MS27 O1

Crystallization of high-pressure polymorphs. Examples of kinetic control.

Elena Boldyreva[a,b]. [a]*Novosibirsk State University, Russia;* [b]*Institute of Solid State Chemistry SB RAS, Novosibirsk, Russia.* E-mail: *boldyrev@nsu.ru*

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The study of the high-pressure polymorphism is still in its infancy. More often than not, the transformations give metastable forms, and not the thermodynamically preferable one. The following facts can indicate at the kinetically, and not thermodynamically controlled transformations:

1. Different forms are obtained at the same conditions from different starting polymorphs.
2. Different forms are obtained on compression and on decompression, transformations are not reversible.
3. Effect of pressure is different for single crystals and for powder samples.
4. The transformation is characterized by a pronounced induction period, a hysteresis, is incomplete, or is extended in a wide pressure range.
5. Different forms are observed, depending on how rapid compression / decompression were; on how long the sample was held at a selected pressure.
6. The transformation is sensitive to the choice of the pressure-transmitting liquid (in which the sample is emerged in hydrostatic loading experiments) / to the presence of even traces of a liquid in a slurry.

This will be illustrated using a few examples. Crystallization of liquids, crystallization from solutions, and solid-state polymorphic transformations will be considered.

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MS27 O2

Crystallization techniques for small molecules compounds: A review.

Juan Manuel García-Ruiz. *Laboratorio de Estudios Cristalográficos. IACT. CSIC-Universidad de Granada. Granada-Spain and Factoria de Cristalización.* E-mail: *jmgruiz@ugr.es*

Keywords: crystallization, small molecules, polymorphism

There is an increasing need of crystals of small molecules compounds for different applications, ranging from their use for X-ray diffraction structural studies to the control of their polymorphic precipitation or crystal habits. Research groups working on structural studies of organometallic, coordination compounds, dendrimers, macrocycle chemistry, etc. require nowadays crystals of specific compounds to advance in the understanding of designing structures with specific chemical properties. In addition, the pharmaceutical industry as well as the manufacturing industries of pigments, cosmetics, foods, etc., requires a precise knowledge of the kinetics aspects of the crystallization of small molecules in order to control and tailor the structural and morphological properties of the crystals. The crystallization of specific compounds are in many cases the bottleneck for advances in crystal engineering and inorganic solid state chemistry research programs. The world of biomineralization and biomimetic compounds not only requires a deep knowledge of the crystallization behavious of mineral phases but also of their interaction with biological molecules or the mimicking synthetic counterparts.

This communication will analyze the current landscape in the research of small molecules crystallization and will offer a review of the crystallization techniques currently used.

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Halogen···halogen interactions in pressure-frozen liquids

Andrzej Katrusiak, Roman Gajda, Anna Olejniczak, Marcin Podsiadło *Faculty of Chemstry, Adam Mickiewicz University, Poznań, Poland.* E-mail: katran@amu.edu.pl

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The research on the crystal structures of halogenated compounds is constantly gaining interest. The short halogen···halogen contacts are considered to evidence attractive forces, considerably stronger than van der Waals interactions, and therefore vital for the molecular arrangement in crystals [1, 2]. According to other theories, the close inter-halogen distances result from molecular packing [3].

Methanes and ethanes are simple carbon compounds with the molecules interact by van der Waals forces, and at the same time small molecules do not impose severe restrictions on their close packing in the crystal structures. In these respects the methanes and ethanes can be considered as models for the aggregation of molecular fragments in many organic substances. Thus structures of halogenated methanes and ethanes can be used for studying the basic aggregation patterns involving halogen···halogen contacts.

A series of crystal structures of dihalomethanes (CH_2XY, where X, Y = Br, Cl, I) have been determined by single-crystal X-ray diffraction. They show clearly systematic isostructural relations resulting from the specific intermolecular interactions in theirs pressure frozen phases: CH_2Cl_2 and CH_2ClBr crystallize in space group *Pbcn* [4], for CH_2Br_2 and CH_2BrI space group *C*2/*c* was observed. CH_2ClI exhibits polymorphism, and forms *Pnma*-symmetric phase α, and also a polar phase β in space group *Fmm*2, isostructural with the pressure frozen-