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  $^\circ C$  and p = 90-150 MPa to improve the solubility of GaN [2]. The temperature effects of the ammonium halogenides NH4X (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  $^\circ \!\! \mathbb{C}$  . 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.

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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  $H_2Ti_3O_7$  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 TiO2 nanotubes were confirmed to be amorphous. However, the amorphous TiO2 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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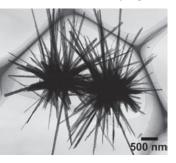
### Selective synthesis of nano-crystalline TiO<sub>2</sub> polymorphs from new water-soluble titanium complexes

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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  $TiO_2$ . Anatase, rutile,  $TiO_2(B)$  and brookite were prepared in a very selective and reproducible way. A simple hydrothermal process was developed for synthesis of  $TiO_2(B)$  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 urchinlike 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