physiological conditions the most stable calcium phosphate is hydroxyapatite ($Ca_5(PO_4)_3OH$, HAP). The growth mechanism of HAP has received considerable attention in view of its importance in understanding the mechanism of hard tissue calcification such as bone and teeth and in many undesirable cases of pathological mineralization of articular cartilage, dental caries and kidney stones [2].

In this work that we investigate the individual effect of polymeric additives for the hydroxyapatite (HAP) crystallization as a model for biomineralization. The higher affinity of PAA for HAP corresponds to the more significant effect of this polymer on the rate of HAP crystal growth.

The results indicate that polyelectrolyte concentration and the larger number of negatively charged functional groups markedly affect the growth rate. The fit of the Langmuir adsorption model to the experimental data supports a mechanism of inhibition through molecular adsorption of polymers on the surface of growing crystals.

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Keywords: hydroxyapatite, biomineralization, crystallization

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Morphological Control of Calcium Oxalate by Hydrophilic Block Copolymers

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Biomineralization processes have attracted considerable attention due to their importance in life sciences, especially with respect to pathological effects[1]. On the aspect of biomineralization, it is of interest to study the crystallization of calcium oxalate monohydrate (COM), because COM crystals have been known as a possible source of urinary and kidney stones[2]. Previous works have shown that the significant influence of urinary macromolecules on calcium oxalate crystallization[3]. Both inhibition and promotion of crystal growth and crystal aggregation by these biopolymers has been reported [4]. An understanding of biological solid-state interactions would be of immense value in many areas.

In this study, we prepared a range of acrylic polymers with different architectures to explore their relative effectiveness in inhibiting crystal growth of calcium oxalate. We investigated the effect of polymers on the particle size, morphology and precipitation of crystals. The presence of copolymers inhibited the crystal growth of calcium oxalate possibly through adsorption onto the active growth sites for crystal growth due to the charge and hydrophilic effects.

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Keywords: calcium oxalate, crystallization, morphology

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Searching the Crystallisation Parameter Space using Evolutionary Algorithms

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When trying to crystallize a new protein, the researcher usually explores a multi-dimensional parameter space using a sparse-matrix or other type of screen. Frequently, the results of such a search consist in a small number of 'promising' conditions. The researcher then conducts a finer mesh search, centered at each of the 'promising' points of the parameter space. If this fails to produce diffracting crystals, other screening conditions must be thought up.

We propose the further probing of such 'promising' conditions, using small-scale Evolutionary (Darwinian) Optimisation Algorithms. Each promising condition is pictured as a 'chromosome', the values of the various parameters (type of precipitant, buffer, pH, temperature, ...) being the alleles on that chromosome. The original 'promising' conditions of the screen constitute a 'first generation' of experiments. A second generation is constituted by random 'recombination' of these 'alleles', i.e. by combining successful values of parameters from different conditions. The most successful of the second generation of experiments will in turn be the 'parent conditions' of a third generation. 'Mutations', i.e. as yet untried values of parameters, can be sparsely introduced in each generation.

This method will not be as robust as for the purely computational optimisation problems for which it is normally used, due to the limitations on the number of 'generations'. It can however lead to optimal combinations of parameters, provided judicious choice of the conditions that will be the parents to each successive generation.

Keywords: biocrystallization, crystallogenesis, crystallization strategies

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Crystallization Platform Integrating Screening & a Novel Optimization Strategy

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Obtaining diffraction quality crystals is a common bottleneck in macromolecular crystallography. With the number of projects increasing exponentially, searching for the right crystallization conditions is a time consuming effort. We have now setup a medium-throughput crystallization platform at the main laboratory in Heidelberg in order to centralize resources, cut costs, and provide efficient and rapid service to EMBL-Heidelberg research groups using X-rays.

The platform is based on use of a nanoliter dispensing robot, standardized crystallization screens with a total of 1800 different conditions, and a database linked to an imaging system for data archiving. The advantages of the service are multiple. It significantly reduces crystallization setup costs by using fewer crystallization solutions and fewer samples. It also saves valuable time. What started as a medium throughput crystallization platform has rapidly grown and 300,000 crystallization drops have already been set up.

As a standard and simple approach for crystal optimization, we are now using the prefilled Nextal Opti-Salts crystallization microplates. This tool allows us to rapidly generate our own new subset of conditions expanded around the hits obtained at initial screening. It works using a combinatorial optimization approach. We will present three projects where the Opti-Salts generate a significant improvement with minimum efforts and investment.

Keywords: crystallization robots, optimization, biomacromolecular crystallization

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$Li_{3.17}(P_{0.69}Ge_{0.24}Mo_{0.07})O_4$: Growth under Electrical Field and the Structure

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The influence of electrical field on crystal growth from flux has been studied in the system Li_3PO_4-Li_4GeO_4-Li_2MoO_4-LiF. Growth occurs on the Pt-rod (anode) immersed into the flux due to temperature decrease with the simultaneous application of direct electrical current. The starting molar ratio between the starting components of the system (Li_3PO_4 : Li_4GeO_4 =1: 1) corresponded to the ratios which provided the stable crystallization of solid solution $Li_{3+x}P_{1-x}Ge_xO_4$ with x=0.31 at the absence of electrical field. When electrical current (V=0.08V) was applied to the growth system, the

compound $Li_{3.17}(P_{0.69}Ge_{0.24}Mo_{0.07})O_4$ has been grown on Pt–rod. For the structure determination there was chosen the single crystal with size 0.13x0.17x0.20 mm.

Crystal structure of analyzed compound is similar to the structure of $Li_{3+x}P_{1-x}Ge_xO_4$ (x=0.31). The partial substitution of $Ge^{4+}(P^{5+})$ for Mo^{6+} follows with the decrease of Li-atom content. In spite of it a significant amount of Li occupy 3 additional sites - 2 tetragonal (very close to 2 main Li-positions which are partially vacant) and 1 octahedral. The fourth additional Li-site found in $Li_{3+x}P_{1-x}Ge_xO_4$ (x=0.31) in our compound is empty.

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Keywords: crystal growth, conductors, electrocrystallization

P.16.04.2

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Phenomenon of Polytypism in Melt Grown Layered Crystals of CdI_2, PbI_2 and $CdBr_2$

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Polytypism has been observed in a large number of materials where the nearest neighbor relationship between identical two-dimensional layers of atoms can be satisfied in more than one way . The phenomenon has posed interesting problem for the Scientists, since the nature of force that causes ordering over the scale ranging from few angstrom to few thousands of angstrom units is not known.

The theoretical and experimental advancements made in the study of polytypism in melt- grown crystals of CdI_2, PbI_2 and $CdBr_2$ in the last few decades have been reviewed. The past work done in this field by us (using optical, Lasers and X-ray diffraction techniques) and update on the aspect of polytypism in the above crystals has been outlined with special reference to the role of:

(1) Purification and effect of impurities (known and unknown);
(2) Solid state phase transitions in the above crystals;
(3) Temperature dependence and their thermodynamic stability.

Keywords: polytypism, X-ray diffraction, melt growth

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Nonstationary Heat field as a new Approach in Bridgman Crystal Growth

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A traditional and axiomatic approach in crystal growth is the creation of a stable and stationary heat field with desired axial and radial temperature gradients. However, an obvious progress in application of Heat Field Rotation Method [1] is reached by development of the non-linear crystal growth technologies of β-BaB_2O_4 (BBO) in Czochralski configuration, LiB_3O_5 (LBO) and $CsLiB_6O_{10}$ (CLBO) in Kyropulos method.

The experiments of $AgGaS_2$ crystal growth by Bridgman method were performed using modified furnace which allows to create cyclic temperature oscillations. Obtained results suggests that moderate temperature oscillations (up to 4°C) favor the crystal quality and are likely to affect generally the hydrodynamic situation in the melt according to Curie principle. More complete mixing resulted to the crystals free of crack, twins and inclusions. Such defects often accompany crystals grown in stationary heat field where the mixing generated by natural convection is slowed due to "stabilized" axial temperature distribution in the melt.

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Keywords: crystal growth apparatus design, convection, nonlinear optical materials

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Growth and Crystal Structure of Bismuth Octaborate, α-$Bi_2B_8O_{15}$

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The objects of this search were a study of $Bi_2B_8O_{15}$ crystallization in the melts of near stoichiometric compositions, a determination of bismuth octaborate solid solutions range and a refinement of crystal structure of low-temperature phase of bismuth octaborate, α-$Bi_2B_8O_{15}$.

The bismuth octaborate crystals were grown from the melts of stoichiometric (20mole% Bi_2O_3 /80 mole% B_2O_3) and near stoichiometric (21.9mole% Bi_2O_3 / 78.1mole% B_2O_3) compositions. The grown crystals of a plate like form were of (5-7) mm in thickness, 27 x 27 mm^2 in cross-section. Comparison of lattice parameters of grown α-$Bi_2B_8O_{15}$ crystals (a=4.3191(9), b=22.175(7), c=6.4739(19)Å, β=105.44(2)°, sp.gr. $P2_1$, z=2) with the data presented in [1, 2] indicates that the phase of non-stoichiometric, Bi_2O_3-rich, composition exists unlike to the α-$Bi_2B_8O_{15}$ phase studied by authors of [1, 2]. Structure was refined as a racemic twin with components 0.80 and 0.20. Range of solid solutions having the 78.1mol.% B_2O_3 – 84.7mol.% B_2O_3 boundaries exists for the $Bi_2O_3{\cdot}4B_2O_3$ compound.

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Keywords: bismuth octaborate, crystalline solid solutions, crystal structure

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Flux Growth and Characterization of Gallium-substituted $YAl_3(BO_3)_4$ Crystals

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Non-centrosymmetric $YAl_3(BO_3)_4$ (YAB) crystals of huntite structure, especially, doped with Tm, Yb, Eu, Er are of most interest as promising multifunctional solids for lasing and non-linear optical applications [1]. So far, no borate of this family is found in the nature, although Italian mineralogists have recently discovered anhydrous rare earth (RE) metaborate with closely spaced chemical composition [2]. For this reason, investigations of crystallogenesis in complex flux systems based on high-temperature RE borates are important from both scientific and technological viewpoints. The present work is focused on flux growth and characterization of $Y(Ga_xAl_{1-x})_3(BO_3)_4$ (x = 0, 0.05, 0.15, 0.2, 0.4) (YGAB) single crystals. YGAB crystals were obtained by top seeded solution growth technique as wel as spontaneous nucleation under different conditions using a $K_2Mo_3O_{10}$ based flux. As a result, transparent and homogenous YGAB single crystals with size up to 3 mm have been grown. From ASEM data, it was found that the average Ga distribution coefficients in YGaAB crystals slightly rises from 0.84 to 0.98 with increase of Ga concentration in the initial borates from 5 to 15 at %.

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Keywords: boron compounds, crystal growth from solution, crystal characterization

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Characterization of Profiled LiNbO3 and SBN Crystals by X-ray Diffraction

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