

## Original articles

Research article

<https://doi.org/10.17308/kcmf.2021.23/3681>

## Investigation of the deposition of calcium fluoride nanoparticles on the chips of CaF<sub>2</sub> single crystals

P. P. Fedorov<sup>1</sup> ✉, M. N. Mayakova<sup>1</sup>, R. V. Gaynutdinov<sup>2</sup>, N. Yu. Tabachkova<sup>1</sup>, G. A. Komandin<sup>1</sup>,  
A. E. Baranchikov<sup>3</sup>, E. V. Chernova<sup>1</sup>, S. V. Kuznetsov<sup>1</sup>, V. K. Ivanov<sup>3</sup>, **V. V. Osiko**<sup>1</sup>

<sup>1</sup>Prokhorov General Physics Institute of the Russian Academy of Sciences,  
38 Vavilova str., Moscow, 119991 Russian Federation

<sup>2</sup>Shubnikov Institute of Crystallography, Federal Scientific Research Centre Crystallography and Photonics,  
Russian Academy of Sciences,  
59 Leninskii pr., Moscow, 119991 Russian Federation

<sup>3</sup>Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,  
31 Leninskii pr., Moscow, 119071 Russian Federation

### Abstract

The deposition of calcium fluoride nanoparticles on single crystal chips of calcium fluoride was studied. CaF<sub>2</sub> nanoparticles were synthesized by co-precipitation from aqueous nitrate solutions using hydrofluoric acid as a fluorinating agent at a batch system. The prepared samples were examined by atomic force microscopy, scanning electron microscopy, transmission electron microscopy and optical transmission. There is an inhomogeneous coating of the substrate surface with submicron particles of about 100–150 nm in size, which are clusters of nanoparticles of 15–20 nm in size. The initial nanoparticles coherently grow on the surface of the crystal substrate. Heat treatment of the substrate-deposited layer composite at 600 °C leads to the coalescence of submicron particles and the formation of a porous layer of a complex structure.

**Keywords:** Fluorite, Single crystals, Nanoparticles, Co-precipitation, Mechanism of oriented attachment growth

**Acknowledgements:** the reported study was funded by RFBR, project number 18-29-12050-MK.

The facilities of the Shared Facilities Center of the Prokhorov General Physics Institute of the Russian Academy of Sciences, the Shared Facilities Center of the Kurnakov Institute of the Russian Academy of Sciences, Shared Research Center of the FSRC “Crystallography and Photonics” RAS and Shared Facilities Center “Materials Science and Metallurgy” of the MISIS National University of Science and Technology (agreement No. 075-15-2021-696) were used.

**For citation:** Fedorov P. P., Mayakova M. N., Gaynutdinov R. V., Tabachkova N. Yu., Komandin G. A., Baranchikov A. E., Chernova E. V., Kuznetsov S. V., Ivanov V. K., Osiko V. V. Investigation of the deposition of calcium fluoride nanoparticles on the chips of CaF<sub>2</sub> single crystals. *Kondensirovannye sredy i mezhfaznye granitsy = Condensed Matter and Interphases*. 2021;23 (4): 607–613. <https://doi.org/10.17308/kcmf.2021.23/3681>

**Для цитирования:** Федоров П. П., Маякова М. Н., Гайнутдинов Р. В., Табачкова Н. Ю., Командин Г. А., Баранчиков А. Е., Чернова Е. В., Кузнецов С. В., Иванов В. К., Осико В. В. Исследование осаждения наночастиц фторида кальция на сколах монокристаллов фторида кальция. *Конденсированные среды и межфазные границы*. 2021;23(4): 607–613. <https://doi.org/10.17308/kcmf.2021.23/3681>

✉ Pavel P. Fedorov, e-mail: [ppfedorov@yandex.ru](mailto:ppfedorov@yandex.ru)

© Fedorov P. P., Mayakova M. N., Gaynutdinov R. V., Tabachkova N. Yu., Komandin G. A., Baranchikov A. E., Chernova E. V., Kuznetsov S.V., Ivanov V.K., Osiko V.V., 2021



The content is available under Creative Commons Attribution 4.0 License.

## 1. Introduction

In recent years, a paradigm change (correction) has taken place in the science of crystal growth: the totality of experimental data reliably indicates that in many cases the growth of crystals in laboratories, in industry, in nature, including in living organisms, is not carried out by attaching of atoms or ions from the environmental medium to the surface of a growing crystal, it proceeds by the oriented attachment of nano-, micro-, or volumetric particles [1–3]. Research on nonclassical crystal growth by the oriented attachment of particles is a “hot topic” of modern materials science [4–14].

One of the main scenarios for nonclassical growth consists of the oriented attachment of small crystalline particles to the surface of a large crystal [15]. The consideration of the possibility of creating surface crystalline layers on a single-crystal substrate in this way is promising.

The aim of this study was the investigation of the deposition of calcium fluoride nanoparticles on chips of calcium fluoride single crystals. The design of experiments was similar to the classic experiment of Shaskolskaya and Shubnikov in 1933 [2, 16] (deposition of small alum crystals on the face of a large alum crystal) with a change in the crystallized substance (calcium fluoride is practically insoluble in water, unlike alum) and particle scale.

## 2. Experimental

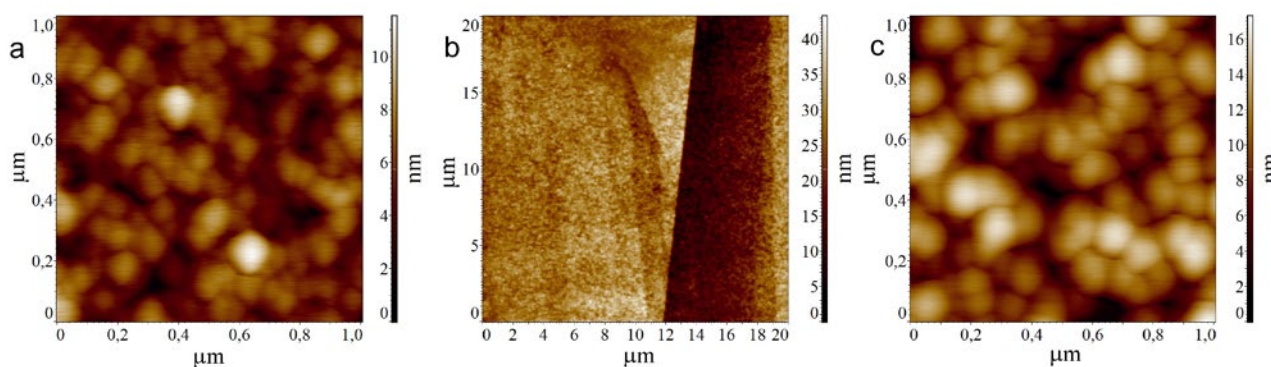
High-purity fluorite single crystals (Hellma, Germany) were split by cleavage by a specially designed manual guillotine [17]. The chip orientation {111} corresponded to the exit of the third-order symmetry axis. The thickness of the

plates was about 2 mm. Atomic force microscopy showed that the surface is atomically smooth and contains steps (Fig. 1).

CaF<sub>2</sub> nanoparticles were synthesized by coprecipitation from aqueous solutions [18] in the batch system. The main parts of the synthesis system were: a polypropylene reactor, a magnetic stirrer, and feed dispensers for initial substances. Hydrofluoric acid was used as a fluorinating agent. Calcium nitrate Ca(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (LANHIT, Russia, 99.99 wt. %), neodymium nitrate Nd(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (LANHIT, Russia, 99.99 wt. %), hydrofluoric acid (extra pure grade 27-5) were used as initial substances. Precipitation at room temperature was carried out by the dropwise addition of a calcium nitrate solution ( $C_N = 0.5$  M) into a solution of hydrofluoric acid ( $C_f = 5$  M) with vigorous stirring with a magnetic stirrer. The colloidal solution was formed as a result of a chemical reaction. The precipitate formed from colloidal solution and then was washed with bidistilled water.

The high specific electrical conductivity of colloidal solutions, which is  $\sim 3$  mS/cm, makes it impossible to experimentally determine their zeta potentials.

A single crystal plate of calcium fluoride was placed horizontally and completely immersed in a colloidal solution (mother solution or wash water with a precipitated reaction product). The plates were placed in the solution one by one: for 1 hour directly during the synthesis process, for a day after the end of precipitation, for 14 days after twice washing the precipitate from the mother solution with bidistilled water. Washes were carried out until the diphenylamine reaction to nitrate ions was negative.



**Fig. 1.** AFM images of sample No. 1 (a) – precipitation, 1 hour, No. 4 (b, c) – precipitation from the mother solution, exposure for 1 day. A step in the chip is visible on the substrate surface

The obtained samples were investigated by atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and optical transmission.

Surface relief of CaF<sub>2</sub> single crystal with deposited nanoparticles was studied using AFM. Measurements were carried out using a scanning probe microscope Ntegra Prima (NT-MDT Spectrum Instruments, Russia) in tapping mode. The silicon cantilevers used (Tipsnano, Estonia) are characterised by the following parameters: resonant frequency  $f \sim 37$  kHz, tip radius  $R \sim 10$  nm and stiffness constant  $k \sim 0.65$  N/m. All experiments on the study of the surface of the samples were carried out under the controlled conditions of the TRACKPORE ROOM-05 measuring complex (class 5 ISO (100), humidity 40 rel. %  $\pm$  1% and temperature  $24 \pm 0.05$  °C).

For scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX), a Carl Zeiss NVision 40 electron microscope (Zeiss, Germany) was used in a high vacuum mode at an accelerating voltage of 20 kV (LaB<sub>6</sub> cathode). Images were formed with a backscattered electron detector (BSE) and a secondary electron detector (SE).

For structural studies, a high-resolution JEM 2100 transmission electron microscope (JEOL, Japan) was used. The JEM 2100 microscope has a spatial resolution of 2.3 Å (point-to-point) and 1.4 Å (lines), a maximum accelerating voltage of 200 kV. The LaB<sub>6</sub> cathode was used as a source of electrons. When obtaining a high-resolution image, an objective lens diaphragm with the diameter of 40 µm was used, which allowed passing a sufficient number of diffracted beams through the optical system of the microscope. For spatial coherence, a condenser lens diaphragm with a diameter of 50 µm was used. The average beam diameter for obtaining images was approximately 100 nm (3 Spot size). Survey images were obtained at low magnifications (5,000–20,000). For a more detailed study of the structure and observation of traces of atomic planes, a direct magnification of 400,000–600,000 was used.

For the investigation of particles on a substrate, samples were prepared in cross section. In order to cut the workpiece from the starting material, ultrasonic cutting was used; the cutting tool was an empty tube with an inner

diameter of 3 mm. Cutting was carried out by excitation of the lead zirconate titanate (PZT) crystals at 26 kHz. The cutting medium was a boron carbide abrasive suspension. Ion etching was performed using a PIPS II system (Precision Ion Polishing System, Gatan) at an accelerating voltage of 3 keV.

The optical transmission of fluorite single crystals, both pure and deposited by layers, was investigated in the IR and terahertz ranges. Measurements were performed using a Bruker IFS113v (IR FT) Fourier spectrometer and a time-domain spectrometer (TDS) described in [19]. Transmission spectra were obtained in the transparency regions of the material in the THz and mid-IR ranges. In the region of high absorption, the reflectance spectra were measured. Reflection spectra were normalized versus a silver mirror reference with a radiation incidence angle of not higher than 6°. All measurements were performed at a temperature of 20 °C. The resolution in IR range was 2 cm<sup>-1</sup>, in the THz range – 0.2 cm<sup>-1</sup>.

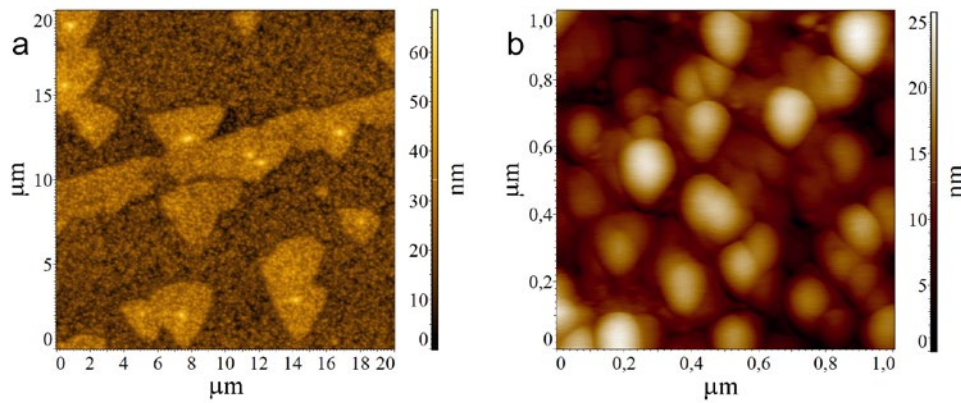
### 3. Results and discussion

Typical AFM data are shown in Figs. 1–3. They slightly varied from experiment to experiment. In general, an inhomogeneous coating of the substrate surface with submicron particles with a size of about 100–150 nm was observed. Particle faceting was not revealed by AFM. The observed pattern is similar to the agglomeration of particles in samples of natural silicites, specifically samples of flints and chalcedony [20].

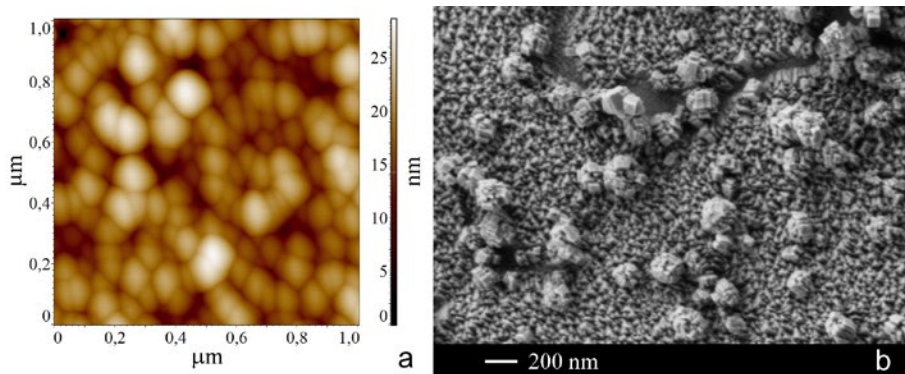
For a sample prepared by deposition with exposure time of 1 h (sample No. 1, Fig. 1a), formations with a size of 40–150 nm were characteristic. When the time of exposure in mother solution was increased up to 24 h (sample No. 4), a significant increase in the size of the formations (70–150 nm) was not observed, however, the general compaction of agglomerates and clearer boundaries between individual formations were noted.

In clusters of particles, agglomerated triangular formations corresponding to the symmetry of the substrate of micron sizes were visible (Fig. 2). SEM data were more informative (Fig. 3). These data allowed visualization of initial small (about 15–20 nm) faceted nanoparticles





**Fig. 2.** AFM image of sample No. 7, precipitation from the washing solution, exposure for 2 weeks



**Fig. 3.** Atomic force (left shot) and scanning electron microscopes (right shot) images. Sample No. 6, mother solution, exposure for 1 day

located on the substrate and mutually oriented. Submicron formations had clusters of these nanoparticles.

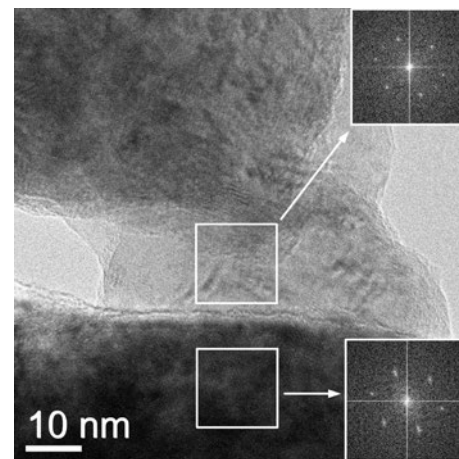
Transmission electron microscopy data (Fig. 4) indicated a coherent growth of fluorite nanoparticles precipitated on a single-crystal substrate. The crystallographic planes of the particles, precipitated on fluorite single crystal had a continuation into the substrate. In addition, the particles of the second deposition layer also retained their orientation relative to the particles of the first layer.

These results confirm the data of the classical experiment of Shubnikov and Shaskolskaya [2, 16] on the oriented growth of small particles during their deposition on the surface of a large crystal.

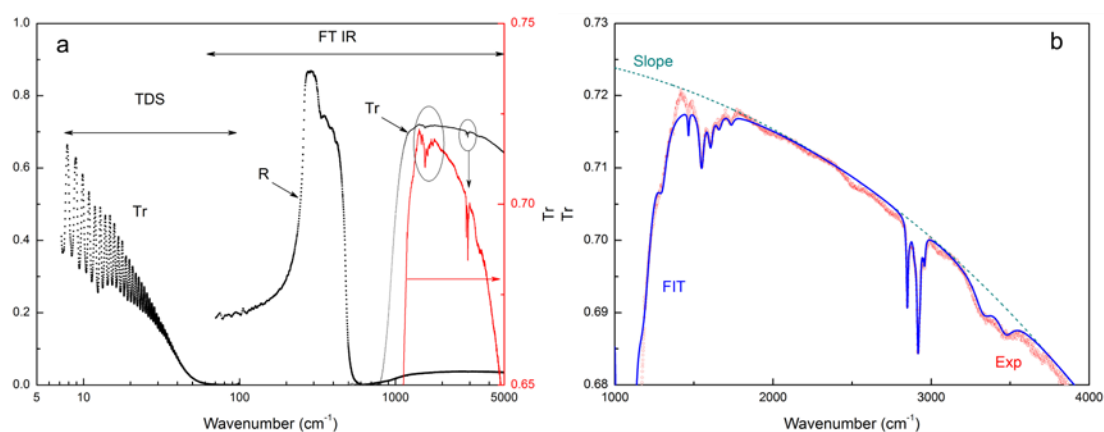
The optical transmission spectrum of a fluorite plate with deposited fluorite particles contains absorption lines in the regions of 1450–1730 and 2850–2930  $\text{cm}^{-1}$  corresponding to vibrations of water molecules and hydroxyl species (Fig. 5). This is natural, since adsorbed water forms tightly bound layers on the surface of

fluorite nanoparticles prepared by precipitation from an aqueous solution.

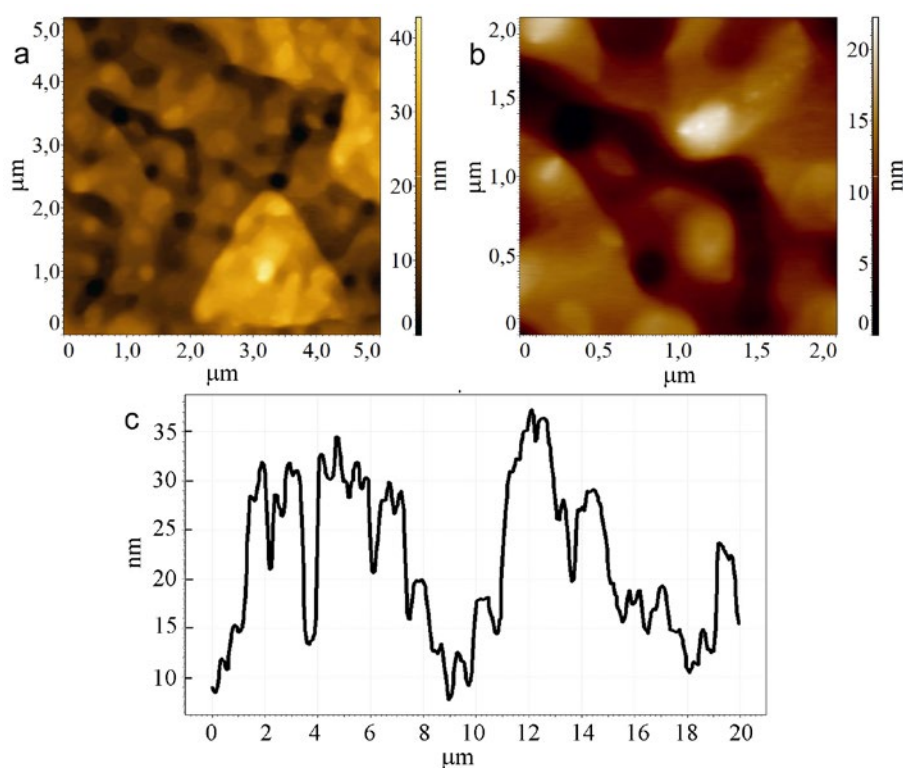
The heat treatment of a fluorite single crystal substrate with a precipitated layer of  $\text{CaF}_2$  at 600 °C was performed. Atomic force microscopy images of the formed layers are shown in Fig. 6. As expected, the attachment growth of the initial particles deposited on the substrate surface with



**Fig. 4.** TEM micrograph, sample No. 1, series “a”



**Fig. 5.** Optical transmission and reflection of a fluorite plate with deposited nanoparticles in the visible, IR and THz ranges



**Fig. 6.** AFM image of the surface of sample No. 7 annealed at 600 ° C for 1 hour (a, b) and the profile of the formed surface (c)

the formation of a single continuous agglomerate of complex topology was observed. The formation of the layer did not finish. The profile of the layer is complex, with strong height differences at the level of 10–30 nm (Fig. 6c).

#### 4. Conclusions

Thus, the deposition of fluorite nanoparticles on the surface of a  $\text{CaF}_2$  single crystal is oriented with a coherent attachment growth to the surface of the single crystal (Fig. 4). However, the formation of associates

of nanoparticles in the initial colloidal solution promotes the chaotic deposition of submicron particles on the substrate surface (Figs. 1–3). The structure formed during the deposition process after heat treatment creates a nanoarchitecture of complex topology. This circumstance prevents the formation of a homogeneous monolithic film suitable for use in photonics on the surface of a single-crystalline substrate. However, this structure of the deposited film can be attractive, for example, for the creation of catalysts.

## Authors contributions

Fedorov P. P. – planning research, writing the article. Mayakova M. N. – carrying out syntheses. Gaynutdinov R. V. – studies by means of atomic force microscopy. Tabachkova N. Yu. – studies by means of transmission electron microscopy. Komandin G. A. – carrying out optical measurements. Baranchikov A. E. – studies by means of scanning electron microscopy. Chernova E. V. – the design of figures, the text, and related materials. Kuznetsov S. V. – discussion of the results. Ivanov V. K. – discussion of the results. Osiko V. V. – the idea of experiments, discussion of the results.

## Conflict of interests

The authors declare that they have no known competing financial interests or personal relationships that could have influenced the work reported in this paper.

## References

- Colfen H., Antonietti M. *Mesocrystals and nonclassical crystallization*. John Wiley & Sons, Ltd: Chichester; 2008. <https://doi.org/10.1002/9780470994603>
- Ivanov V.K., Fedorov P.P., Baranchikov A.Y., Osiko V.V. Oriented attachment of particles: 100 years of investigations of non-classical crystal growth. *Russian Chemical Reviews*. 2014;83(12): 1204–1222. <https://doi.org/10.1070/RCR4453>
- De Yoreo J. J., Gilbert P. U. P. A., Sommerdijk N. A. J. M., Penn R. L., Whitlam S., Joester D., Zhang H., Rimer J. D., Navrotsky A., Banfield J. F., Wallace A. F., Mielke F. M., Meldrum F. C., Cölfen H., Dove P. M. Crystallization by particle attachment in synthetic, biogenic, and geologic environments. *Science*. 2015;349(6247): aaa6760–1–aaa6760–8. <https://doi.org/10.1126/science.aaa6760>
- Garsio-Romero E., Soares M. A structure-based argument for non-classical crystal growth in natural clay minerals. *Mineralogical Magazine*. 2018;82: 171. <https://doi.org/10.1180/minmag.2017.081.031>
- Sushko M. L. Understanding the driving forces for crystal growth by oriented attachment through theory and simulations. *Journal of Materials Research*. 2019;34: 2914–2927. <https://doi.org/10.1557/jmr.2019.151>
- Fedorov P. P., Osiko V. V. Relationship between the faceting of crystals and their formation mechanism. *Doklady Physics*. 2019;64(9): 353–355. <https://doi.org/10.1134/S1028335819090076>
- Neira-Carrillo A., Vásquez-Quitral P., Sánchez M., Farhadi-Khouzani M., Aguilar-Bolados H., Yazdani-Pedram M., Cölfen H. Functionalized multiwalled CNTs in classical and nonclassical CaCO<sub>3</sub> crystallization. *Nanomaterials*. 2019;9(8): 1169. <https://doi.org/10.3390/nano9081169>
- Witts B. D., Clode P. L., Patel N. H., Schroder-Turk G. E. Nature's functional nanomaterials: Growth or self-assembly? *MRS Bulletin*. 1919;44(2): 106–112. <https://doi.org/10.1557/mrs.2019.21>
- Zhou W. Reversed crystal growth. *Crystals*. 2019;9:7. <https://doi.org/10.3390/cryst9010007>
- Liu Y., Geng H., Qin X., Yang Y., Zeng Z., Chen S., ... Kawazoe Y. Oriented attachment revised: Does a chemical reaction occur? *Matter*. 2019;1(3): 390–704. <https://doi.org/10.1016/j.matt.2019.05.001>
- Colfen H. Nonclassical nucleation and crystallization. *Crystals*. 2020;10(2): 61. <https://doi.org/10.3390/cryst10020061>
- Bard A. B., Zhou X., Xia X., Zhu G., Lim M. B., Kim S. M., ... Pauzauskie P. J. A mechanistic understanding of non-classical crystal growth in hydrothermally synthesized sodium yttrium fluoride nanowires. *Chemistry of Materials*. 2020;32(7): 2753–2763. <https://doi.org/10.1021/acs.chemmater.9b04076>
- Mu Z., Tang R., Liu Z. Construction of inorganic bulks through coalescence of particle precursor. *Nanomaterials*. 2021;11(1): 241. <https://doi.org/10.3390/nano11010241>
- Mashiach R., Weissman H., Avram L., Houben L., Brontvein O., Lavie A., Arunacalam V., Leskes M., Rybtchinski B., Bar-Shir A. In situ NMR reveals real-time nanocrystal growth evolution via monomer-attachment or particle-coalescence. *Nature Communications*. 2021;12(1): 229. <https://doi.org/10.1038/s41467-020-20512-6>
- Fedorov P. P., Ivanov V. K., Osiko V. V. Basic features and crystal growth scenarios based on the mechanism of oriented attachment growth of nanoparticles. *Doklady Physics*. 2015;60(11): 483–485. <https://doi.org/10.1134/S1028335815110105>
- Shubnikov A. V. *Kak rastut kristally [How crystals grow]*. Moscow–Leningrad: Publ. AN SSSR; 1935. 176 p. (In Russ.)
- Maslov V. A., Chernova E. V., Fedorov P. P. Search for flux media for crystallization of epitaxial fluorite layers. *Crystallography Reports*. 2020;65(4): 647–652. <https://doi.org/10.1134/S106377452004015X>
- Fedorov P. P., Kuznetsov S. V., Mayakova M. N., Voronov V. V., Ermakov R. P., Baranchikov A. E., Osiko V. V. Coprecipitation from aqueous solutions to prepare binary fluorides. *Russian Journal of Inorganic Chemistry*. 2011;56(10): 1525–1531. <https://doi.org/10.1134/S003602361110007X>
- Komandin G. A., Gavdush A. A., Goncharov Y. G., Porodinkov O. E., Nozdrin V. S., Chuchupal S. V., Spektor I. E. Electrodynamical characteristics of  $\alpha$ -lactose monohydrate in the terahertz range. *Optics*



and Spectroscopy. 2019;126(5):514–522. <https://doi.org/10.1134/S0030400X1905014X>

20. Gaynutdinov R., Voronov V. V., Chernova E. V., Maslov V. A., Mayakova M. N., Chislov A. S., Novikov I. A., Fedorov P. P. Flints as nanostructured chalcedons. *Journal of Surface Investigation: X-ray, Synchrotron and Neutron Techniques*. 2020;14(4):762–770. <https://doi.org/10.1134/S1027451020040084>

### Information about the authors

*Pavel P. Fedorov*, DSc in Chemistry, Professor, Chief Researcher, Prokhorov General Physics Institute of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: [ppfedorov@yandex.ru](mailto:ppfedorov@yandex.ru). ORCID iD: <https://orcid.org/0000-0002-2918-3926>.

*Maria N. Mayakova*, PhD in Chemistry, Researcher of the Laboratory of Technology of Nanomaterials for Photonics, Department of Nanotechnologies at the Research Center for Laser Materials and Technologies, Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [mayakova@lst.gpi.ru](mailto:mayakova@lst.gpi.ru). <https://orcid.org/0000-0003-0713-5357>.

*Radmir V. Gaynutdinov*, PhD in Physics and Mathematics Senior Research, Crystallography and Photonics Federal Research Center of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [rgaynutdinov@gmail.com](mailto:rgaynutdinov@gmail.com). ORCID iD: <https://orcid.org/0000-0002-5384-4026>.

*Natalia Yu. Tabachkova*, PhD in Physics and Mathematics, Senior Research, Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [ntabachkova@gmail.com](mailto:ntabachkova@gmail.com). ORCID iD: <https://orcid.org/0000-0002-0169-5014>.

*Gennadiy A. Komandin*, DSc in Physics and Mathematics, Leading Researcher, Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [gakomandin@mail.ru](mailto:gakomandin@mail.ru). ORCID iD: <https://orcid.org/0000-0003-1101-8225>.

*Alexander E. Baranchikov*, PhD in Chemistry, Head of the Laboratory for the Synthesis of Advanced Materials and Minerals Processing, Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: [a.baranchikov@yandex.ru](mailto:a.baranchikov@yandex.ru). ORCID iD: <https://orcid.org/0000-0002-2378-7446>.

*Elena V. Chernova*, Junior Researcher of the Laboratory of Technology of Nanomaterials for Photonics, Department of Nanotechnologies at the Research Center for Laser Materials and Technologies. Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [e-chernova@yandex.ru](mailto:e-chernova@yandex.ru). ORCID iD: <https://orcid.org/0000-0001-7401-5019>.

*Sergey V. Kuznetsov*, PhD in Chemistry, Head of the Laboratory of Technology of Nanomaterials for Photonics, Department of Nanotechnologies at the Research Center for Laser Materials and Technologies. A. M. Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; e-mail: [kouznetzovsv@gmail.com](mailto:kouznetzovsv@gmail.com). ORCID iD: <https://orcid.org/0000-0002-7669-1106>.

*Vladimir K. Ivanov*, DSc in Chemistry, Corresponding member of the Russian Academy of Sciences, Director of Kurnakov Institute of General and Inorganic Chemistry of the Russian Academy of Sciences, Moscow, Russian Federation; e-mail: [van@igic.ras.ru](mailto:van@igic.ras.ru). ORCID iD: <https://orcid.org/0000-0003-2343-2140>.

*Vyacheslav V. Osiko (1932-2019)*, Academician of the Russian Academy of Sciences, Head of Department of Nanotechnologies at the Research Center for Laser Materials and Technologies, Prokhorov General Physics Institute of the Russian Academy of Science, Moscow, Russian Federation; ORCID iD: <https://orcid.org/0000-0002-3338-6187>.

*Received September 3, 2021; approved after reviewing October 15, 2021; accepted for publication November 15, 2021; published online December 25, 2021.*

*Translated by Valentina Mittova*

*Edited and proofread by Simon Cox*