TEACHING CRYSTAL GROWTH FOR STUDENTS-CRYSTALLOGRAPHERS

Nikolai I. Leonyuk

Moscow State University, Geological Faculty, Dept. of Crystallography and Crystallochemistry, Moscow 119899, Russia, E-mail: leon@geol.msu.ru

Abstract

This crystal growth course has evolved as a self-consistent curriculum of lectures, seminars, training and research in laboratories at Moscow State University in collaboration with other universities, academic institutions and industry for nearly two decades. There are three stages of this long-term crystal growth teaching: 1) general course of lectures and seminars addressed to students at all levels; 2) laboratory courses providing practical experience and making some concepts and techniques more concrete; 3) research work for students who intend to major in crystal growth. This interdisciplinary course unifies various aspects of the recent progress in the physical, chemical and mineralogical materials science.

1. Introduction

Crystal growth is being taught in many universities, and the course scope specifically depends on the profile of interests of the department and/or college. Traditionally, it is mostly a fragmentary and applied tool of interest for materials scientists, solid-state physicists and chemists, inorganic and physical chemists, electrical engineers, gemologists and mineralogists. Often, students and researchers take only a course in crystal growth techniques that is directly related to obtaining selected crystalline materials for their measurements. Mineralogical aspects of this discipline usually concerns the relationships between genesis, morphology and homogeneity of natural crystals, in order to explain several crystallization processes in nature.

However, it is believed that cross fertilization plays a significant role in the development of any teaching and scientific methods, and it is important to keep abreast of new approaches as they appear. Within a few recent decades, the sub-topic of crystal growth has developed from being a largely academic discipline to being one of the key fields in materials science. Single crystals, epitaxial layers and multilayer structures have become the basis for research in solid-state science and for numerous modern technologies. This paper is focused on a new long-term crystal growth course as an example of a self-consistent curriculum containing lectures, seminars, laboratory practices and research work. The course has evolved for nearly two decades, and it has combined the educational and research experience of the author of this course in this field of crystal growth and characterization of materials at Moscow State University (MSU) and in collaboration with other universities, research institutions and the industry.

This course is one component of a full academic load for B.Sc., U.D. (University Degree) and M.Sc. students of the MSU, and it is offered for students at the beginning of the 3rd academic year and through the next eight semesters. However, the students who intend to major in the field of crystal growth and characterization of materials spend on this course 40%, 50%, 70% and 90% of the typical student's time in the 3rd, 4th, 5th and 6th academic years respectively.

2. Curriculum Contents

The field of crystal growth can be divided into fundamentals and growth techniques. Fundamentals addresses the underlying scientific principles relevant to all the techniques of crystal growth and to all materials. It is also devoted to the influence of transport-limited growth on the stability of both isolated growth forms (such as the dendrite) and arrays, and on the cooperative effects which lead to pattern formation. Growth techniques cover Nature's techniques, bulk crystal growth, thin films and epitaxy, and some specific materials for science and modern applications.

The lectures are a general overview of this course material, but may include specific examples that are not given in textbooks and journals. The associated laboratories are intended to demonstrate crystal growth techniques, and to teach the students to perform simple experiments and related procedures on the crystal growth of model materials which can be made easily and safely by students. This training provides a helpful practical experience. The seminars and recitations provide many important details for the course and can help with making some models of crystal growth more concrete. Table 1 provides a topical outline of the scope of the lectures, seminars and laboratory work that now constitute this course. Textbooks and literature recommended for student reference are cited (refs. [1-9]).

3. General Course Milestones

The Crystal Growth course is offered for students in their third year of university education, i.e. at the beginning of the 5th semester. By that time, students intending to major in Materials Science and surrounding disciplines are aware of the most general physical laws and phenomena, and chemical processes, and they may already have taken some mathematical courses. There are no absolute prerequisites for the crystal growth course, but students have taken reasonable introductory courses in areas such as physics and chemistry of the condensed state, crystallography and crystal chemistry, thermodynamics, etc. In addition to lectures and laboratories, knowledge for the crystal growth course will be gained from textbooks, 2 seminars, and 2-3 homeworks for each semester. Also, during each semester the plan suggests one midterm exam and the final exam.

5th Semester: September - January

Three topics such as "Introduction", "Nucleation, structurally attributed shape and equilibrium shape of ideal crystals" and "Growth mechanisms of perfect crystals", held the Fall semester, constitute an introduction to all of the areas of crystal growth.

6th Semester: February - June

Topic "Crystal growth methods", with related training is planned for the 6th Spring semester, through the February - May period. Training in the University's laboratories covers the following topics:

(A) Aqueous solutions: experimental determination of solubility curves for AlK-alums, ammonium phosphate and Seignette's salt ($KNaC_4H_4O_6 \cdot 4H_2O$);
(B) Crystal growth of AlK-alums from aqueous solutions doped with borax and various dyes;
(C) Low-temperature hydrothermal growth of rare earth phosphate crystals;
(D) Hydrothermal synthesis of rare earth silicates;
(E) Flux growth of rare earth phosphate crystals;
(F) Liquid-phase hetero-epitaxial growth of NH_4I, KI, KBr and KCl on mica substrate: microscopic observation;
(G) Czochralski growth of Pb-germanate crystals;
(H) Kyropolous growth of KBr crystals;
(I) Stockberger growth of bismuth crystals.

June is reserved for training in academic research institutions and industrial laboratories. Examples of topics for this research training are:

(A) Hydrothermal growth of piezo-quartz, optical calcite, zincite, berlinite;
(B) High-temperature flux growth of mica crystals;
(C) Czochralski growth of bismuth orthogermanate crystals;
(D) Growth of rare earth aluminate crystals by float zone melting;
(E) Synthesis of diamond.

At the end of March, all students defend publicly their first research project.

7th Semester: October - January

Topics "Growth of real crystals" and "Transport processes and morphological stability" and the laboratories listed below are suggested for this Fall semester.

(A) Computer simulation and computer graphics of external and internal crystal morphology;
(B) The effect of supercooling and supersaturation on the morphology of NaCl, NH_4Cl, $KAl(SO_4)_2 \cdot 12H_2O$ and $HO \cdot C_6H_4 \cdot CO_2 \cdot C_6H_5$ crystals: in situ microscopic observation;
(C) In-situ observation of the $MgSO_4 \cdot 7H_2O$ and $KNaC_4H_4O_6 \cdot 4H_2O$ crystal growth morphology depending on the various admixture concentrations in aqueous solutions;
(D) Microscopic observation of spiral growth on the singular faces of moissanite (α-SiC) crystals;
(E) In-situ observation of etching faces on NaCl, KBr and CaF_2 crystals;
(F) Morphology of germanium epitaxial films: microscopic observation;
(G) Morphological study of twin boundaries and gaseous inclusions in synthetic mica crystals.

8th Semester: February - May

Topics "Experimental equipment" and "Growth of technological single crystals" are scheduled for this Spring semester. In this spring semester, all the students defend publicly their second research project that qualifies for B.Sc.

9th Semester: October - January

Topic "Crystal growth in Earth's Interior" is suggested for the 9th Fall semester, but topic "Growth of technologically important single crystals" is expected to be continued, especially, in the part concerned with crystal growth of novel and unconventional materials. Current problems and future trends will also be discussed.

10th Semester: February - May

This Spring semester is reserved for completing third research project as a base for the final grade towards the University Degree (U.D.). At the end of this semester, the students who intend to obtain the U.D. as their final grade must defend publicly their third/final research project.

6th Academic Year: 11th and 12th Semesters

The final academic year is reserved for completing the Master of Science programme in the field of crystal growth and characterization of crystals.

4. Research Work

Some examples of current research projects which should be performed and defended each year are listed below:

(A) High-Temperature Crystallization in Borosilicate Systems Towards Development of Novel Materials for Science and Modern Technology;
(B) Controlled Flux Growth, Study of Composition and Morphology of Corundum Crystals Doped with Trivalent Metals;
(C) Growth and Morphology of the 123 High-Tc Family's Single Crystals;
(D) Study of Epitaxial Intergrowth of Isostructural Phases in Bi-2212 High-Tc Single Crystals;
(E) Czochralski and Flux Growth of Rare Earth Oxiorthosilicates;
(F) Hydrothermal Growth and Characterization of Zincite Single Crystals Doped with Di- and Trivalent Metals;
(G) Low-Temperature Synthesis and Flux Growth of Rare Earth Pyro- and Metaphosphate Crystals with Laser Device Potential;
(H) Growth and Morphology of Paraffin Crystals Grown under Various Conditions.

The topics are assigned, taking student preferences into account. Students may begin to work on their first projects in research laboratories since the 5th semester. However, during the 5th and 6th semesters they should work beyond their typical student's time for the topics listed in the Section 3, and the defense deadline is at the end of March. For carrying out the second (B.Sc.) and third (U.D.) projects, all students may take the opportunity of nine-week internships and/or visiting assignments in university research laboratories, academic institutions or industry during summer periods after 6th and 8th semesters, respectively. Additionally, the 10th spring semester is reserved for completing the third research project, and the 6th academic year (the 11th and 12th semesters) is reserved to perform their fourth research projects. The second research project (B.Sc.) should be defended at the second half of spring, and the deadline for the third project (U.D.) is set at the end of May. And finally, the fourth research project is directed towards obtaining the M.Sc. degree. Graduates from this program may be invited to work in the field of crystal growth and characterization of materials at universities, at academic institutions or in industry. The most outstanding students are encouraged to pass entrance examinations and to begin their work towards the Ph.D. degree.

5. Conclusions

An attempt was made to apply various aspects of recent developments in physical, chemical and geological materials science in the crystal growth course. This self-consistent course is primarily aimed at students intending to major in crystallography as an interdisciplinary field of science. However, scheme of the course allows interdisciplinary students and engineers to attend this course at any stage for one semester or more, when that need arises. For example, Physics, Chemistry, Materials Science, Mineralogy or Engineering students are welcome to take most of this material in one form or another, as an applied tool to give them knowledge and practical experience concerned with obtaining crystalline materials required for their own experimental programs. Strong interaction and integration between the University Education Program, the Academy of Sciences' Institutions, and Industry seems to be one of the keys to developing effective researchers and engineers for the future.

Acknowledgment

The concept of this curriculum has benefited and was developed from the long-term discussions and assistance of many colleagues in our country and abroad. The author is indebted to colleagues, too numerous to mention, from the Faculties of Geology, Physics and Chemistry at MSU, from the Institutes of Crystallography, Solid State Physics and Experimental Mineralogy of the Russian Academy of Sciences; to colleagues, staff and administration of the All-Russian Research Institute for the Synthesis of Minerals and the Factory of Single Crystals of the Russian Ministry of Natural Resources for the support and four-week training of MSU's students each year for the past two decades. This programme was supported, in part, by Soros' Educational Programme (ISSEP), grants Nos.651p (1997) and p98-1067 (1998).

References

1. *Handbook of Crystal Growth* (in 3 Volumes), edited by D.T.J.Hurle, North-Holland Publ., Amsterdam- London - New York - Tokyo: -Vol. 1. *Fundamentals*: Part A - *Thermodynamics and Kinetics*, Part B - *Transport and Stability* (1993); -Vol. 2. *Bulk Crystal Growth*: Part A - *Basic Techniques*, Part B - *Growth Mechanisms and* Dynamics (1994); -Vol. 3. *Thin Films and Epitaxy*: Part A - *Basic Techniques*, Part B - *Growth Mechanisms* and Dynamics (1995).

2. W. Kurz and D.J.Fisher, *Fundamentals of Solidification*, 3rd ed., Trans Tech Publ. (1989).

3. *Synthesis of Minerals*: Vol. 1 (by V.E.Khadgy, L.I.Tsinober, N.L.Shterenlikht, et al.); Vol. 2 (by Yu.M.Putilin, Yu.A.Beliakova, V.P.Golenko, et al., Nedra Publ., Moscow (1987) in Russian.

4. *Advanced Crystal Growth*, edited by P.M.Dryburgh, B.Cockayne and K.J.Barraclough, Prentice Hall International (UK) Ltd. (1987).

5. J.C. Brice, *Crystal Growth Processes*, Blackie & Son Ltd., Halsted Press (1986).

6. *Modern Crystallography* (in 4 Volumes), edited by B.K.Vainshtein, A.A.Chernov and L.A.Shuvalov. Vol. 3: *Formation of Crystals*, by A.A.Chernov, E.I.Givargizov, Kh.S. Bagdasarov, V.A.Kuznetsov, L.N.Demianets and A.N.Lobachev, Nauka Publ., Moscow (1980) in Russian.

7. D. Elwell and H.J. Scheel, *Crystal Growth from High-Temperature Solutions*, Academic Press, London - New York - San Francisco (1975).

8. R.A. Laudise, *The Growth of Single Crystals*, Prentice-Hall, Inc, Englewood Cliffs, New Jersey (1970).

9. *The Art and Science of Growing Crystals,* edited by J.J.Gilman, John Wiley & Sons, Inc., New York - London (1963).

Table 1. Topical outline of the Crystal Growth course.

Topic	Contents	Semester
Introduction	Condensed and gaseous media. Solids. Ideal and real crystals. Crystallization phenomena. Mass crystallization and bulk (single) crystal growth. Reasons for growing single crystals: the importance of theory and crystal growth technique for science and technology. General aim and outline of the crystal growth course: nucleation, kinetics and mechanisms of crystal growth, selection of growth technique, influence of crystal growth parameters on the size, external morphology, internal perfection and homogeneity of crystals, morphological stability, pattern formation in crystal growth process, etc. Historical development of crystal growth.	5th
Nucleation, structurally attributed shape and equilibrium shape of ideal crystals	Phase equilibria and phase transitions. Crystallization as a first-order phase transition. Phase diagrams. Two-phase equilibrium: isotropic examination of surface excess free energy. The driving force for crystallization. The nucleation work in the homogeneous media. The isotropic critical nucleus. Activation free energy. Nucleation as a result of fluctuations. Geometric model for nucleation. Rate of nucleation in different media. The structurally attributed shape of crystalline nuclei and available approaches for their estimation. Equilibrium shape of crystals. The Gibbs-Thomson-Herring's relationship. The Gibbs-Curie-Wulff's rule. The microscopic approach developed by Stranski and Kaischew.	5th
Growth mechanism of perfect crystals	Heterogeneous media: nucleation on foreign particles. Size and shape of critical nucleus. Two-dimensional nucleation: work and rate. Epitaxy, crystal chemical relation. Anisotropy of surface free energy. Types of crystal faces: flat, rough and slightly misoriented surfaces. Hartman-Perdok's PBC concept: F (flat), S (stepped), K (kinked) faces. Models of two-dimensional interface (mother phase/crystal phase). Two basic growth models: normal growth and layered growth. Conditions for roughness of solid-liquid interface. Boundary layer structure. Stages in growth process. Diffusion process: total and surface diffusion. Anisotropy of layered growth rates. Conditions of layered growth of crystals from vapour, solution and melt.	5th
Crystal growth methods	Classifications of growth techniques based on formal expressions of the driving force for crystallization and on methods used to attain metastability of the mother phase. *Growth of crystals from the melt.* *Czochralski technique:* historical overview, principles, types of heating, rotation, growth rate, shaped growth, crucibles and without crucibles, bulk growth, fibre growth, some examples, merits and demerits of the method. *Kyropolous method:* history, principles, heating, rotation, homogeneity of the composition, crucible, growth rate, crystal size, correlation with Czochralski technique, advantages and disadvantages, some examples. *Bridgman-Stockberger method:* historical background, principles, advantages and disadvantages, some examples. Zone melting: historical development, principles, merits and demerits, examples. *Verneuil method:* historical introduction, advantages and disadvantages. *Principles of solution growth.* General solution concept. Solute-solvent interactions. Choice of solvents. Phase diagrams and solubility curves. Structure of solutions. Classification. *Flux growth:* history, principles, popularity, classical growth from high-temperature solutions, growth from non-stoichiometric melts, solvents and solvent selection, solvent concentration, supersaturation by cooling, heating, evaporation, temperature difference method, different versions/variants of the flux growth epitaxial flux growth, top-seeded solution growth (TSSG), flux growth modified by Kyropolous technique, some examples, merits and demerits, growth rate, crystal quality, crystal morphology, size, etc. *Hydrothermal growth of crystals:* historical background, principles, popularity, advantages, spontaneous nucleation, temperature gradient, solubility, solvents, variants, growth rate, some examples, disadvantages, valency control, use of different nutrients to obtain another modification on the seed of that crystal, for example, cristobalite nutrient on α-quartz, gibbsite on corundum seed. *Growth of crystals from aqueous solutions:* history, principles, popularity, supersaturation through change in temperature, temperature difference, evaporation, chemical reactions, etc. solubility, merits and demerits. *Crystal growth in gels*. *Electrocrystallization.* *Crystal growth in vapour phase.* *Physical condensation:* principles of molecular-beam epitaxy (MBE), cathode sputtering; solid phase epitaxy, bulk crystallization, atomic layer epitaxy, epitaxy with carrier gases. *Chemical condensation:* chemical vapour deposition (CVD), chemical transport, metallo-organic vapour phase epitaxy (MOVPE), chemical synthesis from simple to complex.	6^{th}

Growth of real crystals	The nature of defect formation in crystals. Point defects: vacancies, interstitial and foreign/substitutional atoms, colour centres. Impurity effects on the crystal growth process. Physical and chemical absorption. Incorporation of impurities. Homogeneous and heterogeneous trapping. Equilibrium/non-equilibrium distributions of impurities. The effective trapping coefficients. Line defects: screw and edge dislocations. Screw dislocations as the nucleation centres: spiral growth mechanism is the third of basic crystal growth models. Examples of spiral growth models. Planar defects: low angle boundaries, stacking faults, twin boundaries. Examples of the influence of twinning on the growth mechanism. Formation of bulk defects: mosaic structure, compositional inhomogeneity/striations, foreign inclusions/particles (solid, liquid, gas).	7th
Transport processes and morphological stability	Diffusion, convection, radiative heat transport. Modeling crystal growth processes. Flow and morphological stability. Conditions for stable growth. Unstable growth. Pattern formation in crystal growth: conditions, experimental observation, approaches to modeling. Dendritic crystal growth. Correlation between the theoretical and real crystal forms. Morphology of crystals in relation to growth conditions. Morphology of polyhedral crystals. Surface microtopography. Internal morphology: perfection and homogeneity. Sectorial and zonal growth.	7th
Experimental equipment	Apparatus. Heating and cooling systems. Temperature control. Crucibles. Chemicals. Seed mounting and separation of grown crystals. Stirring techniques. Atmosphere control. High-pressure technology. Other special techniques and procedures.	8th
Growth of technological single crystals	*Classification of growing crystals:* chemical systematic, crystallographic classification, systematic on possible crystal growth technique, functional classification based on technological applications. *Criteria for choice of growth method:* crystal composition, phase transitions, melting temperature level, decomposition at the melting point, solubility, crystal growth rate, size and applicable crystal orientation, desirable real structure, perfection and homogeneity, expected level of dopants, cost of growth, etc. *Oxide materials.* Simple (ordinary) oxides: bromellite BeO, periclase MgO, corundum Al_2O_3, zincite ZnO, rutile TiO_2, ZrO_2 and other high-melting oxides. Chrysoberyl. Spinels and ferrospinels. Aluminates. Rare earth aluminium garnets. Magnetic garnets. Ortho- and hexaferrites. Manganites. Tantalates, niobares and titanates. Cuprates. Silicates: quartz, forsterite, beryl, mica, rare earth oxiorthosilicates, sodalite. Germanates. Borates. Phosphates: berlinite, apatites, KDP, ADP, KTP. Carbonates: calcite. Vanadates, molybdates and tungstates. *Halogenides:* alkali materials, fluorite, rare earth fluorides, barium fluoride. *Diamond, borides, carbides.* *Special considerations:* *Semiconductors.* Silicon and germanium: bulk crystals, shaped crystal growth, space grade single crystals, Si-Ge alloy crystals. Arsenides, phosphides, antimonides: bulk crystals and thin films. Other AIIIBV crystals. Chalcogenides. *Metals:* low- and high-melting. *Superconductors:* LTSC and HTSC. *Organic materials:* proteins and other macromolecules. *Jewellery-cut materials.* *Other novel and unconventional crystals.* Current problems and future trends.	8th 9th

Crystal growth in Earth's interior	The significance of natural crystallization for science and technology: to understand the natural processes and reasons for the association of minerals; to help to plan crystal growth in the laboratory; to improve the crystal properties, size and use; to develope crystal growth techniques; to understand why some minerals have never been synthesized in the laboratory. Theoretical and empirical approaches to growth of crystals in nature. Spatial-temporal (size and time-scales) factors. Conditions and environments of "terrestrial" crystallization: characteristics of crystal growth processes in nature as seen from the laboratory. Simulating the natural conditions in the laboratory. Experimental methods: dynamic crystallization experiments; in-situ observation techniques of magmatic crystallization; in-situ investigation of mineral growth from aqueous solutions. Comparative studies of fluid inclusions in natural and synthetic crystals. Association of minerals. Morphology and perfection of minerals: deductive analysis of growth and post-growth histories. Classification of minerals based on composition, structures, properties. Importance of mineral structures for uses in technological crystals. Terrestrial materials/technological minerals. General characteristic of mineral crystallization: crystal growth in magmas, including structural aspects of crystallization; crystal growth in pegmatites; crystallization under hydrothermal conditions; crystal growth in hydrothermal metasomatic deposits; crystallization in surficial/sedimentary environments; metamorphic crystallization in secondary rocks and during fossilization process. Special consideration: mineral growth of most important technological minerals in nature, for instance, quartz, diamond, calcite, mica, corundum, sphalerite, zeolites, etc. Simulation of extra-terrestrial materials.	9th