Vestnik Otdelenia nauk o Zemle RAN, VOL. 4, NZ9001, doi:10.2205/2012NZ_ASEMPG, 2012

Experimental study of bismuthous minerals crystallization

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The paper presents results of experimental researches on the synthesis and study of the morphology of bismuthous minerals such as eulytite, sillenite, and bismite. These minerals are extremely rare in nature as well-formed crystals, so the study of their morphology is preferable to synthetic analogues.

Key words: bismuth minerals, hydrothermal synthesis

Citation: Marina, E. A., A. A. Marin, A. B. Makhina, V. S. Balitsky. (2012), Experimental study of bismuthous minerals crystallization, *Vestn. Otd. nauk Zemle, 4*, NZ9001, doi:10.2205/2012NZ_ASEMPG.

Bismuth is rare element. It occurs in nature in the form of numerous minerals, mainly of hydrothermal origin, the principal of which are: bismuthinite or bismuth luster (Bi_2S_3), native bismuth (Bi), bismite or bismite ocher (Bi_2O_3), tetradymite (Bi_2Te_3), etc. These minerals are scattered and occur as impurities in the lead-zinc, copper, molybdenum-cobalt and tin-tungsten ores. The deposits of its own ores of bismuth are rare and relatively small in scale. As an exception may be called industrial clusters of native bismuth in the Ore Mountains (Eastern Germany), Bolivia and Australia. There are about 90 bismuth minerals, but the industrial importance has only a few of them.

We have carried out experimental studies to the synthesis of bismuth minerals such as bismite (Bi_2O_3), sillenite ($Bi_{12}M_xO_{20 \pm \delta}$) and eulytite ($Bi_4(SiO_4)_3$). The studied minerals are extremely rare in nature, especially in the form of well-formed crystals, so the growth and study of their morphology is a very urgent task. In addition, bismuthous minerals have a number of important technical features: scintillation (eulytite) and piezoelectric (sillenite), which determines the relevance of research in this area.

The method of hydrothermal synthesis of bismuthous minerals included the preparation of autoclave equipment, preparation of the solution and the charge and direct experimentation. Growth was carried out at relatively low parameters of temperature and pressure (temperature of 250–260 º C, pressure 500 bar).

Eulytite crystals synthesized in aqueous solutions of NaOH (15%), NH_4F (1–5%), and (for the first time in the world) in solutions of hydrogen peroxide H_2O_2 (2–10%). Growth was carried out in high-temperature autoclaves of 50 and 225 ml, from stainless steel and Cr-Ni alloy. Use of contact Teflon fettle was feature of the technique applied by us, allowing excluding ingress of the elements containing in a steel of autoclaves in a solution. As an initial charge used powdered chemicals Bi_2O_3 (84 wt.%) And SiO_2 (16 wt.%).

Sillenite crystals were grown up in 10% solution of NaOH. Synthesis was carried out in Teflon ampoules in volume of 5–8 ml, which in the amount of six pieces was placed in a high-temperature autoclave also with Teflon fettle. The autoclave was filled with the same solution with the same factor of filling as ampoules. As the charge was used Bi_2O_3 or $NaBiO_3$. In addition, to the charge placed various additives $C_4H_{10}O_6Zn$, Ga_2O_3, Fe_2O_3, SiO_2, $Na_3PO_4 \cdot 12H_2O$, K_2CrO_3, $Al(OH)_3$. Bi_2O_3 or $NaBiO_3$ were 95% of the total mass of the charge, and one of the above additives of 5%.

Bismite formed as a by-product at the synthesis of eulytite and sillenite in NaOH (10–15%) solutions. In the absence of sillenite- formative additives bismite formation is 100%.

The initial charge with the necessary additives placed on the bottom of the autoclave (in amount 5–10 g) or in an ampoule (in amount 1 g), further solution with factor of filling 0.85 (that at temperature 260ºC create in the autoclave pressure of an order the 500th bar) was filled in. Charged thus autoclaves was hermetically closed and placed in an electric resistance furnace. Duration of experiments was from 2 to 20 days. At the end of the experiments autoclaves were opened, the contents of the fettle were taken and the process of separating the synthesized crystals from the crystallization medium began.

The obtained crystals were investigated by means of a digital scanning electron microscope Tescan VEGA II XMU with dispersion spectrometer INCA wave 700, by diffractometer DRON-"g" (Co-radiation, iron filter) and by optical microscope Nikon Eclipse LV 100 POL.

Eulytite crystals grown in different solutions (NaOH, NH_4F, H_2O_2) have tetrahedral habitus, but generally that's crystals aggregates with vague marked faces. The crystals that were grown in hydrogen peroxide were most analogous to natural eulytite.

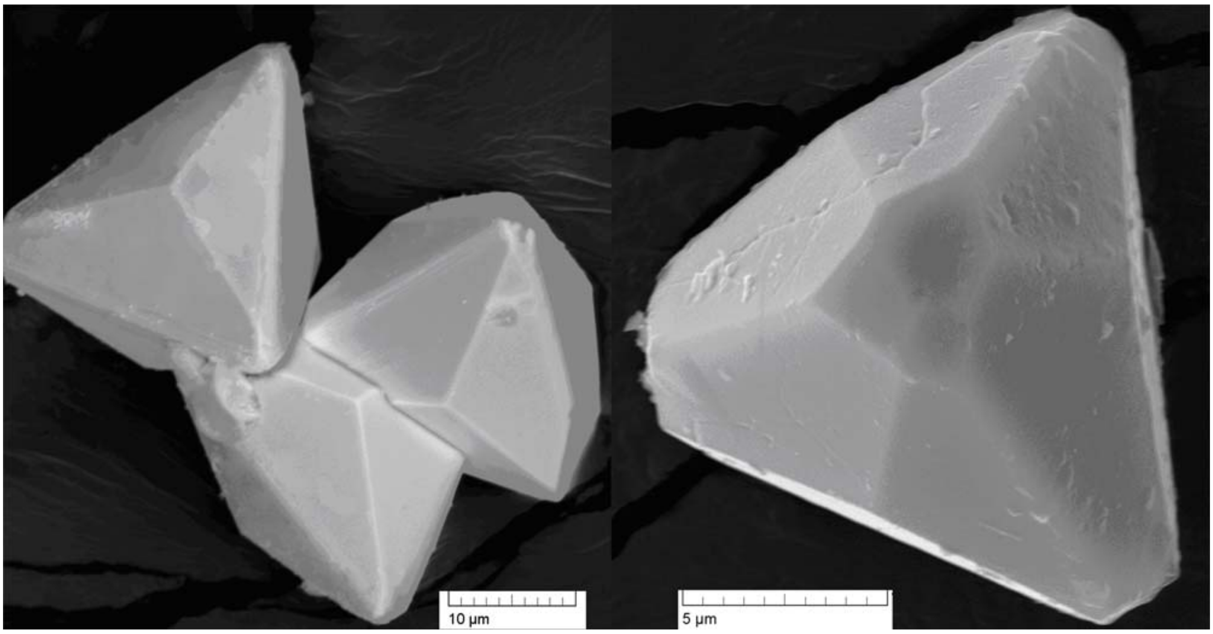

Fig. 1. Eulytite crystals grown in a 5% solution of hydrogen peroxide (photo by scanning electron microscopy)

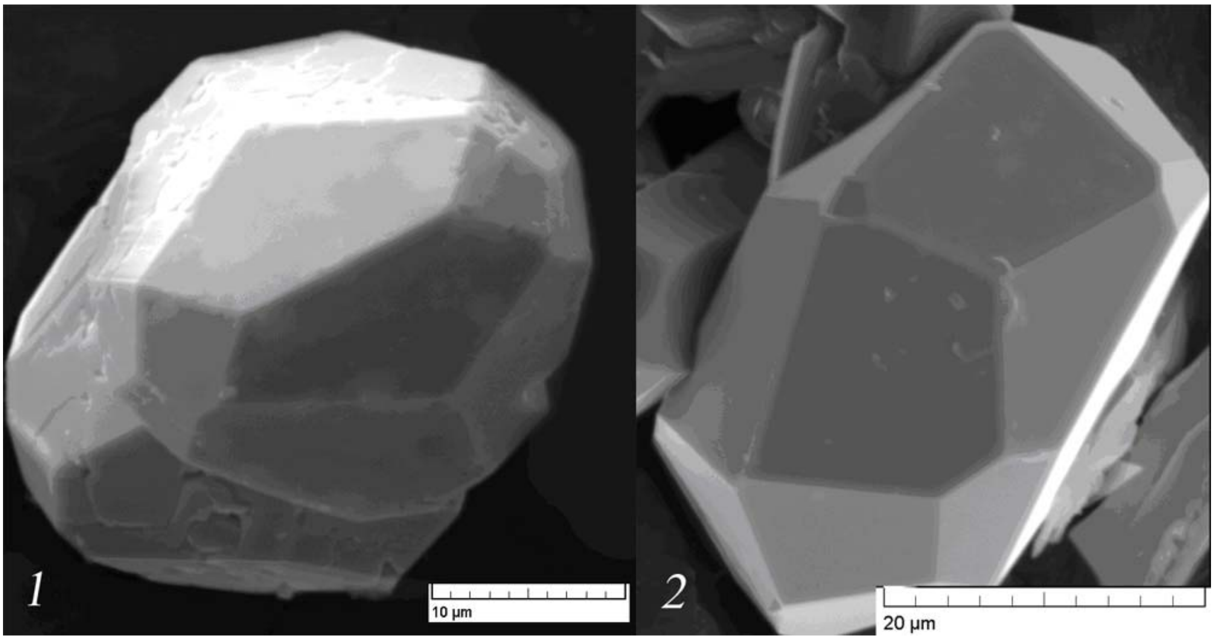

Fig. 2. Eulytite crystals grown in 1 – NaOH and 2 – NH_4F solutions (photo by scanning electron microscopy)

Sillenite crystals grown in NaOH, have trigonal-tritetrahedral habitus. Faces of crystal {100} and {110} are most developed. Since the sillenite occurs as fine-grained earthy masses in the nature, the study of his habitus expedient to carry out on synthetic crystals.

We have synthesized zinc-, gallium-, iron-, silicon-, phosphorus- and chromium-containing sillenite crystals in the size of 0.1–0.5 mm. Zinc-, gallium-, iron- and chromium-containing crystals are usually formed as a tetrahedron, and the silicon- and phosphorus-sillenites as a cube.

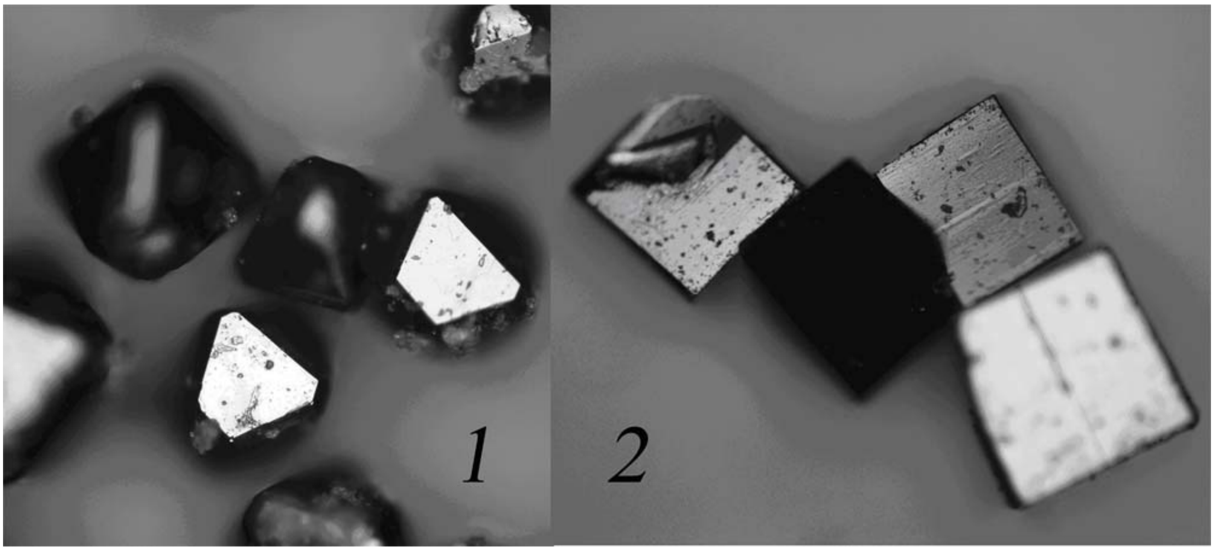

Fig. 3. 1 – gallium sillenite crystals, 2 – phosphorous sillenite (photo by optical microscope)

Bismite Bi_2O_3 crystallizes in the monoclinic syngony. Bismite crystals are pseudorhombic, aggregates are fine-grained and powdery, in nature usually occurs as crusts on the native bismuth. We was synthesized bismite in NaOH. Bismite crystals are pseudorhombic, faces badly formed.

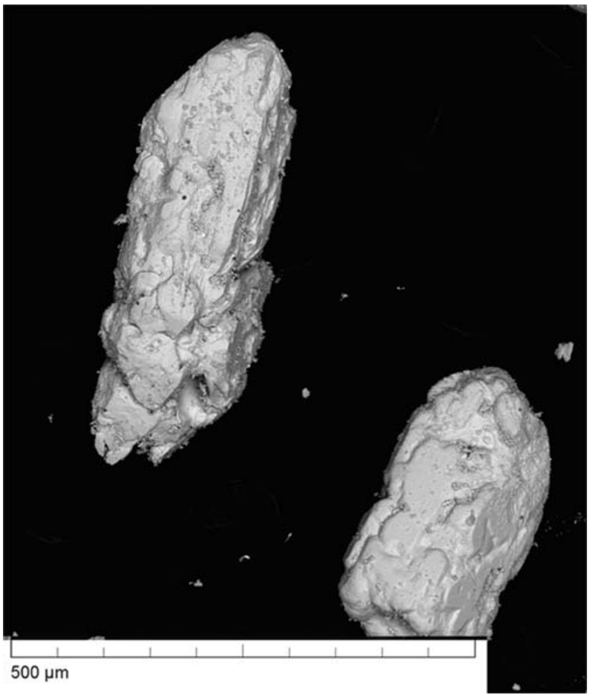

Fig. 4. Bismite crystals (photo by scanning electron microscopy)

The carried-out researches was allowed to obtain of synthetic crystals of the bismuthous minerals which extremely rare in nature, and also to study their habitus.

References

Glembotskiy, V. A. et al (1972). Bismuth: Enrichment of bismuthous-ore, Dushanbe: Donish, p. 150.

Kargin, Y. F., et al (2004). Sillenite crystals. Synthesis, structure, properties, Moscow, Azbuka-2000, p. 316.

Marin, A. A. (1982). The use of hydrothermal synthesis method for the study of crystal-chemical characteristics of sillenite. In the book: Problems in the experimental solid-state and hydrothermal high-pressure apparatus, Moscow, Science, p.214-219.