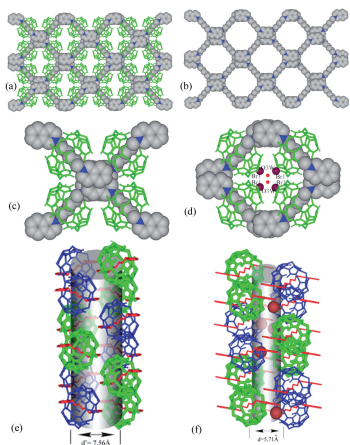


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Q[n]-based supramolecular architectures which have intriguing structures or their potential applications in gas storage or absorption, catalysis, and optoelectronics, have been of great interest in the cucurbit(n)urils (Q[n]s) chemistry.[1-4] In present study a bromide salt of 2,2'-(hexane-1,6-diyl) diisoquinolinium (K6) was introduced to construct a novel framework induced by  $\pi\cdots\pi$  stacking of 2,2'-(alkylene-1, $\omega$ -diyl)diisoquinolinium from Q[6]-based pseudo-rotaxanes. <sup>1</sup>H NMR spectra analysis was performed and confirmed the pseudorotaxane interaction model in which the 2,2'-(alkylene-1,6-diyl) diisoquinolinium guest threads into the cavity of Q[6] with the alkyl chain included inside the cavity and the two end isoquinolyl moieties protruding from the two opening portals. The crystal structure of the compound revealed that the assembled framework based on the Q[6]-2,2'-(alkylene-1,6-diyl) diisoquinolinium pseudo-rotaxanes have stoichiometries of  $\{(K6)@(Q[6])\}^{2+}\cdot 2Br^{-}\cdot 7(H_2O)$  (1). The compound (1) has a novel three-dimensional framework constructed of two different channels – one containing stacked isoquinolyl moieties from the K6@Q[6] pseudorotaxanes and the other containing the bromide anions (See figure below). Absorption spectrophotometric and fluorescence spectroscopic analyses of the host-guest inclusion complex in aqueous solution found that the complexes were most stable at a host:guest mole ratio of 1:1. At this ratio, the complex has binding constants (K)  $\sim 10^6$ .



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**Keywords:** framework,  $\pi\cdots\pi$  stacking, pseudorotaxane

## MS49.P23

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**Study of ZnO nanoparticles thin films deposited by spin-coating**  
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Thin films of zinc oxide nanoparticles, were deposited by spin coating method using glass and silicon as substrates. The obtained films were treated only at 100 °C to evaporate the solvent were the

nanoparticles stay after de deposition. The structural characterization was performed using XRD and SEM techniques in order to observe the differences of film deposition between the substrates. The ZnO thin films showed polycrystalline hexagonal structure when silicon was used as substrate and the other one shows a preferential deposition in 002 ZnO plane. UV-Vis characterization was used to analyze the optical transmittance of the thin films.

**Keywords:** films, ZnO nanoparticles, spin coating

## MS49.P24

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### Crystal Nucleation in X-ray Amorphous Natural Silicates

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The paper reports on crystal nucleation in natural x-ray amorphous silicates – noble and ordinary opals, volcanic and impact glasses. It is known, that opal is unstable and easy dehydrated for its high solubility in geological conditions. It forms crystalbaltite, tridymite and quartz. The transformation occurs under widely known scheme: opal-A – opal-CT – chalcedony – quartz. Usually opals are mixture of amorphous and different degree ordered silica [1-3]. Classical suggestions about structure of noble opals – in regular intervals located spherical particles (size 100 – 500 nm) consisting of small globules in diameter of 10–50 nm, and larger globules are characteristic for opals with crystal structure elements (crystalbaltite – tridymite), and in amorphous opals the sizes of primary globules are estimated in 20–50 nm. However in literature experimental data on electron-microscopic observations of internal structure of small particles in opals practically are not presented. Areas in the size of 10–30 nm with ordered atomic lattice as tridymite or crystalbaltite crystals which are settling down in a disorder opal matrix in amorphous opals [4], are often observed.

We studied hypergenic noble opal from residual soil (Australia), opal of hydrothermal origin from deposit Raduzhnoe, Primorsky Region, Russia, and also ordinary opal from Spain by HRTEM, AFM and IR-spectroscopy.

By means of AFM images on regular basis packed of classical globular structure of noble opals with average diameter of globules 260 nm have been received. It is known, that opal globules are aggregated from smallest particles, however by means of AFM to us them to distinguish it was not possible. HRTEM images of the Australian opal show fragments of round particles which diameter makes from 4 up to 5 nm. These are primary globular particles which form globules observable by means of AFM.

In the Australian opal of the ordered lattice fringes to reveal it was not observed. HRTEM images show all, that the opal substance is amorphous state which shows characteristic irregular contrast. For comparison, in opal which on X-ray and IR-spectroscopic data can be carried to crystalbaltite opal, HRTEM images show continuous amorphous matrix in which are included nanosized areas with crystal ordering. They are chaotically oriented from each other. Lattice distances correspond of crystalbaltite. On contours it is shapeless areas though also polygonal forms in some cases are observed. In the given substance we deal mainly not with nanocrystal, and with ordered fragments of a silica network in disordered environment. It is crystal nucleation center.

The similar ordered areas in natural impact glass have been revealed. Fracture surfaces of the impact and volcanic glasses vary the sizes and the form of the isolations connected with glass nanoparticles.

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**Keywords:** natural silicate, TEM, AFM

## MS49.P25

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### In situ investigation of aragonite formation in atomic resolution by FM-AFM

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The crystallization by the interaction between organic materials and inorganic minerals is called “biomineralization”. The formation of bivalve shell is a biomineralization of calcium carbonate (CaCO<sub>3</sub>) crystal. Some kinds of bivalve shell consist of calcite and aragonite which are polymorphs of CaCO<sub>3</sub> crystal. Although aragonite is metastable at normal temperature and pressure, some mollusks make aragonite stable by organic matrices [1], [2]. Amino acid sequences of some special proteins were revealed which are contained in the organic matrices of the shell, and it was confirmed that many aspartic acids are included in the proteins [3], [4].

In this study, we carried out in situ observation of aragonite formation by addition of the synthetic polypeptide which consisted of 15 amino acid residues and had periodic arrangement of six aspartic acids [3].

First of all, supersaturated solution of CaCO<sub>3</sub> with the synthetic polypeptide and magnesium ( $\sigma=0.86$ ,  $[Mg^{2+}]=0.05$  M, the concentration of the polypeptide = 50  $\mu$ g/ml) was loaded on the calcite crystal which was cleaved on (10-14) face, then the surface was observed in atomic level. In order to observe the change of the surface pattern in atomic resolution, *in situ* and in solution, the Frequency Modulation Atomic Force Microscopy (FM-AFM) was employed. In this solution, we succeeded to observe the moment of aragonite formation at 90 minutes after the solution was loaded. The boundary of the atomic patterns of calcite and aragonite was observed in 10 nm<sup>2</sup>, and aragonite and calcite were in the same layer.

Secondly, the concentration of the synthetic polypeptide was lowered to 30  $\mu$ g/ml. In this solution, some adsorbents were observed on only calcite surface, and they adsorbed along calcium sequence of calcite [010]. The length of adsorbents is 3 - 6 nm. This is close to the length of monomolecular of the synthetic polypeptide.

These results show that calcite transforms to aragonite in the surface layer of seed crystal, and the adsorbents are likely to be the synthetic polypeptide, because aspartic acids in the synthetic polypeptide can bond to calcium atoms on the surface by carboxyl group.

Our results strongly suggest the new model of aragonite formation under normal condition by the transformation.

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**Keywords:** biomineralization, atomic force microscopy

## MS49.P26

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### Quick Pt nanocrystal growth and coalescence on exposition to NO

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The morphology of Pt nanocrystals (10% wt., initial crystallite size approx. 3nm) supported on amorphous silica was studied via in situ XRD during treatment at normal pressure in He, H<sub>2</sub>, O<sub>2</sub> and NO. A specially designed experiment and its analysis enabled detecting of subtle changes in XRD pattern that could be interpreted via atomistic simulations. At the same time a composition of the gas phase could be monitored via Mass Spectrometry (MS). Evolution of Pt fcc peaks position, intensity and width proved to be sensitive to a surface effect and we were able to observe and analyze surface reconstruction of Pt nanocrystals on exposition from H<sub>2</sub> to He [1]. On exposition to NO at temperature 100°C we observe a relatively quick (in a few hours) Pt crystallite growth process. As a result a distribution of an ordered atom column length (closely related to the crystallite size) becomes evidently bimodal with mode size ~3.4nm and ~16.8nm (from 111 reflection). Qualitative analysis (Williamson-Hall plot) revealed only small contribution of microstrain to the peak broadening. Analysis of three reflections 111, 200 and 220 suggests crystal growth process to be anisotropic with preferential growth in 111 direction. During this process MS reveals evolution of N<sub>2</sub>, O<sub>2</sub> and some amount of N<sub>2</sub>O with changing rate (the latter present also in a supplying gas pressure bottle).

A precise analysis shows that the peak position also evolves anisotropically during the growth process. For nanoparticles Bragg law is no longer obeyed precisely and the peak position does not point to the interlayer distance [2,3]. The peak position depends on the crystallites size and on the state of its surface evolving with surface relaxation (and chemisorption phenomena). This also results in a slightly shifted contributions to the peak profile originating from smaller and larger atomic column lengths. Such dependence of a peak position with the crystal size makes classical analysis using Warren-Averbach approach very difficult and sometimes misleading [4].

The observed quick growth of Pt nanocrystals slows down and stops after few hours and the most likely mechanism is coalescence of larger crystallites swallowing the smaller neighbors.

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**Keywords:** in-situ diffraction, crystal growth, surface relaxation

## MS49.P27

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### Synthesis of Nd-Fe-B nanocomposite magnets by reactive mechanical milling

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Nd-Fe-B nanocomposite magnets composed of a Nd<sub>2</sub>Fe<sub>14</sub>B hard magnetic phase and soft magnetic phases such as  $\alpha$ -Fe and/or Fe-B compounds are known to exhibit excellent magnetic properties due to strong ferromagnetic coupling between the magnetic phases [1]. Hydrogenation-decomposition-desorption-recombination (HDDR)