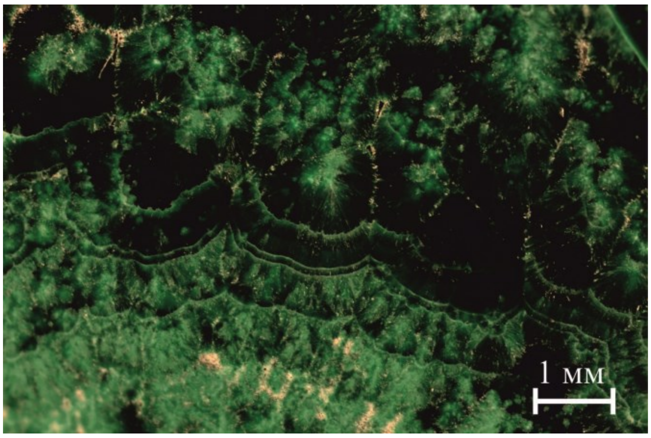

Fig. 3. Fine microspheres of synthetic malachite, grown in an open flow system.

Experiments on the growing of malachite by an open system using low-concentration solutions have not been practically carried out. This is due to the instability of copper-ammonia solutions and a very high labor-intensiveness of the process. Malachite, obtained in a flow system using highly concentrated solutions, is characterized by a less diverse texture with a well-defined zoning (Fig. 3). The mineral outgrowth, on the walls of the vessel and on the seeds of crystals, dense, practically without defects, is composed of small spherolites.

Group growth of spherolites, according to the rule of geometric selection, leads to the enlargement of some and the suppression of growth of other spherolites. However, high rates of crystallization of malachite and additional intensive mixing of the solution with carbon dioxide or other inert gas promote the formation of a large number of new crystallization centers on the growing surface of the mineral and prevent small spherolites from expanding into larger aggregates. The change in the rate of crystallization by variations in the amount of solution supplied to the growth zone allows one to obtain malachite with an intricate, finely-patterned pattern and alternating zones from light to dark green with an emerald or turquoise hue.

The conducted experiments showed the possibility of obtaining malachite of different textural varieties in both closed and open systems. The formation of various textural varieties of synthetic malachite is determined mainly by the method of its synthesis, the crystallization regime and the composition of the solution. Most preferred were copper-ammonia solutions with a high (up to 2 *M* NH_4OH) concentration of ammonia, which provide both high growth rates and the possibility of obtaining malachite with different texture in one experiment.

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