

hydrothermal growth of trigonal SiO<sub>2</sub> and hexagonal ZnO. We are employing a solution of supercritical ammonia and acidic mineralizer at T = 450-550°C and p = 90-150 MPa to improve the solubility of GaN [2]. The temperature effects of the ammonium halogenides NH<sub>4</sub>X (X = Cl, Br, I) as mineralizer on the phase stability of GaN synthesized under supercritical ammonothermal conditions is discussed [3]. The tendency to form cubic GaN (c-GaN) increases from X = Cl to I. Decreasing the temperature supports the formation of c-GaN. Single-phase h-GaN can be grown from X = Cl, Br at 550 °C. The solubility of h-GaN is shown in detail. The use of h-GaN substrate has a phase-stabilizing effect and lowers the temperature range for overgrown ammonothermal h-GaN crystal. High-quality nucleation is detrimental to the growth of GaN. Recent results from luminescence on ammonothermal GaN reveal comparable optical quality to high-quality GaN fabricated by currently-standard hydride vapor phase epitaxy (HVPE). The use of GaN fabricated by the acidic ammonothermal growth as substrate material for the successive growth of GaN device structure is shown.

#### References

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Keywords: gallium nitride, semiconductive A3B5 compounds, solution crystallization

## MS.04.3

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### Vapor-phase hydrothermal preparation of titanate fibers and nanotubes

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Most of hydrothermal syntheses have been performed for many years in solution phases at high temperatures and high pressures. A hydrothermal system in an autoclave, however, is ordinarily comprised of a vapor phase and a solution phase as well as hydrothermal products. In the present study, we focused our research on synthesis and morphology control of fibers and nanotube arrays of titanate compounds in the vapor phases under hydrothermal conditions. In the first place, it was found that some of those crystalline phases which are unstable in the solution phases can be synthesized exclusively in the vapor phases and that some crystalline phases grown in the vapor phases assume morphologies different from those obtainable in the solution phases. K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub> and H<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> fibers with unprecedentedly high aspect ratios (> 100) were successfully obtained so far in the vapor phases of KOH and NaOH aqueous solutions, respectively. Secondly, vapor-phase hydrothermal treatment was found to be very effective to convert amorphous TiO<sub>2</sub> nanotube into highly crystalline anatase phase. Vertically oriented TiO<sub>2</sub> nanotube-arrayed thin films were fabricated first by potentiostatic anodization of titanium metal plates at 10-20 V in 0.3-0.5% HF aqueous solutions at room temperature. With an increase in the applied voltage from 10 to 20 V, the inner diameter of the nanotube increased from 30 to 70 nm and the wall thickness increased from 12 to 17 nm. The nanotube could be grown up to ca. 600 nm in length. All the as-prepared TiO<sub>2</sub> nanotubes were confirmed to be amorphous. However, the amorphous TiO<sub>2</sub> nanotubes were confirmed to be converted into anatase phase in hydrothermal vapor water at 150-200 degree C.

Keywords: hydrothermal method, titanates, nanostructures

## MS.04.4

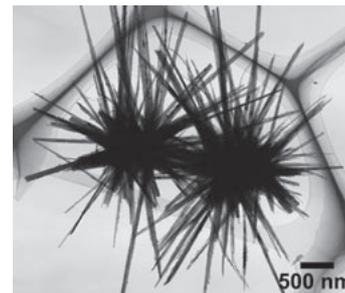
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### Selective synthesis of nano-crystalline TiO<sub>2</sub> polymorphs from new water-soluble titanium complexes

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Currently, solution synthesis of titanium containing oxides has to rely on flammable organic solvents or highly acidic and toxic precursors because all soluble titanium compounds are easily hydrolysable in water. We developed variety of stable titanium complexes, which can be used as environmentally benign precursors for solution based synthesis of titanium containing materials. In these new compounds natural and inexpensive hydroxy-carboxylic acids such as citric, lactic or glycolic acid act as ligands to form stable species. Such compounds are stable against hydrolysis and use of water as a solvent makes them attractive for hydrothermal synthesis of nanocrystalline TiO<sub>2</sub>. Anatase, rutile, TiO<sub>2</sub>(B) and brookite were prepared in a very selective and reproducible way. A simple hydrothermal process was developed for synthesis of TiO<sub>2</sub>(B) and brookite as single phase nano-crystals for the first time and their photo-catalytic properties were studied. The choice of synthesis conditions allowed controlling the direction of crystal growth. Thus, nanowhiskers of rutile were prepared as urchin-like structures (in the Figure below) with extremely high photocatalytic activities.



Keywords: titanium water-soluble complexes, selective hydrothermal synthesis, titanium oxide nanocrystals

## MS.04.5

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### Simple processing of functional ZnO from solution - route towards designed nano-hybridmaterials

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ZnO shows potential as semiconducting scintillator and exploitation of the very fast, sub-nanosecond excitonic emission of ZnO for superfast scintillators was recently discussed in the literature (1). However, efficient collection of emission from bulky scintillation elements is limited. Manipulation of the excitonic emission by shifting the excitonic band to lower energies could be a way to overcome that limitation. We are employing two different techniques

to fabricate crystalline undoped and doped ZnO namely the liquid phase epitaxy (LPE) of thin films on ZnO substrates (2) and synthesis of microcrystals from low-alkaline solutions using mild hydrothermal conditions(3). Photo- and radioluminescence spectra were measured at the undoped and doped with In, Ge, and Sb ZnO thin films and hydrothermal ZnO crystals respectively. The effect of doping, zinc source, and experimental parameters was studied on the phase composition, crystal morphology and size, and luminescence. Molecular imprinted polymer nanoparticles (nanoMIPs) are often referred to artificial receptors. Hybridmaterials based on doped hydrothermal ZnO nanocrystals and nanoMIPs are supposed to work as a specific, nontoxic, and multifunctional label for modern bio-analytics and diagnostics as well as in down stream processing in chemical and pharmaceutical industry.

References

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Keywords: hydrothermal, luminescence, hybridmaterials

MS.05.1

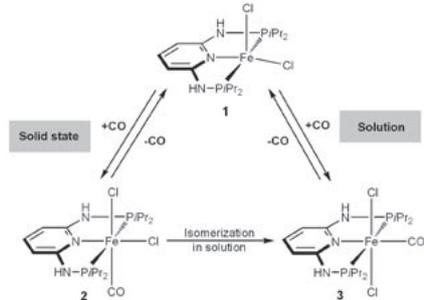
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Solid-state vs solution reactivity of iron complexes: Stereospecific and reversible CO binding

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Chemical transformations that occur in crystalline materials are very rare because most chemical reactions cause intramolecular reorganization, which typically results in the loss of crystallinity. We report here on novel solid-state (and solution) reactivities of iron complexes which maintain their crystallinity even upon CO uptake. When crystalline **1** is exposed to an atmosphere of CO, adsorption of the gas into the organoiron molecules was indicated by a color change of the material from light yellow to deep red, giving cis-[Fe(PNP)(CO)(Cl)<sub>2</sub>] (**2**) as the sole product (Scheme 1). On the other hand, when CO was bubbled into a solution of **1** for two minutes, a blue solid precipitate was formed identified as the corresponding trans complex [Fe(PNP)(CO)(Cl)<sub>2</sub>] (**3**). This process takes place stereospecifically and reversibly depending on the reaction conditions employed triggering changes in the color of the products, in the coordination geometry around the iron center, and in the spin states. Mechanistic aspects are discussed based on DFT calculations, solid-state NMR, and powder diffraction studies.



Keywords: gas sensors, CO binding, solid-state reactivity

MS.05.2

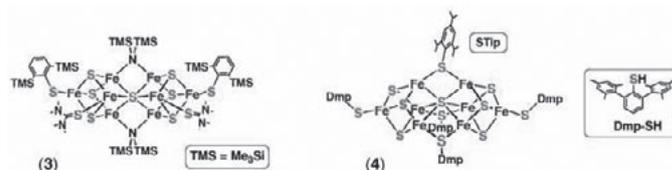
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A new synthetic route to iron-sulfide clusters modeling the active site of nitrogenase

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Recently, we developed a new method to synthesize Fe/S clusters, utilizing Fe{N(TMS)<sub>2</sub>}<sub>2</sub> as the precursor. This route has allowed us to build Fe/S clusters in non-polar solvents, and resulted in a series of unprecedented cluster structures, which resemble closely the active sites of nitrogenase. We succeeded in reproducing the unusual [8Fe-7S] inorganic core structure of P-cluster (PN) of nitrogenase from a self-assembly reaction of Fe{N(TMS)<sub>2</sub>}<sub>2</sub>, SC(NMe<sub>2</sub>)<sub>2</sub>, HSTip, and S<sub>8</sub>, which gave rise to [{N(TMS)<sub>2</sub>}<sub>2</sub>]{SC(NMe<sub>2</sub>)<sub>2</sub>}Fe<sub>4</sub>S<sub>3</sub>]<sub>2</sub>(μ<sup>6</sup>-S){μ-N(TMS)<sub>2</sub>}<sub>2</sub> (**1**). The cluster **1** consists of 6Fe(II)+2Fe(III) irons, while PN carries eight Fe(II)s. Although cluster **1** is unstable under the presence of thiols, it was possible to isolate (NEt<sub>4</sub>)<sub>2</sub>{N(TMS)<sub>2</sub>}<sub>2</sub>(SAr)Fe<sub>4</sub>S<sub>3</sub>]<sub>2</sub>(μ<sup>6</sup>-S){μ-N(TMS)<sub>2</sub>}<sub>2</sub> (**2**) and [(SAr){SC(NMe<sub>2</sub>)<sub>2</sub>}Fe<sub>4</sub>S<sub>3</sub>]<sub>2</sub>(μ<sup>6</sup>-S){μ-N(TMS)<sub>2</sub>}<sub>2</sub> (**3**) from careful treatments of (1) with corresponding thiolates and thiols. Yet another type of [8Fe-7S] cluster (**4**) was synthesized from the reaction of [Fe(Stip)]<sub>2</sub>(μ-SDmp)<sub>2</sub> with S<sub>8</sub> in toluene, the structure of which links topologically FeMoco and P-cluster of nitrogenase and has an intriguing 5Fe(II)+3Fe(III) oxidation state with a doublet ground state.



Keywords: iron-sulfur cluster, nitrogenase, synthesis

MS.05.3

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Advances in electrostatics and application to molecular reactivity

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Most important prerequisites for the reactivity of molecules are the prediction, interpretation and localization of the preferred sites of reactions. Molecular reactivity indicators generally correlate with the atomic charges, the molecular orbital densities and the electrostatic potential. Atomic bonding structures described in the theory of R.F.W. Bader gain acceptance in the field [1]. In this lecture, I will focus on the electrostatic potential, electric field and derived properties to rationalize the molecular interactions. The molecular surface of electrostatic potential defines the nucleophilic and electrophilic attack regions and the electric field assists in predicting the path of reactants in the vicinity of a molecule. The experimental approach of X-ray high resolution diffraction is used to derive these properties. Their computations are based on the Hansen-Coppens model of the electron density [2]. Molecular electrostatic potential

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