

Ba₆WNb₂O₁₄ appears at least in two different polymorphs with the phase transition around 1200°C. The X-ray powder diffraction pattern of high-temperature modification corresponds merely to the niobium homologue of the hexagonal Ba₆WTa₂O₁₄ (ICDD file #35-0187), while the XRD spectra of the low-temperature modification is closely related to the orthorhombic β-Ba₄Nb₂O₉ (ICDD file #35-1155). In order to understand the crystal chemistry governing the formation of Ba₆WNb₂O₁₄, the ceramic prepared by a conventional solid-state reaction, was analyzed by means of X-ray powder diffraction, scanning electron microscopy and transmission electron microscopy. The analysis of microwave dielectric data revealed a low negative coefficient of resonant frequency varying from -25 to -18 ppm/K, dielectric permittivity in the range of 15-20, and the quality factor Qxf distributed over 18 000 GHz.

Keywords: perovskite structures, phase transitions, dielectric materials characterization, TEM, X-ray crystal structure analysis

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Crystallographic direct observation of chemical reactions in a pore

Masaki Kawano

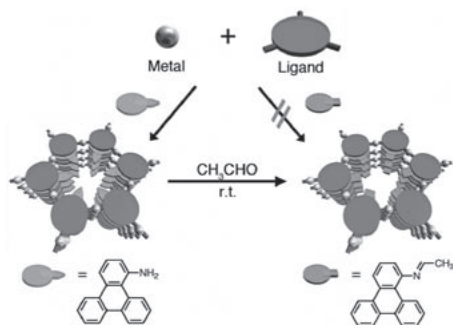
The University of Tokyo, Applied Chemistry, Hongo 7-3-1, Bunkyo-ku, Tokyo, Tokyo, 113-8656, Japan, E-mail : mkawano@appchem.t.u-tokyo.ac.jp

In-situ preparation of labile compounds in a single crystalline state is a unique and effective method for the crystallographic observation.¹ There are, however, several practical problems in this method. Here we utilize the pores of a coordination network. Thanks to the pseudo-solution state in the pores, even bulky substrates can easily interpenetrate into the crystals with keeping single crystallinity. We examined the reaction of acetaldehyde with amines to form acetaldehyde imines that are, normally, easily hydrolyzed or isomerized into enamines.² The aromatic amines were incorporated in the columnar array of aromatic ligands of an as-synthesized porous network complex.³ We also succeeded in observing several condensation reactions of the aromatic amines to produce acylated products in a pore.

References

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Keywords: *in situ* observations, coordination polymers, reactive intermediates



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Phase behavior of block copolymer/inorganic nanocomposites

Pappannan Thiyagarajan¹, Vilas Pol¹, David Bohnsack¹, Chieh-Tsung Lo², Byeongdu Lee¹, Soenke Seifert¹, Randall E Winans¹

¹Argonne National Laboratory, Advanced Photon Source, 9700 South Cass Avenue, Argonne, Illinois, 60439, USA, ²Department of Chemical Engineering, National Cheng Kung University, Tainan 701, Taiwan, ROC, E-mail:Thiyaga@anl.gov

Block copolymers offer as versatile platforms for the fabrication of hybrid composites with ordered phases useful for nanotechnology. Success in this area however requires knowledge on the thermodynamic principles that govern the self assembly of the nanoparticles in the polymer matrix and the resulting morphology and the long range order of the nanocomposites. We carried out a systematic study on the phase behavior of block copolymers with well dispersed grafted nanoparticles enthalpically compatible to one of the domains of the block copolymer. The sequestered nanoparticles in the preferred domain have profound effects on the thermodynamically induced microphase separation of the block copolymers. A number of molecular properties such as polymer molecular weight, segment volume fraction, chi parameter and nanoparticle concentration influence the state of dispersion of the nanoparticles and the degree of segregation of block copolymer morphology. In general, the inorganic nanoparticles tend to weaken the degree of segregation and adversely affect the long range order. We have used a simple method of using small molecular weight homopolymer that can sequester in the same domain as the nanoparticles to overcome the adverse effect of nanoparticles and improve the long range order in the nanocomposites. The basis for this approach is that the small polymers would increase the conformational entropy and swell the preferred domain uniformly which leads to a smoothed interface and improved long range order. The uniform swelling of the preferred domain by the small polymers will also enable higher loading of nanoparticles without losing the long range order. The derived phase behavior will have high impact in the design and fabrication of composites for nanotechnology.

Keywords: block copolymer, nanocomposites, small angle diffraction

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From molecular clusters to nanocrystals - Optical and magnetic properties of metal sulfides

Kian Ping Loh, Junzhong J Wang

National University of Singapore, Chemistry, 3 Science Drive 3, Singapore, singapore, 117543, Singapore, E-mail:chmlhkp@nus.edu.sg

In this talk, I will discuss the transformation of molecular clusters of molybdenum sulfide and arsenic sulfide into novel nanocrystals with new properties. Bulk molybdenum disulfide is known to be a nonmagnetic material. We have synthesized edge-oriented MoS₂ nanosheet-like films that exhibit weak magnetism (similar to 1-2 emu/g) and 2.5% magnetoresistance effects with a Curie temperature of 685 K. The magnetization is related to the presence of edge spins on the prismatic edges of the nanosheets. Spin-polarized calculations were performed on triangular-shaped cluster models in order to provide insight into the origin of magnetism on the edges as well as

the size-property correlation in these MoS₂ nanosheets. Our results imply that nanostructured films with a high density of edge spins can give rise to magnetism even though the bulk material is nonmagnetic. For the first time, we show that Arsenic(ii) sulfide nanocrystal could be fabricated by a wet process of cluster-mediated nucleation method from the bulk material. Arsenic sulfide nanocrystals can show size-dependent fluorescences ranging from 287nm to 450 nm as well as two-photon upconversion. In China, realgar was also reported to be used as a drug in traditional Chinese medicine for more than 1500 years although arsenic is well known to be a highly toxic material. Preliminary pharmacokinetic studies showed that arsenic sulfide quantum dots may afford good potential in anti-cancer treatment.

Keywords: nanocrystals, arsenic sulfide, molybdenum sulfide

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***In-situ* transmission electron microscopy and theoretical studies on the coalescence of nanoparticles**

Ralf Theissmann¹, Gabi P Schierming¹, Martin Fendrich¹, Rouslan Zinetullin¹, Dietrich E Wolf¹, Ralf Meyer¹, Gerrit Guenther²
¹University of Duisburg-Essen, Institute for Nano Structures and Technology, Bismarckstr. 81, Duisburg, North Rhine-Westphalia, 47057, Germany, ²Darmstadt University of Technology, Petersenstr. 21, Darmstadt, Hessen, 64283 Darmstadt, Germany, E-mail: ralf.theissmann@uni-due.de

The production of low-cost nanoparticulate devices based on a bottom-up approach is subject of current research activities. One of the important questions on the way to sustainable devices concerns the question of their mechanical, thermal or electrical stability. Several routes of bottom-up integration of nanoparticulate systems are under investigation, including chemical linking, hybrid integration in a stable matrix and thermal processing. This presentation will focus on aspects of the thermal processing of nanoparticulate films and demonstrate a variety of different processes, which are directly related to the chemical bonding of the material. The thermally activated densification and sintering processes have been studied using time resolved *in-situ* hot-stage transmission electron microscopy of self-supporting films. The experiments were documented as live stream with a TV-rate CCD camera on a hard disc recorder. Varying mechanisms were found for the different materials: a) for ionic ITO particles, an adjustment of the crystal orientation prior to the coalescence is observed at temperatures well below of half the melting temperature; b) for covalent silicon, a melting and subsequent wetting process of the nanoparticles is observed; c) metallic silver particles form area defects during their coalescence, which migrate out of the particles afterwards. These observed mechanisms go clearly beyond the models of classical sintering theory. Our experiments clearly demonstrate that a more sophisticated treatment is necessary in order to understand the sintering processes in nanoparticles, which needs to take into account the chemical bonding and crystallographic orientation. DFT and KMC and MD Simulations support and substantiate the presented experimental results.

Keywords: nanoparticles, sintering / coalescence, *in-situ* transmission electron microscopy

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Structural and magnetic properties of MBE grown MnSb layers

Jadwiga Bak-Misiuk¹, Anna Wolska¹, Krystyna Lawniczak-Jablonska¹, Marcin T. Klepka¹, Janusz Sadowski^{1,2}, Elisabeth Holub-Krappe³, Andreas Persson⁴, Dimitri Arvanitis⁴, Elzbieta Dynowska¹, Przemyslaw Romanowski¹, Jaroslaw Domagala¹, Wolfgang Caliebe⁵

¹Institute of Physics, PAS, Institute of Physics, PAS, Warsaw, Warsaw, 02-668, Poland, ²Lund University, MAX-Lab, Lund Se-221 00, Sweden, ³Hahn- Metner Institute, Glienicke Str., D-141109 Berlin, Germany, ⁴Physics Department, Uppsala University, BOx 530, 75121 Uppsala, Sweden, ⁵HASYLAB at DESY, Notkerstrasse 85, D-22603, Hamburg, Germany, E-mail: bakmi@ifpan.edu.pl

We present results, which open the way towards generating novel materials utilizing the electron spin. We propose to create such materials, by producing the appropriate inclusions in a semiconductor matrix. Bulk MnSb has a TC of 587 K, being therefore a good candidate to form ferromagnetic nano-inclusions in the semiconductor. To establish the best growing condition for MnSb layers and for multiphase materials, we present results of a characterization of MnSb layers grown on GaAs (100) or GaAs (111) substrates by the MBE method. To determine the crystallographic orientation and the local atomic order of the layers, w -2q scans and x-ray absorption studies of the Mn K- edge were performed at DESY-HASYLAB. The phase analysis of the near surface region was performed in glancing incidence geometry (2q scan). In the layer grown on (100) GaAs the existence of two hexagonal MnSb domains with 10.1 and 11.0 orientations and polycrystalline inclusions of zinc-blende GaSb and hexagonal MnSb was detected. The diffraction peaks, observed for a layer grown on (111) GaAs, were indexed as 00.1 MnSb and 111 GaSb. No diffraction peaks originating from polycrystalline inclusions were found. The EXAFS analyze has shown that MnSb layers grown on (100) and (111) substrates have slightly different stoichiometries and/or the number of defects. The magnetic properties were examined by x-ray magnetic circular dichroism at MAX-lab (beamline D-1011). The spin magnetic moment per Mn atom was found to be 1.5 μ_B for both layers but large differences between layers were observed in x-ray reflectivity data, probably produced by a different morphology of these layers. This work was partially supported by a national grant of the Polish Ministry of Science and High Education N202-052-32/1189.

Keywords: synchrotron diffraction, ferromagnetic semiconductor, X-ray absorption spectroscopy

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Leverage analysis: A statistical tool to enhance the control on the crystal structure refinement

Marcello Merli
 Università di Palermo, Dipartimento di Chimica e Fisica della Terra, merli@unipa.it, Palermo, Palermo, I90126, Italy, E-mail: merli@unipa.it

The least-squares crystallographic refinement can be a non-trivial task because of the occurring of some statistical outliers in the data set. This is due to a number of causes: intrinsic noise in the experimental data, not suitable weighting schemes, not valid refinement strategies, problems in the crystallographic model employed and so on. In order to adjust the refinement protocol, a suitable detection of the actually influent outliers is needed. The