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Influence of microwave field on the origin and crystal growth from water solutions was studied. Crystallization by methods of temperature gradient and evaporation of solvent of some inorganic salts (KH_2PO_4 (KDP), NaCl , $\text{Sr}(\text{NO}_3)_2$, KNO_2 , $\text{Ca}(\text{OH})_2$) is investigated. It is established, that growth rates of single crystals in microwave field are much more higher in comparison with growth with the use of other known technologies under the same temperatures and supersaturations. For example growth rate of a prism {100} of KDP crystals reaches 11 mm/day with supersaturations $\sim 1.2\%$, and temperature 70°C . Fine dispersion crystallites of investigated salts were obtained by evaporation of solvent.

Use of microwave field for heating of crystallization water solutions leads to significant increase of crystal faces growth rate.

Microwave field more actively destroys adsorption and diffusion layers on crystal faces in comparison with other methods (mechanic, ultrasonic, etc.) in water solutions, providing more intensive moving of substance in superficial area.

At mass crystallization by evaporation of solvent microwave radiation promotes significant decrease of crystallite size. More distinctly it is shown for hard soluble compounds.

Microwave technique provides uniform heating of the whole crystallization volume with active hashing of the solution and simultaneous origin of a significant amount of crystallites over the whole volume of a crystallizer.

Keywords: crystal growth, microwaves, solutions

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Monitoring Polymorphic Transformations in Solution

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Applying diffraction techniques to the study of crystallisation from solution is a way to study the process of crystallisation under different solvent conditions, supersaturation and cooling regimes. For polymorphs systems this approach provides a means to map the stability of one polymorph in relation to another during the crystallisation process in real time. An issue is the trade off between solid diffraction and solution scatter on the overall pattern obtained, and specifically the overall signal to noise.

Even using the light intensity from a synchrotron the diffraction from the solid phases present, remains buried in the signal due to the solution scattering the x-rays. A novel clarifying crystalliser has been developed which by virtue of the design forms a plume of solid for the beam to probe. Thereby increasing the weight fraction of solid presented to x-ray beam thus the overall signal to noise obtained from the solid present. To date the crystallisation of urea, citric acid, glutamic acid and piracetam has been studied using the cell on station 16.4 at the SRS Daresbury, and the outcome for these systems will be presented. These examples systems highlight how it has been possible to monitor the evolution of morphology, induction times and the rates of inter conversion from one polymorphs to another.

Keywords: polymorphism, insitu diffraction, crystal growth

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Growth of the KDP filamentary crystals from solution with impurities

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The filamentary crystal formation is one of the qualitative indicators of an impurity preferential adsorption.

The effect of different trivalent metal ions impurity on growth of the KDP filamentary crystals at high concentrations (0.4-1.5 g/l) and supersaturations (50-90%) of a solution has been studied. The first stages of whiskers growth formation have been studied by Atomic

Force Microscopy. In aggregate with optical measurements it can help to find out both mechanism of the whiskers formation, and the influence of an impurity. The dependences of growth rate of KDP filamentary crystals on relative supersaturation of a solution and on the impurity concentration for different trivalent metal ions were compared.

Short time submergence of the {101} KDP single crystal substrates in the solution with impurity added and following scanning in air already allowed to trace the dynamics of the growing surface. Being adsorbed on a surface, the impurity interferes with the step motion, that results in non-uniform face growth. The separated bulges at later stage are evidence of this process. The similar relief was constructed by a method of statistical trials for a model Kossel crystal face. Pyramidal asymmetrical growth hills and separated bulges are probably bases of the incipient filamentary crystals.

A model of formation and growth of the KDP filamentary crystals and of the mechanism of the effect of the impurity on the growth process are proposed.

Keywords: crystal growth, impurity additives, AFM

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Crystal Growth and Characterization of Non-linear Optical L-tyrosine Chloride

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L-tyrosine hydrochloride (L-THC) a semiorganic non-linear optical material has been synthesized at ambient temperature and characterized by chemical analysis, melting point measurement and FTIR studies. The solubility of L-THC was determined in different solvents at different temperatures. Bulk single crystals of L-THC were grown by slow evaporation method. Powder X-ray diffraction pattern of the grown L-THC has been recorded. Thermal properties of L-THC were studied by recording TGA/DTA and DSC curves. The Kurtz powder second harmonic generation test shows that the crystal is a potential candidate for frequency conversion in the optical region of electromagnetic spectrum. The L-THC crystal has a wide transparency window in the UV - vis-IR region.

Keywords: crystal growth, L-tyrosine chloride, second harmonic generation

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Growth of $\text{Cs}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and their Characteristics

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At the present time ammonium nickel sulfate hexahydrate (ANSH) and potassium nickel sulfate hexahydrate (KNSH) crystals are successfully used as ultraviolet light filters. However their starting dehydration temperatures are relatively low: 96°C and 97°C for ANSH and KNSH. The purpose of our work is to grow $\text{Cs}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (CNSH) and $\text{Rb}_2\text{Ni}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ (RNSH) crystals for further investigations of their atomic structure, optical transmission spectra and thermal stability. These crystals belong to the Tutton's salts as well as crystals mentioned above.

CNSH and RNSH crystals belong to the monoclinic space group $P2_1/C$. Transparent green CNSH and RNSH single crystals with dimensions of $50 \times 50 \times 25$ mm of good optical quality have been grown from water solutions. First the crystal structure of CNSH was determined by X-ray diffraction method; the lattice parameters are: $a=6.3576(8)$ Å, $b=12.7660(17)$ Å, $c=9.2550(10)$ Å, $\beta=106.97(01)^\circ$, $V=718.4$ Å³, $Z=2$, $D_c=2.887$ g·cm⁻³.

We carried out the comparative analysis of the optical transmission spectra of the CNSH and RNSH crystals. On the whole, their optical characteristics are similar to those of α -NSH, ANSH and KNSH. They have similar transmission bands in visible and UV – ranges of spectrum. Thermo-gravimetric analysis showed that the

starting dehydration temperatures of the CNSH and RNSH crystals are 111°C and 126°C respectively. Real structure of CNSH and RNSH crystals was studied by projection X-ray topography.

Keywords: crystal growth, optical properties, structural analysis

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Protein Crystal Growth in Planar and Integrated Gel Interface Diffusion Device

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A liquid-gel-liquid counter diffusion capillary system has successively used for macromolecular crystallization both on ground and in microgravity environment [1], [2]. This system however shows slow kinetics of crystal growth and non-uniform deposition of crystals in a capillary, which mainly arise from one directional (vertical) mass transport of precipitant reagent into protein solution. This is also not provided for the purpose of high-throughput crystallization/X-ray diffraction data collection experiments, due to the difficulty of handling of each glass capillary.

A novel type of gel counter diffusion device is developed for both purposes of conventional and high-throughput protein crystallization. Precipitant and protein cells are separated by thin gel layer (1-2mm in thickness), and are horizontally arranged in a planar well pate. Protein crystals grown in the protein cell in which dimensions of width/length are about 1mm/100mm, are easily observed by CCD camera and also accessed by loop device so as to mount them. To improve the non-uniform deposition of protein crystals during the counter diffusion process, inert liquid layer [3] is embedded beneath the protein solution cell. Without circulation of the inert liquid layer, protein crystals are distributed uniformly over the whole range of protein solution cell.

[1] Garcia-Ruiz J.M., et al., *J. Crystal Growth*, 2001, **232**, 165. [2] Maes D., et al., *Acta Cryst.*, 2004, **D60**, 463. [3] Adachi H., et al., *Jpn. J. Appl. Phys.*, 2002, **41**, L1025.

Keywords: crystallization of proteins, crystallization methods, structural genomics

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How to Optimize Gel-tube Method

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'Gel-Tube' is a method for a protein crystallization using a simplified counter-diffusion technique as we previously reported [1]. A gel in a silicon tube, through which protein and precipitant solution diffuse each other from different direction, is attached to the end of a capillary. Crystallization experiments with a wide range of conditions can be carried out by only one capillary unless crystallization occurs, which suggests that there is a higher possibility for obtaining crystals by a single experiment than conventional method such as vapour-diffusion. Moreover, if combined with 1-dimensional (1-D) simulation program to know concentration change of protein and precipitant solution in a capillary, it is possible to estimate the concentration of protein and precipitant in a certain position of a capillary when crystallization occurred, so that optimization of crystallization condition for further crystallization experiment can be performed. According to the results of the simulation, polyethylene glycol (PEG) might work well in Gel-Tube method as a precipitant because it diffuses so slowly that crystal grows gradually. The effects of the gel-tube length, sample length in a capillary and type of precipitant will be shown.

[1] Tanaka H., et al., *J. Synchrotron Rad.*, 2004, **11**, 45-48.

Keywords: crystal growth apparatus design, counter-diffusion, gel-tube

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Optimized Crystallization Solution Analyzed from JAXA Cryoprotectant Database

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Techniques for cryofreezing protein crystals are essential for X-ray diffraction experiment to reduce radiation-induced damages caused by X-ray beam in synchrotron facility. However, even though high optical quality crystals are obtained, inappropriate way of adding cryoprotectant to mother liquor often causes deterioration of crystal quality.

If the mother liquor is also suitable for cryoprotectant, the damage caused by soaking in artificial mother liquor before diffraction analysis could be avoided. Therefore, we picked up data from International Space Environment Utilization Research Data Base (ISRDB) (<http://idb.exst.jaxa.jp/>) constructed by Japan Aerospace Exploration Agency (JAXA) and analyzed crystallization solution data which are effective both in crystallization and cryoprotection. We will show the results which will be useful both for crystallizing and for cryofreezing protein crystals without any damages.

Keywords: cryoprotectant database, X-ray diffraction, statistical analysis experimental data

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Optical and Morphological Properties of Lead Sulphide (PbS) thin Films

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In this work we studied the optical and morphological properties of thin films of lead sulphide (PbS). Lead sulfide (PbS) films have been deposited by chemical deposition method on glass substrates from a solution of lead acetate, Pb(CH₃COO)₂, and thiourea, SC(NH₂)₂ diluted in water. The deposition is performed in alkaline medium, using sodium hydroxide (NaOH), the starting solution pH being 11. The advantage of this method is simple, relatively inexpensive and easily controlled method that is producing large area films. Some data about the optical properties, structure, composition of the films and thermal stability of the powder samples have been reported.

The structure and crystallite sizes were determined by X-ray diffraction studies. The optical properties were obtained using Fourier transforms infrared (FTIR) spectroscopy. The films are very adherent to the substrates and are polycrystalline. The surface morphology of the as deposited films was studied with a scanning electron microscope. From two to ten, multiple layers have been deposited. The terminal thickness has been determined. Experiments [1] showed that the shape of the product depended on the initial reactants. Under the same experiment condition, PbCl₂ and Pb(NO₃)₂ were employed as the lead ion source instead of Pb(CH₃COO)₂.

[1] Yonghong Ni, Hongjiang Liu, Fei Wang, Yongye Liang, Jianming Hong, Xiang Ma, Zheng Xu, *Cryst. Res. Technol.*, 2004, **39**, 3, 200.

Keywords: lead sulfide, thin films, chemical bath deposition

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The Effect of Polyelectrolytes on Nano Hydroxyapatite Crystal Growth

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The precipitation and dissolution of calcium phosphate salts is of particular interest because of its importance in industrial water systems, in waste water treatment processes, in agriculture as fertilizers and in biological calcification processes [1]. Under