

## CRYSTAL GROWTH



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Research interests: crystal growth, crystal-chemical design, phase diagrams, material science, nonlinear optics, topological insulators.

### Course description

The vast majority of our planet's solid matter is in a crystalline state, so understanding crystallization processes is an important aspect in the earth sciences. Extraction of information recorded in the real structure of crystals makes it possible to analyze and reconstruct the processes of mineral formation. The study of changes in mineral associations and comparisons with equilibrium phase diagrams can provide important petrological consequences. In addition, progress made in such areas as microelectronics, communications, medical equipment, technologies for space and energy, would not have been possible without previous advances in the production of technical crystals. A further increase in the performance of high-tech devices is due to the improvement of crystal growth techniques and discovery of new promising crystalline substances.

### Course content

**Nucleation processes:** The driving force of crystal growth. Factors determining nucleation. Specific surface energy, work of nucleation, critical supersaturation, size of critical nucleus. Homogeneous and heterogeneous formation of embryos. Metastable and labile regions.

**Crystal growth mechanisms:** Two-dimensional nucleation, layered spiral and normal growth, periodic chain's bonds and surface energy estimation, F, S and K-faces, Jackson's theory, the relationship between the supersaturation value and the crystal morphology (coarsening/roughening of the liquid – crystal interface), the ratio between the supersaturation value

and the growth rate, limiting stage of the growth process, diffusion, and kinetic modes of crystal growth, diffusion field of a polyhedron, and non-constant supersaturation on the edges.

**Defects in crystals:** Equilibrium and nonequilibrium lattice defects, geometric classification of lattice defects. Point defects: vacancies and interstitial atoms, the role of impurities, electrons and holes, and external influences on the concentration and configuration of point defects. Dislocations. Burger's contour and vector, dislocation energy. Dislocation splitting. Block formation in crystals, dislocation structure of block boundaries. Twins. Direct observation of lattice defects: ion microscopy, electron microscopy, X-ray methods, selective etching.

**Effect of impurities and growth conditions on the morphology of real crystals:** kinetics of impurity capture, zonal, sectorial, and structural heterogeneity, diffusion layer, surface processes, concentration overcooling and geometric selection. Observed distribution coefficients. Growth forms. The influence of growth conditions. Edge effect. Defects in real crystals, inclusions, dislocations, temperature stresses, vacancies and impurities, block boundaries.

**Phase diagrams:** Gibbs phase rule, one-component systems (water, carbon, sulfur,  $\text{SiO}_2$ ,  $\text{Al}_2\text{SiO}_5$ ), two-component systems (five types of Gibbs-Roseboom diagrams), three-component systems. Methods for determining compositions on binary and ternary diagrams. The choice of the method for crystal growth. Impurity distribution coefficients (equilibrium, effective).

**Basic physicochemical methods of crystal research:** Sample preparation. X-ray structural and X-ray phase analyzes, Wolfe-Bragg's law, principles of decoding powder diffraction patterns. Micro X-ray spectral (microprobe) analysis, principle of operation, limitations, selection of standards. Thermal analysis, the difference between the melting and crystallization temperatures of a substance, calculation of heat capacity, thermal memory of samples. Approaches to the study of phase diagrams - study of polythermal and isothermal sections.

**Modern application of crystals' properties:** Pyroelectrics (linear and nonlinear dielectrics, ferroelectrics, electro-optical phenomena, electro-optical shutters and modulators), piezoelectric effect, laser media, nonlinear optical effects, and semiconductor properties. The design of the transistor, solar battery, Peltier thermoelement, and principles of operation.

**Laboratory crystal growth methods:** Physicochemical basics of crystallization from a melt, container material, and crystallization atmosphere, heat and mass transfer processes, methods with a large melt volume: Kyropoulos, Czochralski, Stockbarger - Bridgman, methods with a small melt volume: Verneuil, zone melting. Defects in crystals grown from the melt and ways to control the real structure. Growing crystals from solutions. Low, medium, and high-temperature solutions. Defects in crystals grown by the hydrothermal method and ways to eliminate them. Natural

magmatic systems as sequential crystallization of phases from melt-solutions. Crystallization from vapor phase. Methods using physical condensation: cathode sputtering, molecular beam epitaxy, and the bulk vapor phase method, crystallization in an inert gas stream, methods of crystallization with the participation of chemical reactions: chemical transport, methods with decomposition of compounds, and chemical synthesis. Crystallization from vapor through a liquid phase layer.

**Practice in phase diagrams:** Monovariant and invariant equilibria. Extremum points on liquidus and solidus curves. Daltonides and bertholides. Subsolidus transformations. Metastable phases. Isothermal and polythermal sections. Quadruple reciprocal systems.

**Workshop on crystallization in the new laboratory:** Crystallization from aqueous solutions and high-temperature synthesis of oxide compounds.

