SYMPOSIUM Y

Solvothermal Synthesis and Processing of Materials

March 29 - 30, 2005

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* Invited paper

SESSION Y1: Solvothermal Synthesis and Processing
Chair: Sridhar Komarneni
Tuesday Morning, March 29, 2005
Room 3022 (Moscone West)

8:30 AM *Y1.1
Supercritical Hydrothermal Synthesis of Organic Inorganic Hybrid Nanoparticles. Tahereh Mousavando, Seiichi Takami, Mitsuo Umetsu, Satoshi Ohara and Tadafumi Adschiri; Institute of Multidisciplinary Research, Tohoku University, Sendai, Japan.

This paper first describes supercritical hydrothermal synthesis method of nanoparticles. In the method, metal salt aqueous solution is mixed with high temperature water to rapidly increase the temperature of the metal salt solution and thus reduce the reactions and crystallizations during the heating up period. By using this method, we succeeded in the continuous and rapid production of nano meter size single crystals. Specific features of this method is 1) rapid nanoparticles production, 2) morphology control with a little change of temperature or pressure, 3) control of oxidation state by introducing oxygen or hydrogen gas, and 4) highly crystallized single crystal formation. In this paper, we propose a new method to synthesize organic-inorganic fused materials based on the methods of supercritical hydrothermal synthesis. By introducing organic materials in a reaction atmosphere of supercritical hydrothermal synthesis, nanoparticles whose surface was modified with organic materials were synthesized. In supercritical state, water and organic materials form a homogeneous phase, which provides an excellent reaction atmosphere for the organic modification of nanoparticles. Modification with bio-materials including amino acids was also possible. By changing organic modifiers, particle morphology and crystal structure were changed. This organic surface modification provides a various unique characteristics for the nanoparticles: Dispersion of nanoparticles in aqueous solutions, organic solvents or in liquid polymers can be controlled by selecting hydrophilic or hydrophobic modifiers.

9:00 AM *Y1.2
Solvothermal Pathways to Transition Metal Oxides. Greta Ricarda Patzke and Alexej Michailovski; Laboratory of Inorganic Chemistry, ETH Zurich, Zurich, Switzerland.

The development of solvothermal techniques for the morphology control of particles with respect to future nanotechnological applications is a dynamic research area.[1] Transition metal oxides provide a wide range of important properties combined with a rich structural chemistry which can be transferred onto the nanoscale via solvothermal methods.[2] A systematic approach is employed to derive general guidelines for predictive syntheses: firstly, a suitable precursor material is subjected to parameter optimisations. The influence of straightforward ionic additive substances (e. g. alkali halides) is then screened. Furthermore, this step often affords new crystal structures. Finally, the reaction pathways leading to the key products are investigated with in situ- and quenching techniques. This strategy is illustrated for selected examples: (1) Molybdenum oxides [3] $MoO_3 \cdot 2H_2O$ is a powerful precursor material providing a one-step solvothermal access to MoO_3 nanorods. Their morphology can be influenced with ionic additives, such as alkali chlorides and bromides. Furthermore, the corresponding iodides and fluorides open up a spectrum of novel alkali molybdates. in situ XRD- and EXAFS-techniques reveal that the quantitative formation of MoO_3rods proceeds on a minute scale. (2) Tungsten oxides The aforementioned preparative approach was successfully applied upon a spectrum of nanoscale tungsten oxides emerging from the common precursor material ammonium metatungstate. Alkali chlorides were employed to optimise the morphology of hexagonal tungstate nanorods. The resulting fibers are promising materials for AFM-tips, catalysts or sensors. (3) Molybdenum/tungsten oxides [4] A combined solvothermal approach towards mixed nanoscopic (Mo, W)-oxides was devised from (1) and (2). The emerging nanorods exhibit hierarchical growth patterns with a high thermal stability. (4) Vanadium oxides A spectrum of fibrous alkali vanadates is accessible from the solvothermal reaction of vanadium oxide with alkali halides and hydroxides. This class of materials combines a challenging structural chemistry with potentially new magnetic and catalytic properties. [1] K. Byrappa, M. Yoshimura, Handbook of Hydrothermal Technology, Noyes Publications, New Jersey, USA, 2001. [2] G. R. Patzke, F. Krumeich, R. Nesper, Angew. Chem. Int. Ed. 2002, 41, 2446. [3] A. Michailovski, F. Krumeich, G. R. Patzke, Helv. Chim. Acta 2004, 87, 1029. [4] A. Michailovski, F. Krumeich, G. R. Patzke, Chem. Mater. 2004, 16, 1433.

9:30 AM Y1.3
Low Temperature, Hydrothermal Lateral Epitaxial Overgrowth of Zinc Oxide. David Andeen and F. F. Lange; Materials Department, University of California, Santa Barbara, Santa Barbara, California.

Lateral epitaxial overgrowth (LEO) of zinc oxide has been observed at low temperatures in aqueous solutions. The environmentally friendly process is entirely solution based and requires temperatures no greater than 90°C. Initially, a thin (150-200 nanometer), smooth epitaxial layer of c-plane zinc oxide grows hydrothermally on (111) MgAl2O4 (spinel) in a solution containing zinc nitrate, ammonium nitrate, and ammonia, at a pH of 7.5 and a temperature of 80°C. The processing of this base film has been developed from work reported elsewhere.[1] Masked and windowed regions are then defined by Channel Stamping with a PMMA stamp.[2] Subsequent treatment in a solution of zinc nitrate, ammonia, and sodium citrate, at pH 10.9 and a temperature of 90°C, results in both outward and lateral growth of the epitaxial zinc oxide. Films grown under similar conditions without citrate ions exhibit no appreciable lateral growth. Addition of citrate ions to a zinc containing solution was known to alter the height/width ratio of hydrothermally grown crystal particles.[3] The proposed mechanism is selective adsorption of the citrate ions to the zinc oxide basal planes, which inhibits crystal growth in the [0001] direction. Films have been grown laterally up to six microns, across 12-micron masked region, thereby resulting in coalescence across the masked region. The smooth morphology of the overgrown regions indicates a high likelihood of defect reduction when compared to the rough window regions. 1. D. Andeen, L. Loeffler, N. Padture, F. F. Lange, J. Crys. Growth, 259 (2003), 103-109. 2. P. M. Moran, F. F. Lange, Appl. Phys. Lett., 74 (9) 1999, 1332-1334. 3. Z. R. Tian, J. A. Voigt, J. Liu, B. McKenzie, M. J. McDermott, M. A. Rodriguez, H. Konishi, and H. Xu, Nature Materials, 2 (12) 2003, 821-826.

9:45 AM Y1.4
Sovothermal Processes in Materials Synthesis. Demazeau Gerard, Goglio Graziella and Largeteau Alain; ICMCB-UPR-CNRS 9048, Pessac, France.

Solvothermal processes are ,in particular,characterized by the increase of the kinetical factors due to the improvements of the diffusion of chemical species.Consequently such processes can be involved either in the stabilization of new materials or in the development of innovative routes for the synthesis of functional materials. Different exemples will be described: -the stabilization of a new family of bidimensional oxides isostructural of the natural phyllosilicates: the phyllosiloxides, -a new synthesis route for c-BN allowing the decrease of the pressure and temperature conditions, -the development of specific preparation methods of nitrides, in particular the nitrides of the column III, -the control of the size and the morphology of particles used as catalyst.

10:30 AM Y1.5
One-step Solvothermal Synthesis and Characterization of BaTiO3 Nanoparticles. Helen Reveron, Cyril Aymonier, Anne Loppinet-Serani, Mario Maglione, Catherine Elissalde and Francois Cansell; ICMCB, Pessac, France.

In recent years at the ICMCB Institute, solvothermal method has attracted considerable interest to prepare different kinds of materials (ceramics, metals and organic polymers) in several forms (powders, single crystals, fibers, or coatings), due to the relatively low temperatures involved and the possibility to control precisely the stoichiometry, morphology and particle-size (1-2). Barium titanate (BaTiO3) is an important material used in the electronic industry (mainly in multilayer ceramic capacitors and thermistors/thermal switches) due to its high dielectric constant and good ferroelectric properties. Depending on temperature, micrometric BaTiO3 crystallizes in five distinct polymorphic-forms (3). However, among these structures, the tetragonal phase (0 to 130 C) and the cubic phase (130 to 1460 C) are interesting from a technological point of view. Conventionally, barium titanate is synthesized through a solid-state reaction between BaCO3 and TiO2 powders at high temperature (T>1200 C) (4). Nevertheless, the overall reaction involves successive steps of grinding and calcination and usually leads to large particles with inhomogeneous compositions. In the last years, some alternative methods for synthesizing barium titanate powders employing lower temperatures have been developed. The investigations are mainly focused on the preparation of barium titanate nanoparticles with high purity, particularly without barium carbonate pollution; on the one hand, in order to prepare well-sintered ceramics and to obtain outstanding ferroelectric properties and on the other hand, to study the controversial effect of particle-size over BaTiO3 properties. We will describe a novel one-step solvothermal route to obtain pure and well-crystallized BaTiO3 nanoparticles, using a continuous-flow tubular-reactor in the temperature range of 150-380 C and a pressure < 25 MPa. Some of the limitations that are associated with the alternative BaTiO3 synthesis methods, such as long reaction time, post-treatments for powder washing, drying and crystallization, pollution with barium carbonate or tedious synthesis in batch mode, are thus overcome. To synthesize this bimetallic oxide, barium and titanium alkoxides were used as precursors and a mixture of ethanol and water as solvent and reagent. The influence of the operating parameters on the BaTiO3 powder characteristics will be presented by means of transmission electron microscopy (TEM), powder X-ray

diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA). We will show that using this process a cubic, pure, stoichiometric and well-crystallized BaTiO3 nanopowder can be obtained directly without washing or crystallization treatment. Moreover, the ceramic dielectric properties as permittivity and dielectric losses will be also presented. (1) J. Mat. Chem. 12, 958, 2002. (2) J. Mat. Chem. 14, 228, 2004. (3) J. Cer. Proc. Res. 3, 41, 2002. (4) Mat. Chem. Phys. 82, 742, 2003.

10:45 AM Y1.6
High-quality Single-crystalline ZnO Layers Grown by Liquid-phase Epitaxy. Dirk Ehrentraut[1], Hideto Sato[2,4], Miyuki Miyamoto[3], Ikuo Niikura[4] and Tsuguo Fukuda[1]; [1]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; [2]Murata Mfg. Co. Ltd., Shiga, Japan; [3]Mitsubishi Gas Chemical Co. Inc., Tokyo, Japan; [4]Tokyo Denpa Co. Ltd., Tokyo, Japan.

The wurtzite-type ZnO is a wide band gap semiconductor (E_g = 3.37 eV) with a twice larger exciton binding energy (60 meV) than the competing GaN. Therefore, ZnO is highly attractive for UV/violet/blue optoelectronic devices like LED/LD. Moreover, its high piezoelectric coupling constant (k^2 = 8%) is superior over most of commonly used materials, i.e. α-quartz or langasite. SAW and BAW devices of high performance and temperature stability may be produced from ZnO layers with high resistivity. Consequently, the need of highly perfect single-crystalline layers, doped and no doped is obvious. Among all methods to obtain growth of layers liquid-phase epitaxy (LPE), which is using a liquid solvent, is preferable if a proper solvent is found. Highest layer perfection may be achieved since growth appears in the vicinity of the thermodynamic equilibrium at which neither growth nor dissolution occurs. This is in strong contrast to all vapor phase growth techniques where supersaturation is orders of magnitude larger. We grew no doped ZnO layers from alkaline metal (AM, with AM = Li,Na,K,Cs) chlorides and using the chemical reaction of $ZnCl_2$ and AM_2CO_3 to form ZnO. Continous saturation, thus feeding of the solvent is provided over times longer 30 h when working with AM_2CO_3 in crystalline state rather than powder. A growth temperature of 600-650°C under normal pressure and air atmosphere is applied. Facetted layers of 1-15 μm thickness have been grown on 1 cm^2 large (0001) and (11-20) ZnO substrates with off angle α and $0° \leq \alpha \leq 2.4°$. The influence of α on changing the growth mechanism from island to step-flow is discussed. This is confirmed be Nomarski-differential interference microscopy (NDIM), atomic force microscopy (AFM) and scanning electron microscopy (SEM). The concentration of impurities was detected by secondary ion mass spectroscopy (SIMS). The layers exhibit the typical room temperature UV photoluminescence (PL) with the peak signal at 3.31 eV. The substrate quality has crucial impact on the quality of the grown layer. As measure of crystallinity the X-ray full-width-at-half-maximum (FWHM) for (002) is improved to 33 arcsec by proper chemical-mechanical polishing and further down to 25 arcsec by subsequent thermal annealing. Grown LPE layers shows a FWHM of 55 arcsec.

11:00 AM Y1.7
Spectrally Resolved Cathodoluminescence (SRCL) of Hydrothermal ZnO Crystals. Julio Mass[1], Manuel Avella[1], Juan Jimenez[1], Michael Callahan[2], E. Grant[2], K. Rakes[2], David Bliss[2] and Buguo Wang[3]; [1]Fisica Materia Condensada, Universidad de Valladolid, Valladolid, Spain; [2]Fisica Materia Condensada, Universidad de Valladolid, Valladolid, Spain; [3]Fisica Materia Condensada, Universidad de Valladolid, Valladolid, Spain; [4]Air Force Research Laboratory, Hanscom AFB, Hanscom, Massachusetts; [5]Air Force Research Laboratory, Hanscom AFB, Hanscom, Massachusetts; [6]Air force Research Laboratory, Hanscom AFB, Hanscom, Massachusetts; [7]Air Force Research Laboratory, Hanscom AFB, Hanscom, Massachusetts; [8]Solid State Scientific Corporation, Nashua, New Hampshire.

The potential for growth of high quality ZnO single crystals offers a diverse range of applications from dilute magnetic semiconductors to advanced optoelectronic devices. Reliable devices based on ZnO will benefit from the improvements of the materials; in particular, the reduction of dislocations and non-radiative defects. ZnO crystals are presently grown by several different methods: vapor phase transport, melt-growth and hydrothermal. Hydrothermal growth presents the advantage of low dislocation density and high purity. However, the incorporation of impurities and native defects appears highly inhomogeneous. Control of the defect distribution is one of the key issues to improvement of these crystals. We present herein a study of the homogeneity of these crystals using spectrally resolved cathodoluminescence (SRCL). The luminescence spectrum of ZnO consists of an UV NBG (Near Band Gap) part, and a yellow-green broad band. The UV emission of ZnO is very complex and is formed of several excitonic bands and donor acceptor pair recombinations and their corresponding phonon replicas. The visible luminescence consists of two broad bands overlapping each other, the green and the yellowish bands respectively. SRCL images reveal inhomogeneous contributions of the different bands, correlated to different crystallographic faces. 2-D Spatial maps reveal not only the competition with non radiative recombination centers, but also the relative contribution of the different luminescence bands, determined by the distribution of the responsible defects (impurities and native defects). The distribution of defects appears thus strongly dependent on the growth sectors. A full spectral analysis of the CL images is provided revealing the main features of the different growth sectors in the ZnO crystals.

11:15 AM Y1.8
Dielectric Properties of Hydrothermally Grown Epitaxial KNbO3 and KTaO3 Films. Gregory K. L. Goh, Xue Qin Han and Christine S. S. Tay; Materials Science and Characterisation Lab, Institute of Materials Research and Engineering, Singapore, Singapore.

$KNbO_3$ single crystals and epitaxial films have the largest reported electromechanical coupling constants and this makes $KNbO_3$ highly desirable for use as surface acoustic wave (SAW) substrates. SAW devices are used as filters in telecommunications and signal processing, and as sensors for touch screens, automotive and RF identification applications. Unfortunately, it is very difficult and expensive to grow large $KNbO_3$ crystals suitable for making SAW substrates. The alternative is to grow epitaxial $KNbO_3$ films. Due to its close lattice match with $KNbO_3$, $KTaO_3$ films have been used as a buffer layer to improve the alignment of epitaxial $KNbO_3$ films grown on $SrTiO_3$ substrates. In this study, the dielectric properties of epitaxial $KNbO_3$ and $KTaO_3$ films, grown hydrothermally on (100) oriented single crystal $SrTiO_3$ substrates at 200°C and lower, are reported. Epitaxial $KNbO_3$ films were also grown on $KTaO_3$ buffered $SrTiO_3$ substrates. The presence of hysteresis loops confirmed that the as-synthesized $KNbO_3$ films were ferroelectric. Rutherford backscattering spectroscopy of the as-grown multilayer film revealed a channeling yield of 5%, indicating that the hydrothermal method can be used to grow reasonable quality epitaxial films. The $KTaO_3$ films had dielectric constants ranging from 290 to 225 and loss tangents between 8 and 20% (1 to 100 kHz). Although the dielectric constants compared favorably to the bulk value of 240, the loss tangents were unacceptably high. The high dielectric losses were due to conduction of protons (by the Grotthuss mechanism) incorporated during growth in the aqueous environment. As such, heat treatments that led to proton removal from the lattice, as judged from TGA data, also resulted in films with lower loss tangents. For $KNbO_3$ films, the as-synthesized dielectric constants ranged from 249 to 351 and the losses from 14 to 25% for a frequency range of 1 to 100kHz. Just like $KTaO_3$, the minimum loss tangents for the $KNbO_3$ film were attained upon complete proton removal at 600°C. Although heat treatment above 600°C did not lower the loss tangents further, the dielectric constants increased to higher values of 488 to 552.

11:30 AM *Y1.9
Rational Design of Low-Dimensional Nanomaterials: Novel Soft Solution Approaches. Shu-Hong Yu, [1]Department of Materials Science & Engineering, University of Science and Technology of China, Hefei, China; [2]Division of Nanomaterials & Chemistry, Hefei National Laboratory for Physical Sciences at Microscale, Department of Materials Science and Engineering, University of Science and Technology of China, Hefei, China.

Nanosized building blocks with low dimensionality such as nanotubes, nanowires, nanorods, and ultra-thin nanosheets, have emerged as very technically important systems, which provide both fundamental scientific opportunities for investigating the influence of size and dimensionality on optical, magnetic and electronic properties and potential good components for significantly improving the material properties. The exploration of rational routes for controllable synthesis of low dimensional nanocrystals has been an intensive research focus. The latest advances on emerging mild soft solution based strategies for the synthesis of low dimensional nanocrystals such as hydrothermal/solvothermal processes, bio-inspired routes, as well as the emerging oriented attachment mechanism, will be addressed. The formation mechanism of low dimensional nanocrystals (1D and 2D) and more complex hierarchical structures will be discussed. Current advances in this area demonstrated that it is possible to rationally synthesize low dimensional inorganic nanocrystals with controlled shapes, size, phases, as well as their structures. These low dimensional nanocrystals with special shape and structural features could find potential applications in nanoscience and nanotechnology.

SESSION Y2: Solvothermal Synthesis of Nanophases
Chairs: Gerard Demazeau and Richard Riman
Tuesday Afternoon, March 29, 2005
Room 3022 (Moscone West)

1:30 PM *Y2.1
Spin State Switching in Iron Complexes – from Molecular Processes to Possible Applications. Philipp Guetlich, Institut fuer Anorganische Chemie und Analytische Chemie, Johannes Gutenberg-Universitat Mainz, Mainz, Germany.

Coordination compounds of transition metal ions with open-shell electron configurations may exhibit dynamic electronic structure phenomena, depending on the nature of the coordinating ligand sphere. Thermal, light- and pressure-induced changes of spin states [1-6] are among the most fascinating electronic games encountered in transition metal compounds, which are presently under extensive study by chemists and physicists. The switching properties make such material potential candidates for practical applications in thermal and pressure sensors as well as optical devices. The basics of thermal and optical spin transition will be briefly reviewed. Selected examples of thermal spin crossover in mono-, oligo- and polynuclear iron(II) complexes will be discussed, with special emphasis on the importance of cooperative interactions. It will be shown that switching forth and back between different spin states may be effected by irradiation with light of different wave lengths ("Light-Induced Excited Spin State Trapping (LIESST)." The effect of pressure on the spin transition behaviour will be demonstrated. Possible practical applications will be discussed. [1] P.Guetlich, A. Hauser, and H. Spiering: "Thermal and Optical Switching of Iron(II) Complexes", Angew. Chem.Int. Ed. Engl., **1994**, 33, 2024-2054 [2] P. Guetlich, A. Hauser, H. Spiering: "Spin Transition in Iron(II) Compounds", in: Inorganic Electronic Structure and Spectrosocopy Vol. II, A.B.P. Lever, E.I. Solomon eds., John Wiley & Sons, **1999**, 575-622 [3] P. Guetlich, Y. Garcia, H.A. Goodwin: "Spin Crossover Phenomena in Fe(II) Complexes", Chem.Soc.Rev. **2000**, 29, 419-427 [4] P. Guetlich, Y. Garcia, T. Woike: "Photoswitchable Coordination Compounds", Coord.Chem. Rev. 219-221 (**2001**) 839-879 [5] P. Guetlich, Y. Garcia, H. Spiering: "Spin Transition Phenomena", in: Magnetism: Molecules to Materials IV, J.S. Miller, M. Drillon (eds.), Wiley-VCH **2003**. [6] P. Guetlich, H. A. Goodwin (eds.), "Spin Crossover in Transition Metal Compounds", Topics in Current Chemistry, volumes 233, 234, 235, Springer **2004**, Berlin-Heidelberg-New York.

2:00 PM *Y2.2
Molecular Chemical Concepts for Solvothermal Growth of Oxide Nanostructures. Sanjay Mathur and Christian Cavelius; Leibniz Institute of New Materials, Saarbruecken, Germany.

High-purity materials with precise control over chemical composition, morphology and microstructure are fundamental to the development of nanomaterials research. However, the conventional methods (e.g., precipitation, combustion or solid-state reactions) of inorganic materials syntheses are controlled by diffusion of ionic and atomic species through both reactants and products, and therefore not appropriate for the unit-by-unit assembly of nanostructures. In this context, chemistry-based solution approaches such as sol-gel or hydrothermal routes offer promising alternatives especially in terms of control over synthesis parameters and composition-structure-property relationships. Although sol-gel techniques are attractive due to their simple operation, room-temperature processing and scalable throughput, it is rather difficult to obtain crystalline materials without a heat-treatment step and the degree of agglomeration is also high. On the other hand, solvothermal methods allow to combine the advantages of high surface area with high crystallinity in the synthesized materials. However, the large number of process variables associated with solvothermal techniques makes a systematisation rather difficult. We are investigating the transformation of molecular compounds under solvothermal conditions to grow extended frameworks from atomically defined units, which illustrate that predefined reaction chemistry of precursors enforces a precise control over morphology, composition and particle size, in the resulting material. This approach allows to take advantage of both thermodynamic (high pressure and temperature conditions) and kinetic (customized assembly of molecular building blocks) factors for a facile formation of crystalline phases with controlled particle size, shape and dispersion properties. In addition, we have comparatively evaluated the conventional solvothermal synthesis with a micro-emulsion assisted process, in which the metal-organic precursors are pre-hydrolysed in spatially confined "nano-reactors" followed by a solvothermal treatment. The merits of the later hybrid process are evident in non-agglomerated particles and morphology control that can be tuned, for instance, by adjusting the length of the alkyl chains in the surfactant molecules. A brief review of our activities along these lines will be presented.

2:30 PM Y2.3
Morphology Control in the Hydrothermal Synthesis of Nanostructured Titanium Oxides. Calvin J. Curtis, Alex Miedaner, Tanya Kaydanova and David S. Ginley; National Renewable Energy Laboratory, Golden, Colorado.

Nanostructured TiO_2 including nanorods, nanotubes, nanowires and ordered arrays of these structures are of increasing interest as photonic materials and as elements in hybrid organic/inorganic photovoltaic and organic light emitting device structures. Hydrothermal synthesis is a simple and inexpensive method that can be used to produce these structures. We have developed a series of hydrothermal reactions that reproducibly generate a variety of different morphologies for TiO_2 nanostructures, both as free particles and bound to surfaces. Sodium titanate nanowires 10-50 nm wide and several microns in length have been grown on titanium metal substrates. When these nanowires are subjected to further hydrothermal treatment, they are converted to a network of anatase TiO_2 nanorods covering the substrate. These rods are 50-100 nm wide in the center and taper to points at each end, and are 500-700 nm in length. Sodium titanate nanotubes in solution can also be converted hydrothermally to free standing anatase TiO_2 nanostructures. When this conversion is carried out in the presence of various surface modifying agents including organic compounds and other surface coordinating agents, the morphologies produced can be varied to produce blocks, chains, larger rods and wires. These nanorods and nanowires were characterized by transmission electron microscopy (TEM), scanning electron microscopy (SEM), X ray diffraction (XRD) and Raman spectroscopy. Initial attempts to incorporate them in organic photovoltaic devices will be discussed.

2:45 PM Y2.4
Solvothermal Synthesis of Hollow Titania Microspheres. Xin Michael Wang and Ping Xiao; Materials Science Centre, University of Manchester, Manchester, United Kingdom.

Solvothermal synthesis has been used to produce TiO2 with controlled morphology by processing TiCl4 in ethanol and isopropanol. Pure anatase phase nanocrystals of TiO2 was obtained in ethanol whereas nanocrystalline microspheres of TiO2 with hollow interior was produced in isopropanol. There was no templates being used for the synthesis of the hollow microspheres. The morphology of microspheres can be modified by controlling the reaction condition, e.g. temperature, solvent, time and concentration of reactants. Meanwhile, the reaction mechanisms controlling the formation of microspheres were studied.

3:30 PM Y2.5
Hydrothermal Synthesis of ZnO Nanowires for Use in Dye Sensitized Solar Cells. Jason B. Baxter[1], Amanda Walker[1], Kim van Ommering[2] and Eray S. Aydil[1]; [1]Dept. of Chemical Engineering, University of California Santa Barbara, Santa Barbara, California; [2]Department of Applied Physics, Eindhoven University of Technology, Eindhoven, Netherlands.

ZnO is a wide band gap semiconductor with applications in UV optoelectronics, transparent conducting oxide coatings, and photovoltaics. Nanostructured ZnO can enable applications that require high surface area such as sensors and dye sensitized solar cells (DSSCs). We have grown ZnO nanowires hydrothermally from zinc nitrate and methenamine at temperatures under 100 °C on various substrates seeded with ZnO nanoparticles. The seed nanoparticles (~5-10 nm) were grown from zinc acetate and NaOH in methanol. Hydrothermally grown ZnO nanowires are hexagonally faceted single crystals and grow in a dense array vertically from the substrate. Diameter of the nanowires can be tuned by both the growth conditions and the size of the nanoparticle seeds. Using 5-10 nm seeds, ZnO morphology could be varied from 30 nm diameter nanowires to columnar polycrystalline films by increasing concentrations of both precursors from 2.5 mM to 0.25 M. Larger seed particles result in nanowires with larger diameters. Nanowires with 50-100 nm diameters typically grow to lengths of 800 nm in less than four hours, at which point growth slows considerably due to low supersaturation of the precursor solution. However, nanowire growth can be continued by placing the substrate in a new batch of the precursor solution. Nanowires with lengths up to 7 μm were obtained using several growth cycles, with negligible increase in nanowire diameters. The mechanism of nanowire growth depends on the supersaturation of the solution. At high supersaturations, nanowire aspect ratio is determined by the relative 2D island growth rates on the basal plane and the side facets of the nanowires. Seeded nanowire growth also competes with homogeneous nucleation of crystals in solution. As the supersaturation decreases, we see spiral growth on only the basal plane. Current work focuses on obtaining a more detailed understanding of the molecular level interactions responsible for the nanoscopic crystal shape evolution. We have used these dense arrays of nanowires as the high surface area semiconductor in DSSCs, wherein light is absorbed by a monolayer of dye molecules adsorbed at

the surface of a nanostructured wide band gap semiconductor covered by a liquid electrolyte. In a DSSC, the photoexcited electrons are rapidly transferred to the semiconductor conduction band and the dye is regenerated through a redox reaction with a redox couple in the electrolyte. The nanowire geometry may offer improved electron transport compared to conventional sintered nanoparticle films, and the well-defined geometry could provide insight into the mechanisms of charge transport. The photocurrent obtained in these solar cells depends strongly on the semiconductor surface area. DSSCs with 7 μm long nanowires have shown current densities of 1.4 mA/cm^2 and overall efficiencies of 0.3%. Significant improvements are expected when nanowires are grown longer, thinner, and in even more densely packed arrays.

3:45 PM Y2.6
Solvothermal Routes for Synthesis of ZnO Nanorods.
Nelson S. Bell, Chemical Synthesis and Nanomaterials, Sandia National Laboratory, Albuquerque, New Mexico.

Control of the synthesis of nanomaterials to produce morphologies exhibiting unique optical properties will enable device integration of several novel applications including biosensors, catalysis, and optical devices. In this work, novel solvothermal routes for the production of zinc oxide semiconductors with controlled morphology and exhibiting quantized properties will be presented. Much previous work has relied on the addition of growth directing/inhibiting agents to control morphology. This study will also investigate the effect of solvent on speciation, yield, and processablility of these nanomaterials. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company for the United States Department of Energy National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:00 PM Y2.7
Synthesis of Uniform-Dispersed Core-Shell Nano-oxide Suspensions via A Novel Microwave-Micelle Process.
Jack Y. Ding[1], Chao-Kuei Yin[1] and Tsugn-Shune Chin[2]; [1]Department of Materials Science and Engineering, National United University, Miao-Li, Taiwan; [2]Department of Materials Science and Engineering, National Tsing Hua University, Hsingchu, Taiwan.

Uniform nano-oxide particles using a solvothermal synthesis method is reported. The size of such particles is adjustable ranging from 4 nm to 200 nm by mixing various types of organic dispersants. The nano-oxides are composed of a ceramic core with a polymer shell and very stable in aqueous solutions. Poly(vinyl alcohol) dispersants are used in the current method to form micelles that act as micro-reactors encompassing the reactants inside the cell. While the system is irradiated by a 2.45GHz microwave in a microwave oven, chemical reactions and micro-explosions take place in micelles to convert dissolved metal ions into nano-oxides. This method has overcome the problems of aggregation and wide-particle-size distribution that always hapen during the production of nano-sized particles. Effect of molecular weight and OH content of PVA on the particle size distribution of the nano-oxides prepared by this method has been studied and a high resolution transmission electron microscopy (HRTEM) was used to directly observe the core-shell structure. The nano particles were also characterized by thermal analysis and X-Ray diffraction.

4:15 PM Y2.8
Synthesis of Mercury Cadmium Telluride Nanoparticles by Solvothermal Method.
Ranga Rao Arnepalli and V. Dutta; Centre for Energy Studies, Indian Institute of Technology, Delhi, New Delhi, New Delhi, India.

Mercury Cadmium Telluride (MCT) nanoparticles were synthesized by Solvothermal method for the first time. Mercury (I) chloride, elemental Cd, Te and trace amounts of Ferrous Chloride was added into the Teflon-Stainless-Steel autoclave. Ethylenediamine was used as solvent. The autoclave was kept at 180oC for 24hrs, then the reaction product was collected, washed and dried in vacuum for 2hrs. Different compositions of MCT were synthesized by varying the amount of Mercury Chloride and Cd to obtain Hg1-xCdxTe with x varying from 0 to 1. Thus prepared nanoparticles were characterized by RIGAKU Giegerflex-D X-ray diffractometer. X-ray diffraction patterns revealed the formation predominant (111) cubic phase MCT nanoparticles, the intensity of the peak also increased with the increase in the Hg content in Hg1-xCdxTe and for x=0 the X-ray diffraction studies revealed the formation of FCC phase HgTe. The nanoparticles were further characterized by Fei-Philips-260 MORGAGNI Transmission Electron microscope for particle size determination. TEM studies revealed the average particle size of 10nm and for x=0.5 it showed the average particle size of 15nm. Selected Area Electron diffraction patterns recorded for the nanoparticles also revealed the formation of cubic MCT nanoparticles (x=1 to 0.5) and FCC phase HgTe for x= 0. The lattice parameters calculated were well matched with the standard values. The main chemistry involved in the synthesis of MCT nanoparticles by solvothermal method is due to the presence of Ferrous Chloride. In the absence of Ferrous Chloride we got CdTe nanoparticles instead of MCT. We believe the trace amounts of Ferrous Chloride helps in the formation of Mercury ions which then leads to the formation of MCT nanoparticles .Whereas in the absence of Ferrous chloride no mercury ions available for the reaction, only CdTe formation takes place. This was confirmed by X-ray diffraction studies. In conclusion we report on the synthesis and characterization of MCT nanoparticles by solvothermal method for the first time. The role of Ferrous Chloride in the formation of MCT nanoparticles has been established. The reaction mechanism will be discussed in detail.

4:30 PM Y2.9
Computation of Temperature Distribution in Infiltration of Metal in Opal Using a Graphite Furnace Heating Assembly.
Hossein Golnabi, Mahmood Ghornnevis and Nahid Chaboki; Physics, Plasma Physics Research Center, Tehran, Iran.

In recent years metallic photonic crystals have shown many interesting results [1]. It has been mentioned that by decreasing the characteristic size of crystal periodicity, the position of the metallic photonic band gap may be shifted from the microwaves to terahertz frequencies and further into infrared spectral range. The method of the fabrication of opals and the melt infiltration is discussed for the network and cermet topologies. In that report the infiltration of metals in opals are reported in which a special die assembly is used for the melting and infiltration process. It has been shown that the infiltration process is sensitive to the heating temperature and pressing pressure. The use of high temperature furnace assembly used in high temperature high pressure machine [2] is proposed and modeled for such infiltration process. In equilibrium experiments using piston-cylinder a large sample volume with homogeneous temperature distribution is desired. On the other hand, for experiments at transient conditions a true knowledge of the temperature distribution is needed to drive the processes such as induced melt migration or diffusion. With such information and the experimental results provided by different thermocouples in the heating assembly it is possible to control the required temperature distribution in the system with graphite heating assembly. The goal here is to provide useful information about the temperature distribution inside the capsule cell in order to save some time and reduce synthesis cost in the real infiltration process. The heat conduction equation is solved for a cylindrical geometry and the variation of the temperature as a function of radius and axial distances are reported. Both the steady state and transient solutions are given for such an assembly. The 3-D finite element method for a symmetrical assembly is used and the temperature dependence of heat conductivity of multi elements is considered in the calculations. Such information concerning the temperature distribution inside the infiltration assembly is helpful for both the equilibrium studies and performing experiments under transient conditions. Results of such study help the users to properly select the appropriate temperature gradient for the steady state and transient situations. Since the heater can be controlled with a precise controller, thus the adjustment to a precise temperature and temperature gradient is possible. Such temperature and pressure adjustments are helpful for a successful melt infiltration process. [1] A. Zakhidov. R. H Baughman, et al. Three-dimensionally periodic conductive nanostructures: network versus cermet topologies for metallic PBG. Synthetic Metals, 116, 419-426(2001). [2] Depths of the Earth Company, Quick press operating manual and web site www.depthsoftheearth.com.

4:45 PM Y2.10
Cold Water Hydrolysis of Aluminum - Controlled Precipitation and the Preparation of Nano Alumina, Alpha Alumina.
Thiruchitrambalam Manickavasagam[1] and Vijayanthi R. Palkar[2]; [1]Mechanical Engineering, Mahalingam College of Engineering, Pollachi, Tamil Nadu, India; [2]Dept. Condensed Matter Physics and Materials Science, Tata Institute of Fundamental Research, Mumbai, Maharastra, India.

Aluminum metal has been hydrolyzed at room temperature in aqueous-glycerol media and aqueous-methonal media. After hydrolysis, the product i.e., precipitate was aged at room temperature and the ageing medium was diluted periodically. The precipitation and ageing media has influenced the phase composition and morphology of the hydroxides (nano alumina) significantly. The morphology of the hydroxide and alpha alumina powders were examined using TEM and SEM respectively. The microstructural features of the alpha alumina powder like porosity, necking,grain growth were examined using SEM photographs

SESSION Y3: Poster Session: Solvothermal Synthesis and Properties of Materials
Chairs: Gerard Demazeau, Sridhar Komarneni and Masahiro Yoshimura
Tuesday Evening, March 29, 2005
8:00 PM
Salons 8-15 (Marriott)

Y3.1
Methane/Water Adsorption Properties of Synthetic Imogolite Nanotubes. Fumihiko Ohashi[1], Shinji Tomura[1] and Shin-Ichiro Wada[2]; [1]Mat. Res. Inst. Sustain. Devlp., AIST, Chubu, Nagoya, Japan; [2]Agricultural Dept., Kyushu Univ., Fukuoka, Japan.

Imogolite is one of the naturally occurring aluminiumsilicates with a chemical formula of Al2O3SiO2(H2O)n, consisting of hollow nanotubes with an external diameter of about 2.5 nm and length from several hundred nanometers to a micrometer. The imogolite nanotubes has been synthesized from highly concentrated inorganic solutions by a hydrothermal treatment, which can be converted to a mesoporous nanofiber with a pore radius in the range of 0.3-0.6 nm resulting from the nitrogen adsorption isotherm. The 29Si MAS NMR spectra for the synthetic and natural imogolites exhibited a sharp peak centered at -79 ppm. This 29Si chemical shift is typical for the imogolite structures and originates from Si in a Q0 site bonded to one OH group. As other peaks were not detected, the chemical shift strongly suggesting that the SiO4 units are surrounded by mainly Al atoms. The 27Al MAS NMR spectra of the both samples exhibited isotropic peaks centered at -4 ppm and 58 ppm, which indicated the mainly presence of octahedrally coordinated Al (VI) and the slightly presence of tetrahedrally coordinated Al (IV). The electronic environment of imogolite Si is due to the presence of four adjacent oxygens, one attached to hydrogen and other three attached only to octahedral Al, i.e. Si(OAloct)3OH. The results of the water vapor adsorption isotherms, the natural imogolite showed an apporoximately isothermal line where the amount of adsorbed water increased in proportion to P/P0: the maximum amont of adsorbed water was ca. 60 wt%. The synthetic imogolite showed a rapid increase over the range of P/P0 of 0.9-0.95 and achieved a maximum of ca. 80 wt% and with a methane storage property better than that of the usual compressed natural gas storage. In order to obtain a large amount of water adsorption and a high methane storage capacity, it is necessary to control the micro/meso porous structure and the hydrophilic/hydrophobic surface affinity. It is expected that the synthetic imogolite might become a multipurpose adsorbent.

Y3.2
Roles of Glycols on Solvothermal Syntheses and Photoluminescence Properties of YAG:Ce^{3+} Nano-phosphors. Ryo Kasuya[1], Tetsuhiko Isobe[1], Hitoshi Kuma[2] and Junichi Katano[2]; [1]Keio Univ., Yokohama, Kanagawa, Japan; [2]Idemitsu Kosan Co. Ltd., Sodegaura, Chiba, Japan.

We investigate solvothermal reactions of yttrium(III) acetate, cerium(III) acetate and aluminum isopropoxide in various solvents with more than one OH groups to understand the role of solvents on the formation of Ce^{3+}-doped yttrium aluminum garnet (YAG:Ce^{3+}) nano-phosphors and their photoluminescence (PL) properties. The solvothermal reaction at 300°C for more than 1h in 1,4-butylene glycol (1,4-BG) produces crystalline YAG particles of 10nm diameter according to X-ray diffraction profiles and transmission electron microscopy. The crystalline YAG is also obtained by the solvothermal reaction in 1,3-BG. On the other hand, non-crystalline samples are formed by solvothermal reactions in other glycols, $HO(CH_2)_nOH$, with n=2,3,5,6 and alcohols, $CH_3(CH_2)_nOH$, with n=1~4. The coordination states for Al in YAG nanoparticles doped with and without Ce^{3+} are investigated by single pulse excitation (SPE) - MAS ^{27}Al-NMR with high power proton decoupling pulse and the $^1H \rightarrow {}^{27}Al$ cross-polarization (CP) - MAS ^{27}Al-NMR, where solid-state ^{27}Al-NMR experiments are performed in a static magnetic field of 9.39T at the spinning rate of 10kHz. Three ^{27}Al-NMR peaks are observed at 0.6, 50 and 65ppm in the SPE-MAS spectrum, whereas only one peak is observed at 3.5ppm in the CP-MAS spectrum. Each peak at 0 and 3.5ppm is assigned to the six-fold coordination for Al (Al^{VI}), and the peaks at 50 and 70ppm are assigned to the four-fold coordination for Al (Al^{IV}). The integral intensity of Al^{IV} relative to that of Al^{VI} in the SPE-MAS ^{27}Al-NMR spectrum was 1/2, being smaller than 3/2 for the YAG bulk. All the Al sites are observed in the SPE-MAS spectrum, while the Al sites near the surface, i.e., near protons of organic species adsorbed on the surface are observed in the CP-MAS spectrum. Therefore, we conclude that the Al^{IV} does not exist near the surface of YAG:Ce^{3+} nanoparticles. Since the glycothermal reaction of aluminum isopropoxide in 1,4-BG forms alkyl derivative of boehmite (ADB) with the Al^{VI}, the near-surface of YAG:Ce^{3+} nanoparticles appears to have the boehmite-like layer structure. According to the precious observation of lattice images, each primary particle is composed of one single crystal domain, and the same crystalline orientation in the coalescent particles is observed. This might indicate that YAG is formed through the ADB intermediates and the crystalline orientation is kept between YAG and ADB. In other words, these intermediates should play a significant role in the formation of crystalline YAG. The YAG:Ce^{3+} nanoparticles show the asymmetric PL peak at 530 nm corresponding to the 5d ($^2A_{1g}$)→ 4f ($^2F_{5/2}$ and $^2F_{7/2}$) transitions of Ce^{3+} by excitation of blue light. We find out that the surface modification, i.e., the adsorption of YAG:Ce^{3+} nanoparticles with 1,4-BG and acetates plays a significant role in the PL enhancement, and that the solvothermal reaction in the mixture of 1,4-BG and polyethylene glycol can improve the PL intensity.

Y3.3
Ammonothermal Crystallization of AlN Crystals. Alexander Motchanyy, Alexey Reu, Vladimir Kovalenko and Vladimir Balakirev; Russian Research Institute for the Synthesis of Materials (VNIISIMS), Alexandrov, Russian Federation.

III-Nitride (GaN, AlN and other compounds) have attracted vast interest due to their unique properties and potential applications in optoelectronic devices operating in the blue and UV spectral regions and for the construction of electronic devices capable of operating under high power and high temperature conditions [1-3]. In the paper, we report on the synthesis of nanocrystalline AlN in supercritical ammonia at low temperature by ammonothermal method (AMMONO method), which utilizes ammonia as fluid rather than water as in the hydrothermal process. Nanocrystalline AlN powder were obtained by AMMONO method, in which nitridization of Al metal occurs in highly chemical active supercritical ammonia and recrystallization of AlN powder in NH_3 using both NH_4 X (X=Cl, I) as mineralizers. Mineralizers were added to the autoclave in order to accelerate the chemical reactions rate by increasing the amount of anions in the supercritical NH_3 solution. The experiment were performed in the temperature range of 350-550 °C and pressure of 80-120 MPa in stainless steel autoclaves for up to 5 days. Nanocrystalline AlN were spontaneously nucleated on the lower walls of the autoclaves. The obtained AlN powder was characterized by X-ray diffraction. The morphology and size of the nanocrystalline aluminum nitride was observed using both optical microscopy and scanning electron microscopy (SEM). Nanocrystalline AlN powders with average crystallite size 20-30 nm were produced in the temperature range of 450-550 °C. Details of characterization of the AlN are also presented. References [1]. S.J. Pearton, R.J. Shul, F. Pen, MRS Internet J. Nitride Semicond. Res. 5 (2000) 11. [2]. S. Nakamura, Science 281 (1998) 956. [3]. H. Morkoc, Nitride Semiconductors and Devices, (Springer, New York, 1999).

Y3.4
Crystal Growth of RNiO3 Perovskites under High Oxygen Pressure and Hydrothermal Conditions. Jose Antonio Alonso[1], Maria Jesus Martinez-Lope[1], Maria Teresa Casais[1], Angel Munoz[2], Alain Largeteau[3] and Gerard Demazeau[3]; [1]Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Cientificas, Madrid, Spain; [2]Depto. de Fisica, EPS., Univ. Carlos III., Madrid, Spain; [3]Institut de Chemie de la Matiere Condensee de Bordeaux, Universite Bordeaux 1, Bordeaux, France.

The family of RNiO3 perovskites (R= rare earths) offers an excellent opportunity to study a metal-to-insulator (MI) transition in narrow s* band oxides, in which the bandwidth can be significantly varied as the eg (Ni)- 2ps(O) covalent mixing is progressively reduced from R= La to Lu. The materials containing R3+ cations smaller than La3+ present a rather rich phenomenology associated with the MI transition, including the occurrence of a charge disproportionation (CHD) of Ni3+ cations associated with the electronic localization in YNiO3 (TMI= 582 K). In the delocalized carriers regime, above TMI, the structure is orthorhombic (Pbnm), similar to that of RNiO3, R= Pr, Nd. Below TMI the symmetry changes to monoclinic (P21/n). Most of the preceding findings have been studied on polycrystalline RNiO3 samples; only NdNiO3 has been growth in single crystal form (1), at 4 GPa under high oxygen pressure resulting from the in situ decomposition of KClO4. In the present work, we describe the crystal growth of the more distorted perovskites YNiO3, HoNiO3 and LuNiO3, with an average crystal size of 10-20 microns, starting from mixtures of R2O3 oxide, Ni(OH)2 and KClO4. The use of starting reactives in the form of hydroxides would be crucial for the dissolution and crystallization process under high pressure conditions, water vapor transport driving reactions under hydrothermal-like conditions. The evaluation of the cooling-time on the crystal-growth process is also in progress. (1) J.A. Alonso, A. Munoz, A. Largeteau, G. Demazeau, J. Phys: Cond. Matter 16, S1227 (2004)

Y3.5
Solvothermal Synthesis of Titania, Zirconia and Titania/Zirconia Composite. Xin Michael Wang and Ping Xiao; Materials Science Centre, University of Manchester, Manchester,

United Kingdom.

Solvothermal synthesis has been used to produce titania, zirconia, and titania/zirconia composite nanophase particles. The relationship among crystallite size, particle phase, particle size and synthesis condition have been established. In addition, particle morphology was also modified by change of the synthetic condition. Meanwhile, titania/zirconia composite particles have been produced by co-precipitation and a sequential precipataion methods. The produced composite particles show uniform nanoscale phase distribution and in some case a core-shell structure. For the synthesis of the composite, the effect of titania or zirconia on the crystallisation of zirconia or titania has been examined.

Y3.6
Synthesis of Calcium Carbonate in Ethanol-Ethylene Glycol Media. Mi-Young Ryu[1], Hyoung-Ho Lee[1], Sang-Bop Lee[2] and Hwan Kim[1]; [1]Seoul National University, Seoul, South Korea; [2]Korea Electronics Technology Institute, KyungGi-Do, South Korea.

Calcium carbonate widely utilized in various industrial applications, has several polymorphs and particular particle shapes with the different synthesis conditions. Especially needle-like aragonite particles are evaluated as high-performance fillers in paper and rubber. Therefore, there have been many researches concerning the preparation of metastable phase, such as aragonite and vaterite, or the synthesis of the elongated calcite. In this study, calcium carbonate powders of various elongated shapes were successfully synthesized via two-step process in ethanol-ethylene glycol solvent system which is known to stabilize metastable calcium carbonate phases by inhibiting the transition to the stable calcite phase. In first stage, we prepared gel-type calcium carbonate with liquid-vapor reaction method (carbon dioxide gas flow in the Ca^{2+}/ethanol/ethylene glycol solution) and in the next place, the resultant gel was aged at different temperatures for 3 days. We obtained the final products through washing, filtering and drying. The phases and the morphologies of samples were analyzed with XRD, SEM and TEM. The spherical particles and the elongated ones were observed to coexist in all samples, and the latter changed its specific shape from peanut-like through columnar to spindle, with aging temperatures of 40°C, 70°C and 100°C, respectively. Electrom beam diffraction patterns confirm that the peanut-like and the columnar particles are aragonite and the spindle are vaterite single crystals.

Y3.7
Characterization of Indium-Tin-Oxide Films Grown by Polymer-Assisted Deposition. Y. Li, J. Xie, Y. Lin, Q. X. Jia, A. K. Burrell and T. M. McCleskey; Los Alamos National Laboratory, Los Alamos, New Mexico.

Indium-tin-oxide (ITO) thin films have been deposited successfully on glass substrates by a polymer-assisted deposition (PAD) technique we developed recently. We have used ellipsometer, in-situ transport measurement, and thermogravimatric analysis (TGA) to characterize the films. Systematic changes in the thickness, the electrical resistivity, and the mass of the films have been observed during the early stage annealing process. We have investigated the decomposition of the polymer and the formation of metal-oxide with right phase during the heat treatment process. This study is important to understand the growth mechanism of metal-oxide films grown by PAD.

Y3.8
Growth Behavior of Tin Oxide Nanoparticle Suspensions Induced by Hydrothermal Treatment. Eduardo Lee, Caue Ribeiro, Elson Longo and Edson Roberto Leite; Universidade Federal de Sao Carlos, Sao Carlos, SP, Brazil.

Tin oxide is a very interesting material from the technological point of view. The combination of its chemical, electrical and optical properties enable a great number of potential applications, such as gas sensors, catalysts and opto-electronic devices. There is a great number of studies reported in the literature regarding the synthesis of tin oxide nanoparticles. In spite of the fact that it is essential to understand the growth behavior of nanocrystals, in order enable the preparation of controlled nanostructures, investigations on the growth behavior of tin oxide nanocrystals are scarce. In this work, tin oxide nanocrystal suspensions were synthesized by the controlled hydrolysis of tin chloride II. The room temperature-synthesized nanoparticles presented nearly spherical morphologies and a mean particle diameter in the range of 3-5 nm. The growth of the as-prepared nanoparticles was induced by means of hydrothermal annealings. The hydrothermal treatments were carried out at 100, 150 and 200oC for different periods of time. The growth of the nanoparticles was investigated by characterizing the hydrothermally annealed suspensions by transmission electron microscopy. The particle size evolution of the annealed samples showed that growth by the Ostwald ripening mechanism is not significant in the conditions investigated in this study. On the other hand, the morphological evolution from nearly spherical particles, in the as-prepared samples, to irregular nanocrystals, in the hydrothermally-annealed samples, indicates that growth by the oriented attachment mechanism should be very significant. The particle size growth was analyzed, as a function of time, by a simple model that describes growth by the oriented attachment mechanism. The results are strong indications that growth in tin oxide nanocrystal suspensions occurs solely by oriented attachment, which is in accordance with the extremely low solubility of this material. Moreover, it was possible to observe that longer periods of hydrothermal treatments may also induce some anisotropic growth of nanocrystals.

Y3.9
Hydrothermal Preparation of the Layered Material of $Li_xV_yO_2$ (x = 0.84 and y = 0.78) and its Electrochemical Properties. Kiyoshi Ozawa[1], Hiroki Fujii[1], Lianzhou Wang[2], Mika Eguchi[3], Hitoshi Yamaguchi[1] and Yoshio Sakka[1]; [1]National Institute for Materials Science, Tsukuba, Ibaraki, Japan; [2]The University of Queensland, Brisbane, Queensland, Australia; [3]Ibaraki University, Hitachi, Ibaraki, Japan.

A new type of layered compound of $Li_xV_yO_2$ (x = 0.84 and y = 0.78) was prepared by the hydrothermal reaction of V_2O_3 with $LiOH{\cdot}H_2O$ at 180 °C. The Rietveld refinement based on the X-ray diffraction data revealed that this material has a layered rhombohedral structure corresponding to space group symmetry of R3m with unit cell parameters of a = 2.9101(4) and c = 14.230(2) $\AA$ in the hexagonal system, where the V atoms occupy 3a (0, 0, 0) and 3b (0, 0, 1/2) sites. The charge and discharge properties of the material were investigated using a coin-type cell. It was found that the material shows a relatively large capacity of about 100 $mAhg^{-1}$. Such electrochemical properties are discussed compared to those of the related compounds such as $LiNiO_2$.

Y3.10
Ferromagnetism in Cobalt-Contained Nanoparticles/Nanorods Prepared Hydrothermally. X. F. Wang[1,2], J. B. Xu[1,2], Jin An[1,2], Y. W. Lai[1,2], N. Ke[1,2], S. P. Wong[1,2] and Rong Zhang[3]; [1]Dept. of Electronic Engineering, Chinese University of Hong Kong, Hong Kong, Hong Kong; [2]Materials Science and Technology Research Center, Chinese University of Hong Kong, Hong Kong, Hong Kong; [3]Dept. of Physics, Nanjing University, Nanjing, China.

A new cobalt-contained phase (blue color) was synthesized directly via the facile hydrothermal method from aqueous solutions of cobalt acetate and hexamethylenetetramine (HMT), and was systimatically characterized by XRD, SEM, and TEM measurements. The results reveal that this new phase interestingly has the identical crystalline diffraction-peaks as those of ZnO crystal, and has the morphology of nanoparticles/nanorods in a size around 50 nm. The nanorods are preferentially oriented along the c-axis direction and exhibit a single-crystalline hexagonal (wurtzite) structure. Also the magnetic properties of the fabricated nanostructure were characterized by exploiting vibrating sample magnetometer (VSM) technique. The results surprisingly show that the new phase possesses a strong ferromagnetic behavior from 5 K to 300 K (room temperature), very different from the well-known antiferromagnetic characteristics of CoO. Detailed structural investigation of the as-formed cobalt compound and the mechanism of its formation are in progress.

SESSION Y4: Solvothermal Synthesis
Chairs: Tadafumi Adschiri and Masahiro Yoshimura
Wednesday Morning, March 30, 2005
Room 3022 (Moscone West)

8:30 AM *Y4.1
Soft Chemical Route to Zinc Oxide Nanocrystals with Various Morphologies. Jin-Ho Choy, Nanoscience, Ewha Womans Univeristy, Seoul, South Korea.

Zinc oxide (ZnO) with a large excition binding energy (60 meV) and a direct wide band gap (ΔEg = 3.37 eV) has a renewed interest owing to its broad range of applications as an ultraviolet laser, gas sensor, solar cell, light emitting diode, catalyst, and so on. In particular, scientific and technological interests in one-dimensional ZnO nanomaterials with various morphologies such as nanowires, nanotubes, nanocombs, and nanobelts have been rapidly increased since the electrical and optical properties depend sensitively on the size, shape and orientation of the nano-bulding blocks. However, most of their successful syntheses were achieved under high temperature conditions at around 1,000^{circ}C. Recently, we reported that various ZnO nanoarrays and nanomaterials such as nanorod arrays, nanowall arrays, nanocoral reefs, and nanofibers with a remarkably enhanced

ultraviolet lasing properties could be realized by hydrothermal reaction under significantly lower temperature than that of thermal evaporation procedure. Such a hydrothermal method has an excellent advantage in terms of easy scale-up, low production cost, and environmental friendliness. However, a reasonable explanation for the morphology variation of ZnO crystal under hydrothermal reaction is rarely reported due to lack of experimental and theoretical study. Such a difficulty comes from the fact that morphology of ZnO crystal in aqueous solution is affected by various factors such as pH, nutrient solution, temperature, reaction time, and so on. In this study, the evolution of morphology, from prismatic rod shape to rectangular belt one, was examined from hydrothermally grown ZnO at 95^{circ}C in the presence of nutrient solution of zinc acetate and hexamethylenediamine mixture (pH = 6.7). In order to carry out the mechanistic study on morphological evolution, the intermediate reaction products were carefully analyzed by field emission scanning electron microscopy, powder X-ray diffraction, mass spectroscopy combined thermal analyzer, and high resolution transmission electron microscopy.

9:00 AM *Y4.2
Electro-Synthesis of Metal Encapsulated Carbon Nano-Cells in Organic Solvent under Local Solvothermal Conditions.
Tomoaki Watanabe, Yasuaki Yamakawa, Naota Sugiyama and Masahiro Yoshimura; Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama, Japan.

Nano carbons and related materials have recently been received a considerable amount of attention due to their novel properties. For example, carbon nano capsule encapsulated metal particles might have important applications in areas such as magnetic data storage, magnetic resonance imaging and medical appreciations so on. The role of the carbon layer would be to isolate the metal particles from each other and to provide the oxidation resistance of the bare metal nanoparticles. Moreover, the carbon coatings can give the biocompatibility and stability in many organic and inorganic media to the metal nanoparticles. Therefore those carbon nano capsule encapsulated metal particles are interesting candidates for many bio-engineering applications including drug delivery, biosensors, and magnetic contrast agents for magnetic resonance imaging. In the past a few years, carbon nano capsule encapsulated metal particles have attracted a great number of research interests all over the world. In order to realize practical application of those carbon nano capsules encapsulated metal particles, it is necessary to establish a process for large production. Generally, those nano-particles are produced by arc discharge method with metal/carbon composite electrode in inert gas [1]. Recently, some new method has been developed like the method using reaction between nano-diamond and metal powder at high temperature in the vacuum [2] and using reaction of metal powder with CO gas at high temperature [3]. All of the method allow to fabricate the particles but not suitable for mass production because of their low yields, low efficiencies of source materials, and energy efficiency or difficulties to collect pure products. We have developed a direct fabrication method for carbon-encapsulated metal nanoparticles from organic solvent. Our method allow to fabricate the nano particles without carbon electrode and vacuum with applying radio frequency power between metal electrode in the ethanol. Figure shows the nano-particle carbon nano capsule encapsulated cobalt metal particles. In this presentation, we will present feature of our method and product with some characterization results. [1] S. Yamamoto, T. Yoshikawa, M. Okuda and N. Fujimoto, J. Appl. Phys. 75 (1), 1 (1994) [2] S. Tomita, M. Hikita, M. Fujii, S. Hayashi, K. Yamamoto, Chem. Phys. Lett. 316 (2000) [3] J. Jiao, S. Seraphin, J. Phys. Chem. Solids. 61 (2000) 1055

9:30 AM Y4.3
Solvothermal Synthesis of Bulk Wide-Bandgap Single Crystals for the Production of Semiconductor Substrates.
Michael J. Callahan[1], Kelly Rakes[1], David Bliss[1], Erik Grant[1], Loniel Bouthillette[1], Buguo Wang[2] and Sheng-Qi Wang[2]; [1]SNHC, Air Force Research Lab, Hanscom AFB, Massachusetts; [2]Solid State Scientific, Nashua, New Hampshire.

Since the demonstration of the first transistor by Bell Laboratory researchers in 1947, the semiconductor market has grown to one of the largest world wide industries, with annual sales in the hundreds of billions of dollars. Semiconductors are now ubiquitous in everyday life, which would not be possible without single crystal substrates in which all current commercial semiconductors devices are manufactured on. The majority of commercial substrates are derived from large bulk single crystals grown from molten techniques such as the Czochralski and vertical gradient freeze techniques. These traditional molten techniques produce high yields of large boules with high crystallinity at a low cost, which yield many thousands of substrates annually. Wide-Bandgap semiconductors such as gallium nitride, diamond, and silicon carbide can potentially fulfill many of the needs in the semiconductor community such as; high speed-high power electronic devices; dilute magnetic semiconductors operating above room temperature; radiation hardened electronics; and optoelectronic devices that, depending on the type of device manufactured, have applications from the terahertz to the deep ultraviolet. Most wide-bandgap compounds have high melting points with large equilibrium pressures, which makes melt growth improbable unlike traditional semiconductors such as Si, GaAs, and InP. Thus other techniques must be used to produce wide-bandgap substrates on a commercial scale. Large scale solvothermal growth of single crystals for production of wide-bandgap substrates potentially has several advantages over other growth techniques such as physical vapor transport, hydride vapor phase epitaxy (HVPE), and flux growth. Here we will review two wide-bandgap bulk crystals synthesized solvothermally, zinc oxide crystals grown in high pressure alkaline water and gallium nitride crystals grown in supercritical alkaline ammonia. A brief review of current research and commercialization of solvothermal growth of ZnO and GaN by other groups will be reviewed. Our own research will then be discussed in some detail. We have grown up to 25mm x 1mm ZnO boules in our laboratory and are concentrating on developing a methodology to allow large volume production of uniform conducting and semi-insulating ZnO substrates with less than 1000 dislocations/cm by the hydrothermal method. Characterization of growth morphology, optical, and electrical properties of the bulk crystals will be discussed. Finally we will discuss growth of single crystal GaN up to 1mm x 10mm x 10mm deposited on HVPE seeds. Retrograde solubility will be demonstrated with our current conditions and efforts on optimizing the technology to increase growth rates and reduce impurities will be discussed. These results will show that solvothermal growth has several advantages over other growth techniques for the large scale production of single crystals for the manufacture of wide-bandgap semiconductor substrates.

9:45 AM Y4.4
Solvent Effect on Microstructure of Yttria-Stablised Zirconia Particles in Solvothermal Synthesis.
Zile Hua[1,2], Xin Michael Wang[1], Ping Xiao[1] and Jianlin Shi[2]; [1]Materials Science Centre, University of Manchester, Manchester, United Kingdom; [2]Shanghai Institute of Ceramics, Chinese Academy of Science, Shanghai, Shanghai, China.

Using methanol or methanol/2-propanol mixtures as reaction media, YSZ particles were synthesized with solvothermal processing. The particles structures were characterized with X-ray diffractometry (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), laser particle-size analysis, and nitrogen adsorption isotherms. Results indicated that cubic/tetragonal YSZ nanocrystals with crystal size lower than 5 nm were obtained and their sizes were controlled solvent compositions, reaction temperatures and reaction durations. In addition, Solvent composition controlled the morphology of the YSZ agglomerate/aggregate particles. According to DLVO theory and zeta potential results, solvent effect on microstructures of YSZ particles in solvothermal synthesis has been examined. Moreover, based on these results, particle structure evolution in solvothermal synthesis has been discussed.

10:30 AM Y4.5
Structure, Morphology and Photocatalytic Activity of Novel Hydrothermal ZnBiVO4.
Bharat B. Kale[2,1], Jin-Ook Baeg[1], Sang Mi Lee[1], Hyunju Chang[1], Sang-Jin Moon[1] and Jin-Soo Yoo[1]; [1]Advanced Chemical Technology Division,, Korea Research Institute of Chemical Technology (KRICT), Daejon, South Korea; [2]Nanocrystalline Materials, Centre For Materials For Electronics Technology (C-MET), Pune, Maharashtra, India.

We offer a synthesis of novel nanocrystalline ZnBiVO4 using hydrothermal method. The same novel catalyst was synthesized using solid-state route for the first time. We have exemplified the hydrothermal synthesis of this new compound using zinc nitrate, bismuth nitrate and ammonium metavanadate. The ZnBiVO4 was synthesized using zinc oxide, bismuth oxide and vanadium oxide by solid-state route. The resultant product was characterized by X-ray difractometry for its structural study and Scanning Electron Microscopy for the particle morphology. The prima facie observations reveled the formation of tetragonal crystallites of hydrothermal ZnBiVO4 ranging from 40-50nm. The BET surface area of hydrothermal ZnBiVO4 was increased 900 times as compared to solid state ZnBiVO4. The steepness of the UV-visible DRS (Diffuse Reflectance Spectra) absorption edge, suggests the good crystalline nature of the material. From the photodecomposition of H2S, it was noteworthy that the hydrogen evolution was enhanced by 70% in hydrothermal ZnBiVO4. A tentative structure has been suggested for such hitherto unstamped material as a promising photocatalyst.

10:45 AM Y4.6
Synthesis and Surface Modification of Metal Oxide Nanoparticles in Sub and Supercritical Water.
Seiichi Takami,

Tahereh Mousavand, Satoshi Ohara, Mitsuo Umetsu and Tadafumi Adschiri; Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Miyagi, Japan.

We report synthesis and surface modification of metal oxide nanoparticle in sub and supercritical water. Surface modification of metal oxide nanoparticles was performed by the dehydration between an organic molecule and a hydroxyl group on the growing surface of metal oxide nanoparticles under hydrothermal conditions. We note that organic reagents become miscible with water at higher temperature due to decreased dielectric constant of water. Therefore, metal oxide nanoparticles can be tethered with longer alkyl chains that are not miscible with water at room temperature. We synthesized iron oxide nanoparticles that were modified with C10 alkyl chains. The end of alkyl chains was changed to -CH_3, -NH_2, and -COOH, controlling the surface properties of the oxide nanoparticles. We also successfully attached peptides on the surface of metal oxide nanoparticles. We confirmed that the similar approach is effective for various metal oxides including TiO_2, Co_2O_3, NiO, and Ce_2O_3.

11:00 AM Y4.7
Synthesis, Particle Morphology Control and Optics Properties of LnBO3:Eu3+(Tb3+) by Hydrothermal Process. Y. H. Wang and J. C. Zhang; Material Science, Lanzhou University, Lanzhou, GanShu, China.

After more than 50 years of extensive research on the luminescent materials applied in lamps and displays, compounds are obtained with almost ideal physical properties. Contrary to classical areas of application, nowadays the search for new materials is most important for tomorrow's fields of light generation for displays and illumination. Consequently, the search for new materials, for example, vacuum ultraviolet (VUV) phosphors on plasma display panels (PDPs) is performed vigorously in industry and university laboratories. In addition, an environment disadvantage of fluorescent lamps is fact that they involve Hg plasma, the VUV phosphors may very well be a potential candidate for mercury-free lamps.Phosphors used in PDPs strongly resemble the phosphors applied in fluorescent lamps. In PDP, three primary colors are generated by using three types of inorganic phosphors, which are excited by a discharge of the Xe gas. The phosphors currently used for PDPs are BaMgAl10O17: Eu2+ (blue), Zn2SiO4:Mn2+ (green) and (Y,Gd)BO3:Eu3+ (red). They have their own merits and drawbacks and high efficiency phosphors are desired. Thus considerable efforts are underway to develop new phosphors as well as to improve existing phosphors. For the application of high resolution display, phosphors properties were deeply affected by their morphologies and particles size. Furthermore, the phosphor particles must have narrow size distribution, non-agglomeration and spherical shape for good luminescent characteristics. In this paper, the novel red and green LnBO3:Eu3+(Tb3+) (Ln=rare earth) phosphors were successfully prepared by a mild hydrothermal process. By changing and controlling the condition of hydrothermal reaction, not only sphere, rod and plate morphology LnBO3:Eu3+(Tb3+) phosphors in micron but also nanoscale phosphors have been obtained. Their photoluminescence was investigated under UV (254nm) and VUV (147nm) excitation. The result indicated that the spherical phosphors show excellent luminescence properties both in UV and VUV region. This could be due to its uniform particle size without milling process as well as better properties of spread and high photoluminescence efficiency.

11:15 AM Y4.8
Nanoscale Structural Features of Ultra-fine Zirconia Powders Prepared via Precipitation-Hydrothermal Treatment Route. Vladislav A. Sadykov[1], Vladimir I. Zaikovskii[1], Dmitrii A. Zyuzin[1], Ella M. Moroz[1], Elena B. Burgina[1] and Valerii A. Matyshak[2]; [1]Heterog. Catalysis, Boreskov Inst. of Catalysis, Novosibirsk, Russian Federation; [2]Semenov Inst. of Chem. Physics, Moscow, Russian Federation.

Genesis of the structure of zirconia fine particles prepared by precipitation of amorphous hydrated zirconia by ammonia from nitrate solution followed by hydrothermal treatment of precipitate, washing and calcination under air up to 1000 C has been studied by HRTEM, X-ray diffraction, Raman, FTIRS. Dehydration at 300 C causes crystallization of cubic zirconia domains (2-3 nm) in amorphous matrix, while at 400 C nanoparticles (5-10 nm) of both cubic and monoclinic phase appear. Sample annealed at 500 C is comprised of nanosized monoclinic zirconia particles with fairly perfect structure. This is confirmed by Raman and FTIR spectra revealing bands corresponding only to monoclinic-type structure. Calcination at 600-650 C causes removal of residual lattice hydroxyls. Ordering of thus generated point defects is reflected in appearance of closed voids as well as in multiple (polysynthetic) twinning of monoclinic zirconia particles. In these particles, thin (1-5 nm) slabs alternate being separated by (001) mirror plane. HRTEM analysis revealed pronounced strain-induced relaxation of the structure of these slabs leading to more symmetric arrangement of atoms resembling that in tetragonal zirconia. This is reflected in reappearance of XRD (111) diffraction peak of a cubic phase, though integral intensity of the monoclinic phase reflexes remains constant. Such a disordering leads to disappearance of Raman spectrum, while the local distortion of coordination polyhedra characterized by FTIRS of lattice modes remains identical to that in monoclinic phase. Simulation of X-ray diffraction patterns using a program for the layered structures modeling revealed that indeed multiple twinning in m-zirconia is able to generate reflexes corresponding to both cubic and monoclinic phases, provided certain relations between slab thickness and mirror-related slabs alternation sequence is kept. After annealing at 1000 C polysynthetically twinned particles disappear, which removes a cubic (111) reflex from XRD pattern. Hence, nanosized m-zirconia particles prepared from hydrothermally treated amorphous precursor appear to be stabilized by residual hydroxyls decreasing their surface energy. The loss of hydroxyls and accompanying generation of point defects enhances their surface energy, which is decreased by multiple nanoscale twinning leading to more symmetric average arrangement within thin slabs. This specificity of nanostructure is reflected in the adsorption properties of surface Lewis and Broensted acid sites, which are important for catalysis of acid-base reactions. Moreover, coordination and clustering of supported transition metal cations (Cu, Co) and/or precious metals are also sensitive to the zirconia nanostructure, which is reflected in performance of such catalysts in red-ox reactions (methanol synthesis/steam reforming, NOx reduction by hydrocarbons etc). This work is in part supported by Integration Project 8.17 of Presidium RAS.

11:30 AM Y4.9
Phase Composition and Grain Size Distribution in Zirconia Nanopowders Produced in a Microwave Driven Hydrothermal Reaction. Agnieszka Opalinska[1], Roman Pielaszek[1], Hubert Matysiak[2], Cristina Leonelli[3], Witold Lojkowski[1] and Krzysztof Kurzydlowski[2]; [1]Institute for High Pressure Physics, Warsaw, Poland; [2]Faculty of Materials Science, Warsaw University, Warsaw, Poland; [3]Faculty of Engineering, University of Modena and Reggio Emilia, Modena, Italy.

Hydrothermal synthesis of nanopowders is a well established method. Recently the microwave driven hydrothermal reactions are extensively studied. Application of microwaves permits to heat substrates in the liquid form uniformly over the entire volume with a high heating rate. This advantage of microwave heating can best be exploited for reactions carried under high pressures, which permit charging high microwave energy density prior to reaching the boiling point. Rapid heating implies also significant reduction of the energy lost to the reactor vessels walls. Hence, even short reactions can be carried out in well defined conditions: the reaction temperature and reaction time are independent variables. In this paper we report results of the studies of microwave driven hydrothermal synthesis of zirconia powders. The reactions have been carried out at a fixed reaction time of 30 min and variable synthesis pressure. The reactions were performed in aqueous solutions by neutralising ZrOCl2 with NaOH. The solution volume was 70 ml, and the microwave power applied was 250 W under three reaction pressures: 4.2 MPa, 5.5 MPa and 8 MPa. The Grain Size Distribution (GSD) of the fabricated powders was measured both using transmission electron microscopy and a newly developed method for X-ray Diffraction Line Profile analysis (X-DLPA). It was found that the reaction product consisted of 70 - 80 wt.% of tetragonal phase and balance of monoclinic phase. The average grain size of the tetragonal phase was virtually not affected by the processing conditions (varying in the range 10 - 12 nm, with dispersion 3 nm), while the monoclinic phase grows both with reaction time and pressure, leading to a bimodal GSD with individual grains with size in the range 20 - 50 nm. The materials obtained by microwave driven hydrothermal reaction with precise control of the process conditions exhibit interesting physical properties and further studies are carried out on their applications. The new XRD methods for characterisation of nanopowders used in this study gave better insight in the formation mechanism of zirconia nanopowders during hydrothermal synthesis.

11:45 AM Y4.10
Hydrothermal Synthesis of Mechanically Strong Porous Composites of MeOx/Al2O3/Al-Type. Sergei F. Tikhov, Vladislav A. Sadykov, Yulia V. Potapova, Ivan V. Yudaev, Olga B. Lapina, Sergei V. Tsybulya, Aleksei N. Salanov and Akeksei I. Titkov; Heterog. Catalysis, Boreskov Inst. of Catalysis, Novosibirsk, Russian Federation.

Basic features of the process of metallic aluminum oxidation into hydroxides by the gas phase or liquid water at temperatures up to 210 C and pressures up to 20 atm have been elucidated. The effect of powdered oxides of Mg, Ca, La, Ti, Al or their nitrate salts on this process kinetics has been studied. The experimental procedure consists in mixing Al powder with additives and putting this mixture

into a stainless steel press-form allowing free access of water and removal of evolved hydrogen, this form being then placed in an autoclave. To incorporate other elements into emerging aluminum hydroxides, autoclaves instead of pure water were filled with solutions containing nitrate salts of promoters. Hydrothermal treatment leads to aluminum oxidation and, thus, to increase of the solid phase volume. As the result of self-pressing, a mechanically strong monolith with macroporous structure is produced. After decomposition of hydroxides by calcination in air, the microporous structure is formed. Effects of powdered and soluble additives on the aluminum reactivity as well as structure and texture of obtained alumina were clarified. The processes of the redistribution of soluble additives between solid phase in the press-form and autoclave solutions were revealed and described. Relations between the parameters of the macroporous structure and mechanical strength of granulated composites were considered.

SESSION Y5: Solvothermal Synthesis, Corrosion and Processing
Chairs: Jin-Ho Choy and Philipp Gutlich
Wednesday Afternoon, March 30, 2005
Room 3022 (Moscone West)

1:30 PM *Y5.1
Engineered Hydrothermal Crystallization of Ceramic Coatings. Richard Erick Riman and George A. Rossetti; Materials Engineering, Rutgers, The State University, Piscataway, New Jersey.

The field of hydrothermal coatings provides a rich area for new materials development. Key advantages of this technology include its ability to control chemical and physical microstructure, simplicity, cost and its effective role in industrial ecology. Opportunities abound in the area of polycrystalline films, textured materials and epitaxial films. This talk will cover focused efforts in our laboratory that encompass applications which include electronics, bioceramics and conversion coatings. Our paradigm for process engineering encompasses the use of thermodynamics to drive experimental research by specifying processing variable phase space for the stability of the desired ceramic material. These calculations also drive experimental designs for kinetic investigations by mapping out conditions that regulate crystallization kinetics, reaction rate and define species concentrations that potentially rate limit its process. This talk will describe show examples of this approach as it relates to the engineering of lead zirconate titanate, acmite, and hydroxyapatite coatings.

2:00 PM *Y5.2
Low Temperature Hydrothermal Corrosion of Mullite. Hartmut Schneider[1], Nadine Eils[2], Claus Reuscher[2] and Martin Schmucker[1]; [1]Institute of Materials Research, DLR, Koeln, Germany; [2]Institute of Mineralogy, University of Hannover, Hannover, Germany.

Single crystal and polycrystalline mullite samples were hydrothermally treated at 780°C and up to 7 days sealed in gold capsules (water (H_2O) pressure up to 2 kbar "stationary conditions") and under low water pressure but gas flow at temperatures of 1600°C ("dynamic conditions"). Optical and electron microscopy and infrared spectroscopy have been used to characterize the hydrothermal corrosion of mullite. The corrosion (2 kbar water pressure) produces an about 20 μm thick layer with typical "lip-shaped" features consisting of sillimanite and hexagonal plates of α-alumina (corundum). The newly formed sillimanite displays strict orientational relationships to mullite, which is reasonable since both phases belong to the mullite family of crystal structures. Things are completely different in open systems with water gas flow at 1600°C. These corrosion experiments of mullite in a first step lead to a certain hydroxylation of the mullite crystal structure and after longer high temperature treatments to the formation of α-alumina plus volatile silicon hydroxide ($Si(OH)_4$).

2:30 PM Y5.3
Hydrothermal Growth of High-quality 3-inch ZnO Single Crystals. Dirk Ehrentraut[1], Akira Yoshikawa[1], Hiraku Ogino[1], Tsuguo Fukuda[1] and Ikuo Niikura[2]; [1]Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan; [2]Tokyo Denpa Co. Ltd., Tokyo, Japan.

ZnO ia a wide band gap semiconductor (E_g − 3.37 eV) with a large exciton binding energy of 60 meV. Although the high potential for application in optoelectronics, piezoelectric and as scintillator is recognized for longer time stronger interest emerged recently when large size single crystalline substrates become available. We report the growth of high-quality 3 inch ZnO crystals on industrial scale by using hydrothermal method. Autoclaves with Pt inner container are used to isolate the mineralizers (1 mol/l LiOH and 3 mol/l KOH) containing supercritical solution from the Inconel walls of the autoclaves. The feedstock is high purity sintered ZnO, separated by a baffle from the ZnO seeds. Applying the growth temperatures 300-400°C at pressures of 80-100 MPa a growth rate about 30 μm h^{-1} is obtained. The growth time extends up to 60 days. Wafers of ⟨0001⟩ are cut and than further machined by applying a chemical-mechanical polishing procedure. The last step is thermal annealing at 1100°C. The excellent quality of the wafers is confirmed by low etch pit density (epd) of 80 cm^{-2}. The X-ray full-widt-at-half-maximum (FWHM) for (002) is 18 arcsec. To our knowledge this is the best value for FWHM ever reported for ZnO large bulk material. Atomic force microscopy (AFM) reveals the superior quality of ready-to use wafers. A root-mean-square roughness of 0.12 nm for Zn terminated (c+) and 0.15 nm for O terminated (c-) face is measured. Optimized thermal annealing leads to the formation of steps on c+ with width of 150-200 nm and the height of 0.5-1 nm or 1-2 unit cells, respectively. Moreover, despite polarity of hexagonal ZnO, steps of similar size were obtained on c-. The optical transmittivity is 80% at λ = 410 nm and further increasing to 90% in the infra red. The room temperature photoluminescence (PL) signal shows a sharp peak at 3.3 eV, FWHM = 1.76 10^{-3} eV, and emission around 2.2 eV originating from deep levels as result of measureable impurity concentration is not observed. A residual impurity in the crystal was analyzed by inductively coupled plasma mass spectroscopy (ICP-MS) with 0.9 ppm Li and 0.3 ppm K both from the mineralizers and 11 ppm Fe and <3 ppm Al. The electrical characteristics is made by determining the distribution of electrical resistivity, carrier mobility and carrier concentration over 2 inch wafers. The values are 380 Ωcm (15% tolerance), 200 $cm^2V^{-1}s^{-1}$ (10% tolerance) and 8 10^{13} cm^{-3} (20% tolerance), respectively.

2:45 PM Y5.4
Crystallinity of Solution Deposited TiO_2 Films. Gregory K. L. Goh[1], Xue Qin Han[1] and Cheryl P. K. Liew[1,2]; [1]Materials Science and Characterisation Lab, Institute of Materials Research and Engineering, Singapore, Singapore; [2]Republic Polytechnic, Singapore, Singapore.

TiO_2 films are important for photocatalytic applications such as self-cleaning, anti-fogging and solvent purification, and as switches and interferometers in optical communication devices. A simple and cost effective method for film growth is the use of low temperature (<200°C) solution methods like hydrothermal synthesis and liquid phase deposition. Films grown by these methods are crystalline as-deposited, and irregular surfaces and porous bodies can be coated evenly. In this study, it is shown that the as-synthesized crystallinity is not very high and can be improved by raising the growth temperature from 60 to 200°C. This potentially means that post deposition temperatures more than 300°C can be avoided so that the solution deposition method remains truly a low temperature technique. Low film processing temperatures are important so that temperature sensitive substrates (e.g. polymers) can be used to increase the combination between materials systems that could lead to new and/or improved functionalities. Rutile and anatase TiO_2 material were grown on glass substrates from acidic titanium precursor solutions at 60 to 200°C. The TiO_2 films had a c-axis preferred orientation that was greater for higher deposition temperatures. Also, both anatase and rutile lattices were expanded, apparently due to proton incorporation. The rutile film was determined to have a refractive index of 2.4 compared with the known bulk value of 2.9. This was because the as-synthesized rutile material was only 29% crystalline and also contained nano-sized pores. Anatase synthesized at 60°C had a crystallinity of 15% that increased to 54% for a growth temperature of 200°C. A similar crystallinity by conventional heat treatment of the 60°C material was attained only at 400°C. Since crystalline TiO_2 is formed by continuous linking of titanium complexes in solution, it is believed that more complete dehydration of these complexes at higher growth temperatures leads to less disruption of the long range attractive forces required for the formation of a periodic array.

3:30 PM Y5.5
The Concentration Quenching Effect in Spherical YBO3:Ln (Ln=Eu3+,Tb3+) Phosphors Synthesized by a Mild Hydrothermal Process. J. C. Zhang and Y. H. Wang; Material Science, Lanzhou University, Lanzhou, GanShu, China.

YBO3:Ln(Ln=Eu3+,Tb3+) phosphors with uniform size and sphere morphology were successfully prepared by a mild hydrothermal process. A new phenomenon was observed that there is a much higher quenching concentration in hydrothermal phosphors compared with that in solid-state derived phosphors under 254nm excitation, and the optimum luminescence intensity of hydrothermal phosphors is much stronger than those prepared by solid-state process under 254nm or 147nm excitation. The concentration quenching was explained by energy transfer theory. The result indicated that the high quenching concentration is due to the less traps in hydrothermal phosphors. However, the low quenching concentration was observed in YBO3:Eu3+ prepared by hydrothermal process under 147nm excitation. This indicated that the energy relaxation pathway to the Eu3+ sites should be different under VUV excitation.

3:45 PM Y5.6
Direct Fabrication of Nanocrystalline Anatase Deposited Hydroxyapatite by Mild Hydrothermal Reactions.
Masahiro Yoshimura, Pornapa Sujaridworakun, Naoki Sakamoto and Tomoaki Watanabe; Materials and Structures Laboratory (Center for Materials Design), Tokyo Institute of Technology, Yokohama, Japan.

TiO_2-deposited Hydroxyapatite (HAp) nano-composites have been successfully synthesized by direct, one step hydrothermal treatments of $CaCO_3$, H_3PO_4 suspension or by two-step ones with adding 10 vol% Tas-fine (Titanium amine complex) to HAp powder (hydrothermally stnthesized HAp and reagent HAp) at 180°C for 6h or 120°C for 18-24h, in neutral solution. The obtained products were characterized by XRD, SEM, FT-IR, Vis-raman and TEM. XRD and Vis-raman results showed the formation of HAp and TiO_2-anatase phases after hydrothermal treatments both in one and two steps. Small rod-like anatase nanocrystals deposited on HAp observed by SEM, TEM in the sample prepared by two steps. The present work revealed that treated process, temperature and time had effected the crystallization of anatase crystals. The resultant products, TiO_2/HAp nanocomposites might have the ability to adsorb bacteria and/or organic materials, thus it might have superior photocatalytic properties to decompose the contaminants resulting good in antibiotic applications and environmental purification.

4:00 PM Y5.7
Hydrothermal Preparation of Nanocrystalline $Zr_{1-x}Ce_xO_2$(0<x<1) Tetragonal Phase.
Masahiro Yoshimura, Anwar Ahniyaz and Tomoaki Watanabe; Materials and Structures Laboratory (Center for Materials Design), Tokyo Institute of Technology, Yokohama, Japan.

Zirconia based ceramics are widely used due to their excellent mechanical and electrical properties. Recently, zirconia-ceria system has been attracted as a catalyst promoter for automobile exhaust gas treatment. Though these properties strongly depend on the crystal structures and phase changes, they are not completely understood. Several synthetic methods have been developed for nanocrystalline ceria-zirconia powders/particles, such as hydrothermal method [1], high-energy ball milling [2], polymerized complex method [3], sol-gel[4] and gel-combustion [5] and precipitation-sonification [6] methods. Although nanostructured fine powders can be successfully synthesized in limited composition by all above-mentioned methods, some of them cost either environmentally or energetically during the over all synthesis process. Moreover, some discrepancies and misunderstandings can be found in these works since several authors have found problems in distinguishing between t" and t'-forms of tetragonal phase or between t"-forms and the cubic phase. In order to understand structural nature of nanocrystalline zirconia-ceria, homogenous fluorite type complete zirconia-ceria solid solutions ($Zr_xCe_{1-x}O_2$ .nH_2O, x = 0∼1.0) were prepared at 120°C by using both hydrothermal [7] and hydrothermal ball milling method [8]. The as prepared samples were hydrous and included water up to 15 wt %. However, most of them can be expelled by heating the samples above 600°C. In present work, we have focused on precipitation process and metastable phase formation as well as structural evolution against temperature [9]. As prepared and heat-treated $Zr_{0.5}Ce_{0.5}O_2$ samples below 900°C have been confirmed as t"-form of metastable tetragonal phase, while the heat-treated ones above 1100°C was confirmed as the mixture of metastable form of tetragonal phase, t"-form and t'-form. Combination of XRD and Raman techniques is proved to be a very useful tool to study the structural changes in the zirconia-ceria system. References: 1. A. Cabanas, J. A. Darr, E. Lester and M. Poliakoff, J. Mater. Chem., 2001, **11**, 561. 2. S. Ezno, F. Delogu, R. Frattini, A. Primavera, and A. Trovarelli, J. Mater. Res., 2000, **15**, 1538. 3. M. Yashima, K. Ohtake, M. Kakihana and M. Yoshimura, J. Am. Ceram. Soc., 1994, **77**, 2773. 4. S. Rossignol, F. Gerard and D. Duprez, J. Mater. Chem., 1999, **9**, 1615. 5. D. G. Lamas, G. E. Lascalea, R. E. Juarez, E. Djurado, L. Perez and N. E. Walsoe de Reca, J. Mater. Chem., 2003, **13**, 904. 6.A. S. Deshpande, N. Pinna, P. Beato, M. Antonietti, M. Niederberger, Chem. Mater., 2004, 16, 2599. 7. A. Ahniyaz, T. Fujiwara, T. Fujino, M. Yoshimura, J. Nanosci. Nanotech. 2004, 4(3), 233 8. A. Ahniyaz, T. Fujiwara, T. Fujino and M. Yoshimura, Solid State Ionics, (accepted). 9. A. Ahniyaz, M. Yoshimura, Nano Lett. (submitted).

4:15 PM Y5.8
Solvothermal Processes of Doping of Oxides during Synthesis.
Marina Nikolaevna Danchevskaya, Yurii Dmitrtievich Ivakin, Sergei Nikolaevich Torbin, Galina Petrovna Muravieva and Olga Gumarovna Ovchinnikova; Chemistry, Moscow State University, Moscow, Russian Federation.

The researches of fine crystalline simple and complicated oxides synthesis in water medium in sub- and supercritical conditions have shown obligatory presence of a crystalline intermediate phase, which is characterized by the certain degree of hydroxylation [1]. In reactionary medium of dopant water solution, the diffusion of ions into an aluminous matrix happens at the stage of existence of intermediate. Then, during transformation of intermediate into thermodynamic stable oxide, the doping elements occupy nodal positions of structure of obtained oxide. Par example, during synthesis of corundum from Al(OH)3 in water solution of dopant at first at T>200C boehmite AlOOH is forming, into which doping ions diffuse. At T>360C the boehmite is transforming into corundum and doping elements are incorporating into the nascent corundum crystal structure. As doping additives were using: compounds of chrome, manganese, cobalt, magnesium, strontium, barium, cerium, yttrium and the rare earths elements (La and Eu). Optimal synthesis regimes were found to produce the doped corundum of higher mechanical (strength and abrasive ability) and optical(color and luminescence) performances. By varying of composition of the doping components and conditions of synthesis the corundum can be obtained of different crystals size - in the range of 0.3-400 microns, and of habitus, bipyramidal, plate, prismatic or in the shape of truncated bipyramid. The developed technology is ecologically safe as the by-product is only water. The synthesis of gahnite (ZnAl2O4) consists in two-stage treatment of an mixture of precursors (ZnO and Al(OH)3): in hydrothermal, and then in supercritical conditions. This method allows to obtain fine crystalline powders single-phase both pure and doped gahnite, and composites on a basis of gahnite. The gahnite doped by cerium and barium and binary system from gahnite and copper oxide are catalytic agents exhibit thermal stability and stability to abrasion. The gahnite doped by rare earth elements is intensive luminophor. [1] M. N. Danchevskaya, Yu.D. Ivakin, S.N. Torbin, G.P. Panasyuk, V.N. Belan, I.L. Voroshilov, High Pressure Research 2001, 20, 229-239.

4:30 PM Y5.9
Preparation of Fine Crystalline Alpha Aluminium Oxide.
George P. Panasyuk, Victor N. Belan, Igor L. Voroshilov and Timur V. Grusha; Russian Academy of Scinces, General & Inorganic Chemistry, Moscow, Russian Federation.

The method of preparation of fine crystalline alpha aluminium oxide from preliminary synthesized boehmite was developed. Boehmite was synthesized from commercial hydrargillite in an autoclave in hydrothermal solutions at temperature 150-200°C and under pressure of saturated water vapor. Synthesis of boehmite was carried out in neutral, acid and alkaline mediums. As result we received boehmite with the crystal size from 100 nanometers to 5 microns. This boehmite was treated under vacuum thermal and thermovapor conditions. On thermal processing of the boehmite above 1100°C in vacuum alpha alumina formed. Its crystal size approximately corresponded to the crystal size of initial boehmite. The habitus of alpha alumina grains also corresponded to the shape of initial boehmite crystals (lamellar, isometric and needle) and so remained until heating up to 1400°C with insignificant sintering of particles. After heating above 1400°C the alumina grains became more rounded and at the same time there started a sintering of alumina particles. This process occurred more readily for equally orientated crystals. For thermovapor treatment the boehmite was steamed in autoclaves at temperature 350-450°C under pressure 2-30 MPa. By varying parameters of process we prepared fine corundum crystals in the range of 0.8-5 microns with approximately isometric habitus. These methods of boehmite processing we also successfully used for preparation of alpha alumina and fine crystalline corundum, doped by manganese, chromium, titanium and other elements. The obtained results could be used for development of industrial technology of pure and doped alpha alumina and corundum in a wide range of crystal sizes from 0,3 up to 5 micron. These materials could be used for abrasive processing of materials, in manufacture of high-quality ceramics and as raw material for single crystal sapphire growth.