

## Nanotechnology and material science

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The general features of nanotechnology processes are summarized. There are three key problems that require theoretical understanding: crystal faceting, crystal shaping and hierarchical organization of matter

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Nanomaterials in general, in particular nanofluorides, exist in the realm of non-equilibrium states. They are products of special technologies and are obtained by non-equilibrium physical and chemical transformations. Very often, the latter leads to the formation of previously unknown phases of variable composition and enhanced reactivity [1]. For example, nanofluorides are prone to light pyrohydrolysis [2].

High reactivity can create significant problems for the reproducibility of results and in their interpretation, thus challenging the experimenter's skill. Conversely, these circumstances also make possible unsurpassed opportunities for manipulation in the design of materials, functional features and architecture of the resulting products. It is often possible to produce completely different materials using the same starting reagents. The realm of nanotechnology demonstrates unusual connections between composition, structure, and properties that differ from those found in previously known bulk materials.

Control over nanotechnology-based processes requires – in addition to a cybernetics component (i.e., targeted process control [3]) – mandatory accounting for the spontaneously occurring synergetic transformations [4]. The latter includes, in particular, agglomeration of nanoparticles, which usually demonstrates a clear stepwise hierarchy [5–7].

The available data refute the well-known postulate of thermodynamics, namely, it is generally accepted that labile states are unrealizable, because its transition to the equilibrium state is not associated with overcoming the potential barrier, there is no force that returns the system to its original state, and after the fluctuation out of equilibrium, the system moves away from it with acceleration [8,9]. For example, the crystalline solid solution  $Ba_{1-x}Ca_xF_2$  samples, prepared by mechanochemical treatment, can exist in a non-equilibrium state indefinitely. After heating, the system goes to the equilibrium state, namely, the decomposition of the solid solution takes place, and it is accompanied by heat release (exothermic effect) [10]. Apparently, the relative stability of the crystalline samples of the  $Ba_{1-x}Ca_xF_2$  solid solution is due to the extremely low values for the diffusion coefficients of the cations. The system is “falling”, but very slowly.

Ostwald's step rule [11] works unequivocally for the nano-objects, and phase transformation sequences always start with the most non-equilibrium amorphous products that turn into more stable phases in a stepwise manner.

A separate problem is to establish the true picture of phase equilibria at low temperatures. Very long equilibrium times, in many cases, make experimental studies impossible [12]. The use of molten salt synthetic techniques allows ones to significantly expand the temperature range available to the study [13, 14]. It is worth noting that, according to the third law of thermodynamics, all solid solutions are non-stable phases at low temperatures [12].

The nanotechnology realm systematically displays non-classical crystallization by oriented attachment crystal growth [15, 16]. These processes are implemented as in the primary formation of nanoparticles (see Fig. 1), and the behavior of nanoparticle ensembles during their thermal treatment [17]. The formation of associated crystals with an increased content of defects can trigger the classical Barton–Prim–Slichter mechanism of crystals growth [15].

The lack of a theoretical description of non-classical crystallization processes is acutely felt. At least three problems remain to be solved.

- (1) The problem of crystal faceting. Nanoparticles conceived do not obey the Curie–Wulf principle [18]. It is possible that there is another dimensional effect [19], which consists in lowering the temperature of the phase transition of the faceting while reducing the particle size.
- (2) The problem of shaping. A number of experiments show that agglomerating nanocrystals tend to assume the correct microcrystal shape (habit) in advance, followed by filling the volume with a crystalline material [14].

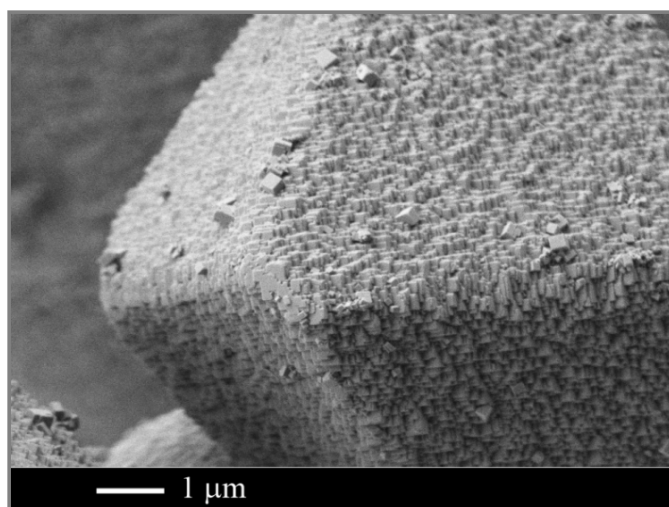


FIG. 1. SrF<sub>2</sub> microcrystal, consisting of nanocubic particles, which were synthesized by the reaction of SrCl<sub>2</sub> + KF = SrF<sub>2</sub> ↓ + KCl at 1000 °C. Synthesis was performed by V. A. Maslov and SEM was performed by A. E. Baranchikov

- (3) The problem of understanding the hierarchical organization of matter and quantization of particle size: in the processes of agglomeration and dispersion in the range of 10<sup>-9</sup> – 10<sup>8</sup> m, a spectrum of the most probable particle sizes corresponding to the geometric progression is regularly observed [20].

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