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Acta Cryst. (2008). A64, C585**A novel approach to specifically crystallize anhydrous compounds: Crystal structure of adenine**

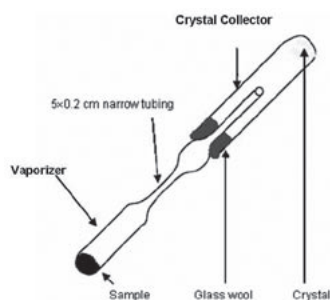
Sudarshan Mahapatra, Susanta K Nayak, S. J. Prathapa, Guru Row N Tayur

Indian Institute of Science, SSCU, Prof T. N. Guru Row Lab, Bangalore, Karnataka, 560012, India, E-mail: sudarshan@sscu.iisc.ernet.in

Crystallization without solvent incorporation is a key requirement to study anhydrous forms of compounds. The structures of all the anhydrous nucleobases were not available as adenine was very hard to crystallize without solvent incorporation. X-ray powder diffraction data both from conventional source as well as synchrotron radiation was found inadequate to solve the structure in the anhydrous form. Crystals of anhydrous adenine were grown by a new approach using the principle of sublimation and gradient cooling. Anhydrous adenine crystallizes in a monoclinic space group $P2_1/c$ with $a=7.891(3)$, $b=22.242(8)$, $c=7.448(3)\text{\AA}$, $\beta=113.193(5)^\circ$, $V=1201.6(3)\text{\AA}^3$ and $Z=8$.

There are two molecules in the asymmetric unit linked via N-H \cdots N hydrogen bonds. The crystal structure is stabilized by two additional sets of N-H \cdots N hydrogen bonds, one across the center of symmetry connecting the imidazole moiety to the pyridine moiety and the other linking the next asymmetric unit resulting in a sheet motif.

Keywords: crystallization, X-ray powder diffraction, synchrotron radiation



P16.13.17

Acta Cryst. (2008). A64, C585**Polymorphism and crystal structure of BPT propyl ester in various solvents**Mitsutaka Kitamura¹, Takayuki Hara^{1,2}, Kousuke Adachi¹, Midori Takimoto-Kamimura²

¹Department of Mechanical and System Engineering, University of Hyogo, 2167 Shosha, Himeji, 671-2201, Japan, ²Pharmaceutical Discovery Research Laboratories, Teijin Parma Limited, 4-3-2, Asahigaoka, Hino, Tokyo, 191-8512, Japan, E-mail: mkitamura@eng.u-hyogo.ac.jp

BPT propyl ester (Propyl 2-(3-Cyano-4-(2-methylpropoxy)-phenyl)-4-methyl-thiazole-5-carboxylate) (Pr-est(CN) and propyl 2-(4-(2-methylpropoxy)-phenyl)-4-methyl-thiazole-5-carboxylate) (Pr-est(H)) were synthesized, and solvent effect in the polymorphic crystallization was investigated by rapid cooling crystallization method. The crystallization for Pr-est(CN) was carried out from ethanol (EtOH), acetonitrile (MeCN), and cyclohexane (c-Hxn) solutions. From EtOH and c-Hxn solutions at high initial concentrations, meta-stable form first appeared, and after then, the transformation to a stable form occurred. On the other hand, at low concentrations the stable form crystallized directly. The crystallization from MeCN solutions resulted in only a stable form, indicating the solvent effect on the polymorphism. X-ray analysis indicated that both of the stable and meta-stable forms are constructed by stacking the sheet structures of the molecules. In the meta-stable form, no hydrogen bonding is observed, whereas the stable form

is stabilized by the hydrogen bonding through nitrile and carbonyl group. Polymorphic crystallization behavior was also examined for Pr-est(H) in MeOH, EtOH and MeCN solutions. In this system only one form crystallized in each solvents, i.e. no solvent effect appeared. The crystal is constructed by stacking the zigzag sheets of the molecules, and the hydrogen bonding between carbonyl group and hydrogen atom in phenyl ring is observed. These results indicate that for the formation of polymorphs the nitrile group in Pr-est(CN) is very important, because it contributes to the formation of distinctive hydrogen bonding and the thermodynamic stability of the solid phase.

Keywords: crystallization, polymorphic structure, pharmaceuticals

P16.13.18

Acta Cryst. (2008). A64, C585**Photoinduced phase transition between polymorphic crystals of a photochromic diarylethene**Seiya Kobatake^{1,2}, Itsuka Yamashita¹

¹Osaka City University, Department of Applied Chemistry, Graduate School of Engineering, 3-3-138 Sugimoto, Sumiyoshi-ku, Osaka, Osaka, 558-8585, Japan, ²PRESTO, JST, Kawaguchi Center Building, Honcho 4-1-8, Kawaguchi-shi, Saitama 332-0012, Japan, E-mail: kobatake@a-chem.eng.osaka-cu.ac.jp

Diarylethenes undergo thermally stable photochromic reactions even in the crystalline phases. 1,2-Bis(2-methyl-6-nitro-1-benzothiophen-3-yl)perfluorocyclopentene (1a) has two kinds of polymorphic crystals, which are named as 1a-alpha and 1a-beta. Both of crystals change color upon irradiation with ultraviolet light. Single crystals of 1a-alpha are obtained by recrystallization from hexane. When the alpha-crystals were heated over 180 degree C, the crystals changed to beta-crystals by a phase transition. The difference of the crystal structures of 1a-alpha and beta was confirmed by X-ray crystallographic analysis. At 170 degree C, alpha-crystals do not change to the crystal structures of 1a-beta. However, upon irradiation with ultraviolet light, the alpha-crystals took place the phase transition to form beta-crystals even at 170 degree C. It is due to the decrease in the phase transition temperature because of the presence of a few ten mol% of the closed-ring isomers. The beta-crystal has a needle-like crystal form. The contact angle to water in the beta-crystals was larger than that of alpha-crystals. The thin film of polystyrenes doped 1a was prepared. The contact angle changed from 134 degree to 154 degree by the phase transition to form the beta-crystals even in the film.

Keywords: photochromism, polymorphism, phase transition

P16.14.19

Acta Cryst. (2008). A64, C585-586**In situ observation of CH₄ hydrate growth by neutron powder diffraction**Akinori Hoshikawa¹, Hiroshi Fukazawa², Naoki Igawa², Hiroki Yamauchi², Yoshinobu Ishi³, Toru Ishigaki¹

¹Ibaraki University, Frontier Research Center for Applied Nuclear Sciences, 4-12-1 Nakanarusawa-cho, Hitachi, Ibaraki, 316-8511, Japan, ²Japan Atomic Energy Agency, 2-4, Shirakata-shirane, Tokai-mura, Ibaraki, 319-1195, Japan, ³Radiation Application Development Association, 2-4, Shirakata-shirane, Tokai-mura, Ibaraki, 319-1106, Japan, E-mail: akinori.hoshikawa@j-parc.jp

Growth process of methane hydrate from D₂O ice powder was measured under pressurized CH₄ gas by in situ neutron powder diffraction. We used HRPD and HERMES [1] at JRR-3 in Japan. To avoid melting ice, the CH₄ gas was gradually applied at 240 K as an isothermal process. The diffraction peaks of methane hydrate were observed at 2 MPa. The pressure was kept at 2 MPa for several hours. After that, the pressure was increased until 6 MPa. However, the growth rate of methane hydrate did not change. Accordingly, the pressure did not affect the growth rate under the sufficient pressure for the crystal growth. Following, the temperature was changed under nearly isobaric process (6-7 MPa). When temperature was changed from 265 K to 270 K, an increase of the growth rate was observed. At 275 K, the D₂O ice was melted and the growth rate drastically increased. After 4 hours, almost all of the D₂O ice was changed to methane hydrate. As a result, temperature is more effective parameter for the crystal growth of methane hydrate. Moreover, we will discuss the size effect of ice grain.

[1] K. Ohoyama, T. Kanouchi, K. Nemoto, M. Ohashi, T. Kajitani, Y. Yamaguchi: Jpn. J. Appl. Phys. Vol37(1998)3319-3326.

Keywords: crystal growth, neutron powder diffractometry, *in situ* observations

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Abiotic growth and biological dissolution of pyrite surfaces

Katja R Etzel¹, Andreas Klingl², Harald Huber², Reinhard Rachel², Michael Thomm², Wulf Depmeier¹

¹Institute of Geosciences, University Kiel, Olshausenstr. 40, Kiel, Schleswig-Holstein, 24114, Germany, ²Institute of Biochemistry, Genetics and Microbiology, University Regensburg, E-mail: ke@min.uni-kiel.de

The relevance of microbial pyrite oxidation processes has resulted in a large number of studies by which microbial oxidation of Bacteria and Archaea were experimentally examined. Because pyrite is a potential, nontoxic candidate for photoelectrochemical and photovoltaic applications, it is important to know how the surfaces of pyrite can be controllably altered. Natural pyrite crystals are often impure, thus, the synthesis of high quality pyrite single crystals is of interest. A potential technique to synthesize pyrite single crystals is the CVT- technique. With this technique it was possible to produce crystals with edge lengths of up to 8.5 mm and habits of up to five forms ({100}, {111}, {210}, {211}, and {221}). The composition and stoichiometry of the crystals were observed near to ideal FeS₂ (S : Fe = 1.98(8)) and studies of the topography of crystal surfaces indicated the high quality of the synthesized crystals. To enhance our understanding of effects of pyrite dissolution mediated by Archaea and various influence parameters (time, temperature, crystallographic orientation surfaces), etching experiments on synthetic pyrite crystals were performed. As biological oxidants two archaeal strains, namely *Metallosphaera sedula* and *Sulfolobus metallicus*, were employed. Studies with Scanning Electron Microscopy (SEM) showed cell attachment and etching effects during the whole time period. Surface alteration forms features up to several tens of microns in size, while the shape of the features varies with face-symmetry and edges of etch pits follow distinct directions. However, control experiments with abiotic oxidants showed, that the shapes of the euhedral etch pits are similar, but smaller in sizes, indicating a higher dissolution rate for microbial than abiotic etching.

Keywords: growth from gaseous phase, dissolution etch phenomena, biological activity

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Synthesis and structural characterization of ZnO deposited by chemical bath

Gabriel Juarez¹, Javier Martinez², Oscar Portillo-Moreno³, Raquel Castillo³, Reina Galeazzi², Constanza G Carrillo², Lenin Pena², Jose A Henao⁴

¹SEES-CINVESTAV, Centro de Investigacion y de Estudios Avanzados del IPN, Centro de Investigacion en Dispositivos Semiconductores, Av. IPN 2508 Col. San Pedro Zacatenco, Mexico, Distrito Federal, 07360, Mexico, ²CIDS-ICUAP, 14 sur Esq. San Claudio, Ciudad Universitaria Edif 137, Apdo. Postal 1651, 72000, Puebla, Pue. Mexico, ³Facultad de Ciencias Quimicas Benemerita Universidad Autonoma de Puebla, Mexico, ⁴Universidad Industrial de Santander-Bucaramanga Santa, Colombia, E-mail: gabriel.juarez@icbuap.buap.mx

Thin films of zinc oxide (ZnO) were deposited on glass substrates by chemical bath deposition technique (CBD), varying the contents of nitrate zinc (Zn(NO₃)₂) and thiourea ((NH₂)₂CS) in the bath solution. The deposition temperature was 80 °C keeping constants the pH value, volume, deposit time and mechanical stirring speed. The samples were characterized by X-ray diffraction (XRD) and transmittance. By X-ray is found that the material is polycrystalline with a Wurzita type structure and with a preferential crystallographic direction (100) for smaller amounts of Zn(NO₃)₂, while for larger amounts of Zn(NO₃)₂ the material presents a preferential crystallographic direction (002), also the diffractograms show that the presence of thiourea stimulates the reaction desired between precursors. By transmittance is found that with a larger amount of Zn(NO₃)₂ the material presents a tendency to increase its energy band gap.

Keywords: semiconductor thin films, zinc oxide, chemical deposition of oxides

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Influence of bath composition in structure of ZnO deposited by microwave activated chemical bath

Javier Martinez¹, Reina Galeazzi¹, Gabriel Juarez², Constanza G Carrillo¹, Ramon Pena-Sierra², Francisco Flores¹

¹CIDS-ICUAP, Benemerita Universidad Autonoma de Puebla, Centro de Investigacion en Dispositivos Semiconductores del Instituto de Ciencias, Av. Sn Claudio esq. 14 sur, Edif. 137 Ciudad Universitaria, Col Sn Manuel, Puebla, Puebla, 72570, Mexico, ²Depto. de Ing. Electrica-SEES, CINVESTAV-IPN, Av. IPN 2508, Apdo. Postal 14-740, 07300 Mexico 14 D. F., Mexico., E-mail: javier.martinez@icbuap.buap.mx

ZnO films were deposited on glass substrates by microwave activated chemical bath deposition technique (MW-CBD), varying the composition of the bath in the relationship 1:1, 1:2, ... 1:10 of (Zn(NO₃)₂):CO(NH₂)₂, while the reagents that makes the solution become basic are maintained constant as well as the power and time deposit. Samples were characterized by X-ray diffraction (XRD), photoluminescence and transmittance; XRD diffractograms show that material is polycrystalline, hexagonal wurzite type, and the lattice constants and the unit cell volume increases as relationship is varied from 1:1 to 1:10. Furthermore, the samples show a preferential orientation along the c-axis indicated by the intensity of 002 reflection, the same was observed in the residual powder of the reaction that was not deposited on substrate. Photoluminescence spectra show a yellow-red emission of deep-levels related to defects, but there is not significant variation due to relationship of precursors.