

suggest that the temperature may influence the nucleation and growth by changing the supersaturation level or by inducing liquid-liquid phase transitions [3].

In this study the effects of temperature in the nucleation and in the growth of crystals of different proteins were investigated. Protein crystals grown using batch technique over a temperature range from 277K to 297K were measured and counted. The preliminary results indicate that under the same crystallization conditions, a remarkable change in the number of crystals is observed when the crystallization temperature is modified. Dynamic Light Scattering experiments were performed for *in situ* determination of the size of aggregates during the crystallization process [4]. According to the fluctuation theory, the diffusion coefficient(s) of the sample solution can be obtained from the correlation times of the second order Auto Correlation Function (ACF) of the scattered light intensity. In this application, the ACF decays like the square of sum of exponentials [5] and the size distributions are determined using the Einstein-Stokes relation for diffusion when polydisperse aggregates are considered rigid spheres moving through the sample with low Reynolds number. Data analysis was performed using the program SEDFIT and according to the maximum entropy [6] the square of sum of two exponentials better adjust the data.

The results of DLS experiments indicated no temperature dependence of the growth rate of the scatters (crystals, nuclei) in the investigated temperature range. However, the scattered light intensity during the crystallization essays suffers a crucial change with temperature. Thus, temperature seems only to affect the crystallization process by altering the number of nuclei exceeding the critical size.

[1] (a) www.pdb.org (b) A. McPherson, *Crystallization of Biological Macromolecules* **1999**, CSHL Press, New York. [2] M. Charles, S. Veessler, F. Bonneté, *Acta Cryst.* **2006**, D62, 1311-1318. [3] (a) J.R.Luft et al. *Protein Science* **2007**, 16, 715-722. (b) R. Giegé, V. Mikol, *Trends biotechnolology* **1989**, 7, 277-282. (c) C. Haas, J. Drenth, *J. Phys. Chem.* **2000**, B104, 368-377. [4] (a) N. Asherie, *Methods* **2004**, 34, 266-272. (b) E. Saridakis, *Acta Cryst.* **2002**, D58, 1597-1600. [5] (a) P. Licinio M.B.; M. Delaye, *Chem. Phys.* **1987**, 91, 231-235. [6] (a) P. Schuc et al., *Biophysical Journal* **2002**, 82, 1096-1111. (b) A.K. Livesey, P. Licinio M.B.; M. Delaye, *Chem. Phys.* **1986**, 84, 5102-5107.

Keywords: protein crystallization, dynamic light scattering

MS35.P21

Acta Cryst. (2011) A67, C463

Growth kinetics of the {100} face of potassium chloride crystals

Daria Bogdashkina,^a Dmitriy Vorontsov,^b Elena Petrova,^a ^a*Physics department of Moscow State University, Moscow, (Russia).* ^b*Nizhny Novgorod State University.* E-mail: dashabogd@gmail.com

There are different kinds of particles (atoms, molecules, molecular clusters, etc) in the solutions but it is not known exactly what particles are the building units of the ion crystals. The work [1] suggests a theory which connects the growth rate with the Kossel or non-Kossel models of growth. So, the study of the dependence of the step velocity on supersaturation and other parameters may help to verify the models of ionic crystal growth.

The growth kinetics of the {100} faces of potassium chloride crystals was studied by atomic force microscopy (AFM) and Michelson laser interferometry.

Interferometric observations have shown that potassium chloride exhibits skeletal growth morphologies. Solution inclusions and segmented faces have appeared even at low supersaturation. The growth steps mostly came from the edges and quickly gained domination over growth hillocks on the face. At higher supersaturations of solution the growth hillocks appeared on the face, as well, but they often overlapped.

According to [2] the growth rate of potassium chloride decreases in the presence of lead chloride. Also PbCl₂ additive makes more stable the {100} faces of KCL crystal, preventing them from segmentation, and stimulates the appearance of growth centers on the surface.

Lower growth rates of the {100} faces in PbCl₂ doped solution allowed *in situ* study of surface crystallization processes by AFM. These experiments showed that lead chloride influenced significantly surface morphology of potassium chloride crystals.

[1] L.N. Rashkovich, E.V. Petrova, T.G. Chernevich, O.A. Shustin, A.A. Chernov., *Crystallography reports* **2005**, 50, 1, S78-S81. [2] G.D. Botsaris, E.A. Mason, R.C.. *The journal of chemical physics*, **1966**, 45, №6, 1893-1899.

Keywords: crystal, surface, kinetics

MS35.P22

Acta Cryst. (2011) A67, C463

Crystal growth using low temperature gradient sublimation

Jolanta Karpinska, Andrea Erxleben, Patrick McArdle, *School of Chemistry, National University of Ireland, Galway, Galway, Ireland.* E-mail: karpinska.jolanta@gmail.com

Many organic compounds are known to exist in different crystalline forms both as polymorphs and solvates [1]. Since processing steps in pharmaceutical industry raise many opportunities for phase transformations or solvate formation which may affect their physico-chemical properties it is important to be able to obtain pure crystalline forms.

A method for growing high quality single crystals in the gas phase has been developed. The combination of low (and very low) temperature gradients with vacuum sublimation has several important advantages over other crystallization techniques. Sublimation (which is also a purification technique) can give good quality single crystals in few hours without the necessity of using solvents. The crystalline form and morphology of crystals grown from gas phase are far less affected by solvents and impurities than crystals grown from solution.

The method has been successfully applied to several different classes of compounds. These include systems which exhibit polymorphism, pseudo-polymorphism (sulfathiazole, carbamazepine), have difficulties with crystal packing (stanazolol and ethinyl estradiol [2]) or have problematic morphologies when grown from solution (4-hydroxy-N-phenyl-benzenesulfonamide).

All compounds were analyzed using single crystal X-Ray diffraction, X-Ray powder diffraction, FT-IR spectroscopy and differential scanning calorimetry.

[1] S. R. Vippagunta, H. G. Brittain, D.J.W. Grant, *Advanced Drug Delivery Reviews*, **2001**, 48, 3-26. [2] C. Guguta, I. Eeuwijk, J.M.M. Smits, R. de Gelder, *Crystal Growth & Design*, **2008**, 8, 823-831.

Keywords: crystallization, sublimation, steroid

MS35.P23

Acta Cryst. (2011) A67, C463-C464

Effect of cooling rate on thermal crystallization of energetic materials

Lev Kalontarov, Gloria Yagudayev, Yossi Evri, Sharon Dvir, *Israel Military Industries (IMI) Ltd., Ramat Hasharon (Israel).* E-mail: lkalontarov@imi-israel.com

Particle morphology of energetic materials to a great extent defines their sensitivity and reactivity properties. The morphology in its turn strongly depends on the crystallization process. In the present research the thermal crystallization of pentaerythrol tetranitrate (PETN) explosive and ammonium perchlorate (AP) was studied by differential scanning calorimetry (DSC) and FT-IR spectroscopy. DSC test usually included the heating of the sample with the constant rate of 5°C/min to the temperature which was several degrees higher than the melting temperature and then the cooling of the sample with the different cooling rates. The cooling led to the crystallization. The crystallization temperature, heat and rate were measured. The newly crystallized samples were then subjected to microscopic inspection and FT-IR spectroscopy.

It was found that the crystallization of AP takes place in two stages. The first high temperature stage proceeds at temperatures higher than the melting temperature and starts just after beginning of cooling. The second low temperature stage occurs at temperature significantly less than the melting temperature, e.g. the crystallization is realized from the overcooled liquid. The relative contributions of these types of crystallization strongly depend on the cooling rate. At low cooling rate (0.2°C/min) the crystallization takes place through the high temperature mechanism solely whereas at high cooling rate (15°C/min) only low temperature process is realized. At intermediate cooling rates both types of crystallization exist. The ratio of the heat of low temperature crystallization to the high temperature one ($H_{\text{lowtemp}}/H_{\text{hightemp}}$) increases exponentially with the cooling rate. FT-IR spectroscopy showed that the AP sample crystallized through the high temperature mechanism has strictly the same spectrum as the initial material. The spectrum of AP crystallized from the overcooled melt demonstrates certain differences (line shapes and frequencies) in the range of NH_4^+ stretching ($\approx 3200 \text{ cm}^{-1}$) and bending ($\approx 1400 \text{ cm}^{-1}$) vibrations and ClO_4^- stretching ($\approx 1100 \text{ cm}^{-1}$) vibrations. These facts testify perhaps that the different mechanisms of crystallization result in formation of different crystal structures.

Crystallization of PETN in all experiments takes place from the overcooled melt and proceeds in one stage. The value of the overcooling depends on the cooling rate. At low cooling rates (up to 4°C/min) the crystallization temperature is approximately constant and concentrates near 120 °C ($T_{\text{melt}}=141 \text{ °C}$). The further rise of the cooling rate (from 5°C/min and up to 15°C/min) results in the sharp increase of the overcooling ($T_{\text{cryst}} \approx 100 \text{ °C}$). It was found that the rate of crystallization has the same step like dependence upon the cooling rate. The high overcooling leads to the significant increase of the crystallization rate. FT-IR spectra do not show any differences between initial and newly crystallized samples. However visual and microscopic inspection show that in the case of low rate crystallization (low overcooling) the newly formed crystals have a regular needle like shape, while the high rate crystallization (high overcooling) results in formation of irregular mainly small-sized particles.

Keywords: crystallization, energetic, DTA

MS35.P24

Acta Cryst. (2011) A67, C464

Growth decorations on facets of Al-Cu-Fe single quasicrystals

Marian Surowiec,^a Włodzimierz Bogdanowicz,^a Paweł Zamrzycki,^a Bolesław Formanek,^b Maria Sozańska,^b ^a*Institute of Material Science, Univ. of Silesia, 40 007Katowice*, ^b*Faculty of Materials Engineering and Metallurgy, Silesian Univ. of Technology, 40-019 Katowice (Poland)*. E-mail: msurowie@us.edu.pl

The contribution reports on investigations of facet decorations formed during crystallization of polygonal single quasicrystalline ψ phase occurring in Al-Cu-Fe alloy. The perfectly stable icosahedral

single quasicrystals of ψ phase are formed in the range of compositional triangle $\text{Al}_{62.4}\text{Cu}_{24.4}\text{Fe}_{13.2}$, $\text{Al}_{65}\text{Cu}_{23}\text{Fe}_{12}$ and $\text{Al}_{61}\text{Cu}_{28.4}\text{Fe}_{10.6}$ [1-4].

Polyhedral equilibrium single grains of the ψ phase were obtained inside of ingots of an Al-Cu-Fe alloy, for which the nominal composition was 65 at. % Al, 20 at.% Cu and 15 at.% Fe. The specimens were synthesized in a helium atmosphere using the Bridgman-Czochralski-Growth (BCG) apparatus equipped with an induction furnace. The growth morphology was investigated by the scanning electron microscopy (SEM) using primary and secondary electrons. The selected area diffraction (SAD) as well as X-ray powder diffraction were applied [5].

Single quasicrystals of ψ phase $\text{Al}_6\text{Cu}_2\text{Fe}$ exhibit icosahedral symmetry with pentagonal dodecahedral growth forms - 12 faces perpendicular to the 5-fold axes (Fig. 1 (a)). The dodecahedra have irregularities and different dimensions of edges extending up to 160 μm . The faces of dodecahedra are not perfectly smooth and show residual flux. Some of the dodecahedra are uniformly covered by primary cellular decorations gradually covering almost all facets. During the next stage of crystallization, the secondary fractal like decorations appeared on the quasicrystals surfaces (Fig. 1(b)). There was no evident difference in chemical composition between the inner dodecahedra, primary cellular decorations as well as the secondary fractal like decorations.

The facets of dodecahedra are decorated in similar way as fivefold facets of quasicrystals units of Al-Pd-Mn found by Beeli and Nissen [6]. Contrary to their conclusion we don't found a relationship between facet symmetry and the symmetry of dendrites. The decorations can be formed during the last stage of crystallization, when residual flux crystallizes on the quasicrystal facet in a form of solid dendrites.

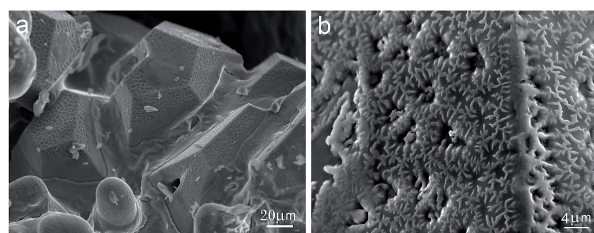


Fig. 1. Decorations on pentagonal faces of the ψ phase. Primary cellular decoration (a) and secondary fractal like decoration (b).

- [1] F.W. Gayle, A.J. Shapiro, F.S. Biancanello, W.J. Böttinger, *Metall. Trans.* **1992**, A23, 2409-2417. [2] A.P. Prevarskiy, *Russ. Met.* **1971**, 4, 154-156. [3] D. Gratias, Y. Calvayrac, J. Devaud-Rzepski, F. Faudot, M. Harmelin, A. Quivy P.A. Bancel, *J. Non-Cryst. Solids*, **1993**, 482, 153-154. [4] C.P. Wang, X.J. Liu, L. Zhang, K. Ishida, Landolt – Börnstein New Series, IV/11 A2, *Springer* **2005**, 1-37.[5] M. Surowiec, W. Bogdanowicz, J. Krawczyk, B. Formanek and M. Sozanska, *Phil. Mag.* DOI:10.1080/14786435.2010.528460. [6] C. Beeli and H.-U. Nissen, *Phil. Mag. B*, **1993**, 68, 487-512.

Keywords: Al-Cu-Fe system, quasicrystal growth morphology, decoration of facets.

MS35.P25

Acta Cryst. (2011) A67, C464-C465

Uncoupling nucleation and protein crystal growth using microfluidic chips

Pascal Rigolet,^d Malika Lounaci,^a Yong Chen,^{b,c} ^a*Laboratoire Sciences Analytiques, Bioanalytiques et Miniaturisation, ESPCI, 10 Rue Vauquelin, 75231 PARIS, (France)*. ^b*Ecole Normale Supérieure of Paris, CNRS-ENS-UPMC UMR 8640, 24 rue Lhomond, 75231 Paris, (France)*. ^c*Institute for Integrated Cell-Material Sciences, Kyoto University, Yoshida-Ushinomiya-cho, Sakyo-ku, 606-8507 Kyoto*