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Microfluidic devices reduce protein consumption required for identifying crystallization conditions and obtaining well ordered crystals. This nanoliter volumes approach has nevertheless some inconvenient, generally involving higher levels of supersaturation than equivalent experiments at the microliter or milliliter scales.

As the influence of channel depth of the PDMS microcircuits has not yet been evaluated, we have undertaken a comparison of the nucleation depending of this parameter. We observed that it is indeed correlated with the supersaturation needed to get crystals [1]. When the depth of the microchannels is decreasing the number of lysozyme crystals is dramatically reducing whereas their mean size is increasing.

Consequently, in order to uncouple nucleation and crystal growth, we propose original microfluidic chips which can be used to initiate nucleation in its deepest section and facilitate crystal growth in its shallow end.

The data presented in this work can contribute to a better control of the crystallization in microfluidics and shed light for the design of new microcircuits uncoupling nucleation and crystal growth that should facilitate the appearance of single crystals suitable for X-ray diffraction. They can also be used for macroseeding and microseeding experiments to improve the quality and size of crystals obtained after a first random screening.

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Keywords: crystallization, microfluidics, nucleation

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Cubic growth of natural diamond

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Natural diamond grows by at least three different modes: (a) Faceted growth on {111} planes giving octahedra; (b) Fibrous growth in <111> directions giving cubes [1]; and (c) Cuboid growth on crinkly surfaces approximating to {100}, which also produces cubes [1]. Combinations may also occur: growth by (a) followed by (b) gives coated stones [2]; and (a) and (c) growth modes may occur together to give combined morphologies. Twinning of (a) gives spinel-type contact twins (called 'macles') [3] and twinning of (b) gives fluorite-type interpenetrant cubes [4]. Subsequent dissolution may greatly modify the morphology: for example, octahedral diamonds grown by mode (a) may dissolve into rounded rhombic dodecahedra [5].

Here we report the existence of a fourth mode of growth: (d) Faceted growth on {100} planes. Flat cube facets are a common occurrence for *synthetic* diamonds grown by high-pressure high-temperature techniques, especially at the lower range of temperatures at which diamonds are formed; but cube facets are so rare in nature that some have denied that they are a true growth form. It is true that they have been seen only on small diamonds (< 1 mm). Their absence from larger diamonds may simply be the result of their growth rate being much larger than that for octahedral facets and thus they grow out.

We also report another finding [6]: a diamond which has grown by fibrous mode (b), followed by octahedral growth (a): an unusual occurrence, whereas (a) followed by (b) is quite common.

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Keywords: diamond, morphology, X-ray topography

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Calculating the interaction energy between 1-D hydrogen bond motifs using semi-empirical methods

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One dimensional hydrogen bond motifs often, but not always, tend to display needle-like morphologies which extend in the motif direction. Perhydropyrimidin-2-one and a highly substituted derivative display identical 1-D hydrogen bonding motifs. However, the former displays a block morphology while the latter grows exclusively as needles. These observations have been investigated by calculating the interaction energy between a motif and its surroundings.

A 7 motif pack was constructed. Each motif was 6 molecules long and the central one was surrounded by its 6 nearest neighbours. MOPAC2009 [1] was used to optimize this pack using the AM1 method. The pack was then split into a core and a shell and these energies were also computed. The difference in the energy of the core + shell and the energy of the pack is taken to be the interaction energy. The interaction energy per 100 Å^2 of core surface (Connolly) was calculated. There is a significantly lower interaction energy calculated for the substituted system. This suggests that in nucleation and crystal growth the structure will advance slower normal to the 1-D motif direction.

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Keywords: 1D, hydrogen_bonding, morphology

MS35.P28

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Morphology of synthetic tourmaline crystals

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Single crystals of colored Co-, Ni-, Fe-, (Ni,Cr)-, (Ni,Fe)-, and (Co,Ni,Cr)-bearing tourmalines have been grown on a seed in boric, boric–alkaline, boric–fluoride, boric–chloride–fluoride, and boric–chloride hydrothermal solutions at 400–750°C and 100 MPa [1]. The morphology of spontaneous tourmaline crystals formed in experiments in solutions of different composition has been studied.

Crystals synthesized in boric-chloride solutions, are characterized by the long prismatic habit (needles) formed by the trigonal pyramid {10-11} and the hexagonal prism {11-20} faces. Long prismatic crystals also form in boric-fluoride solutions; they show hexagonal and trigonal prisms. As a rule, analogous (-) ends of crystals are broken or monohedron. Crystals formed in boric acid solutions show higher number of faces. The trigonal pyramid {02-21}, the trigonal prism {10-10} and the trigonal pyramid {02-21} are formed in boric acid solutions. Habit of crystals is from short to long prismatic. Unlike natural tourmalines the crystals synthesized in boric-bearing hydrothermal solutions show fewer numbers of faces, which exclusively develop the following main habit forms: trigonal {10-10} and hexagonal {11-20} prism and trigonal pyramids {10-11}, {02-21} and {02-2-1}.

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Keywords: synthetic, crystal, habit

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Synthesis of 13C - diamonds in $CaCO_3$-C system

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Isotope-pure 13C-diamond was synthesized in melts of the Ca13CO3 - 13C system at 8.5 GPa, 2000 K (in anvil-with-hole apparatus) and 20 GPa, 2500 K (in multianvil press). Starting carbonate and graphite (metastable phase) materials were based on 100%-rich 13C-carbon isotope. A"solution-melt" mechanism of 13C-diamond crystallization was realized. The mechanism is characterized by formation of oversaturated in respect to diamond labile carbon solution in carbonate melt (under experimental PT conditions, melting of Ca-carbonate is congruent). Diamond synthesis with the use of mainly 12C –based starting Ca-carbonate and graphite at 8 – 9 GPa, 2100 – 2300 K has been reported previously [1]. Colorless, transparent diamond single crystals of octahedral habit and 5-30 micron size have been grown and are shown in the fig. 1 together with the quenched Ca-carbonate melt. Raman spectra of the synthesized diamond (fig. 2) contain a narrow intensive peak 1280 cm-1, which is characteristic for 13C-diamond based on 100%-rich 13C-carbon isotope.

The experimental results are in agreement with phase diagram of CaCO3. A stable phase region of congruent Ca-carbonate melts within 2300 and 3500 K is determined at 20 GPa by the newest experimental studies [2]. This is of specific interest for the problem of "super-deep" diamond genesis in carbonate-rich growth media of the transition zone and lower mantle of the Earth.

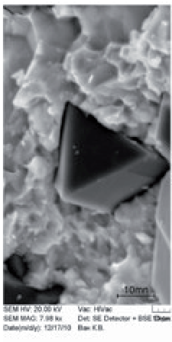

fig.1

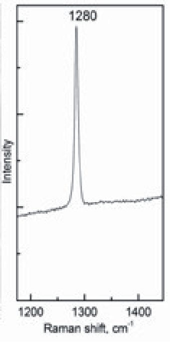

fig.2

Support: Grants of RF President MK-913.2011.5, RAS Presidium P02, RFBR 10-05-00654 and 11-05-00401.

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Keywords: carbonate-synthetic 13C-diamond, carbon, isotope

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Growth and morphology of eulytite crystals synthesized in hydrothermal solutions

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Eulytite ($Bi_4(SiO_4)_3$) is one of the rarest minerals in the nature. It forms as single crystals, aggregate of crystals and radial fiber spherolites. The crystals usually have tetrahedral habitus. Faces of crystal (2-11) and (211) are most developed. Less developed faces are (100), (110), and (111) and rarely developed faces are (511). [1]

Crystals of bismuth orthosilicate (eulytite) are using for scintillator in the high-energy physics, computer tomography, and dosimetry. Eulytite is one of the most promising materials for these purposes, but the problem of production still remains unsolved due to crystals growing from high viscosity melt.

Previously eulytite was synthesed in NaOH solution [2], but subsequent researches in this field did not carry out then.

We have performed hydrothermal synthesis of the fine crystalline bismuth orthosilicate (eulytite) at temperature 250 - 260°C and pressure 500 bars in solutions of sodium hydroxide (NaOH), ammonium fluoride (NH_4F), and hydrogen peroxide (H_2O_2). The stochiometric mixture of standard Bi_2O_3 and SiO_2 chemicals has been used as a starting material. Fine crystalline eulytite has been obtained in the experiments with duration from 7 to 12 days. In our experiments eulytite crystals were growing in ammonium fluoride and hydrogen peroxide solutions for the first time in the world.

Analysis of the run products has shown that hydrogen peroxide is the most perspective solvent for eulytite synthesis since in the system there are no elements strange in composition to eulytite.

SEM investigation of obtained crystals has shown that eulytite single crystals are growing in different solutions have tetrahedral habitus, and crystal aggregates generally grow with vague marked faces.

The crystals growing in oxygen peroxide were most analogous to natural eulytite.

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Keywords: morphology, bismuth, growth

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Conformational polymorphism in the crystal structure of $HgBr_2$ adducts of dppf

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