

### Ferromagnetism above Room Temperature Discovered in Mn-Doped ZnO

Ferromagnetism at and above room temperature in magnetic semiconductors is a property of significant interest for spintronic applications and devices. Mn-doped ZnO and GaN have been predicted, based on theoretical calculations, to be potential candidates for exhibiting ferromagnetism above room temperature, leading to an intense search for the right material. The first observations of ferromagnetism above room temperature for dilute Mn-doped ZnO have now been reported. K.V. Rao, P. Sharma, and their colleagues from the Royal Institute of Technology (Sweden) and from the Armament Research Center (United States), Arizona State University (United States), University of Uppsala (Sweden), and the University of Sheffield (United Kingdom) report this discovery in both bulk and thin transparent films of Mn-doped ZnO in the October issue of *Nature Materials*.

The incorporation of ferromagnetism in ZnO, a known piezoelectric and electro-optic material, may lead to various multifunctional properties. Doping ZnO with Mn, a 3d transition metal, can make possible the injection of a large amount of spins and carriers, making Mn-doped ZnO an excellent candidate for spintronic applications.

In this study, the material was made by mixing appropriate amounts of ZnO and MnO<sub>2</sub> powders. The powder mixture was then calcined at 400°C for 8 h and then sintered at temperatures ranging from 500°C to 900°C for 12 h to obtain Zn<sub>1-x</sub>Mn<sub>x</sub>O ( $x = 0.01, 0.02, \text{ and } 0.1$ ). For samples sintered below 700°C, superconducting quantum interference device measurements revealed ferromagnetic ordering. Elemental mapping using electron dispersive spectroscopy showed that the Mn was uniformly distributed and the material was homogeneous with a single phase. Sintering the samples above 700°C suppressed the ferromagnetism to below room temperature. This was attributed to the formation of Mn clusters, which are antiferromagnetic, and/or the formation of other phases. Ferromagnetic resonance (FMR) measurements indicated that the 2 at.% Mn-doped ZnO is a ferromagnetic semiconductor with a Curie temperature  $T_c$  well above 425 K. The researchers said that this is likely the first FMR measurement of room-temperature ferromagnetism in a semiconductor.

Thin films of the Zn<sub>1-x</sub>Mn<sub>x</sub>O were deposited on fused quartz substrates using a pulsed laser ablation technique. The films, which were transparent, also exhibited

room-temperature ferromagnetism and phase homogeneity. High-resolution transmission electron microscopy on the thin films showed that the ZnO was ordered and oriented perpendicular to the  $a$ - $b$  plane of a hexagonal lattice with a matching lattice parameter. The results suggest that the Mn substitutes for the Zn in the structure. This discovery of above-room-temperature ferromagnetism in Mn-doped ZnO semiconductors opens up a number of possibilities for spintronic applications and novel magneto-optical components.

GOPAL RAO

### Large Diamond Crystals Grown at Low Temperatures

Synthetically made diamond is widely used for technological applications ranging from abrasives, tool coating, microelectronics, and optics to corrosion protection. Yet most techniques for making this material require high temperatures and pressures. Qianwang Chen, a professor of materials science and engineering at the University of Science and Technology of China, and his colleagues have made diamond crystals as large as 510  $\mu\text{m}$  in size by reducing magnesium carbonate with sodium at temperatures as low as 500°C.

As reported in the September 29 issue of *Angewandte Chemie*, the researchers were able to carry out the reaction in an autoclave using autogenetic pressure. The preferential formation of diamond over graphite was found to be very sensitive to conditions of temperature, pressure, and starting concentration of reactants. The researchers think that magnesium carbonate is first pyrolyzed to yield the oxide and supercritical carbon dioxide. The latter is then reduced on the surfaces of molten sodium at high pressures to give the polyhedral diamond crystals, which are usually about 120  $\mu\text{m}$  in length and can be as large as 510  $\mu\text{m}$ . At 500°C and 860 atm pressure, reaction yields of up to 6.6% were attained. Raman spectroscopy and x-ray diffraction showed the formation of high-purity, well-crystallized diamond particles. Moreover, the researchers said, the diamond crystals are transparent and colorless. No diamond could be detected at process temperatures below 500°C.

Chen said, "It was in 1796 that it was shown that diamonds could be stoichiometrically converted to carbon dioxide by burning in oxygen, only now has it been possible to achieve the reverse conversion of dense carbon dioxide to large diamond crystals."

While the mechanism for carbonate reduction and diamond growth is not fully understood, the low cost of the

starting materials and low temperatures used in this process make this technique particularly attractive for industrial diamond production.

SARBAJIT BANERJEE

### Arrays of Binary and Ternary Particles Fabricated by Use of Patterned Microchannels

Patterned arrays of nano- and micron-sized particles have great potential as materials for high-performance electronic and optical devices. In the November 4 issue of *Chemistry of Materials*, researchers Seung-Man Yang and co-workers from the Korea Advanced Institute of Science and Technology report a method for fabricating binary and ternary particle arrays using patterned microchannels. This method began with a poly(dimethylsiloxane) mold containing V-shaped grooves of precise dimensions. These grooves were filled with silica spheres 320 nm or 600 nm in diameter or with polystyrene (PS) spheres 1.01  $\mu\text{m}$  in diameter using a dip-coating technique. The spheres are driven into close-packed arrays in the V-shaped grooves by capillary forces. The confined geometry of the grooves also directs the spheres into a fcc structure with the (100) plane toward the facing surface. After these V-shaped arrays of particles are transferred to a polyurethane film, the resulting new grooves can be filled with spheres of other types and diameters to produce binary particle arrays. For example, 1.01  $\mu\text{m}$  diameter PS spheres could be placed into the grooves between V-shaped arrays of the 320 nm or 600 nm silica spheres. Alternatively, filling those grooves with a mixture of 50 nm diameter silica spheres and 1.01  $\mu\text{m}$  diameter polystyrene spheres leads to a ternary particle array. Subsequent oxygen plasma etching selectively removes the polystyrene particles, leaving patterned, inverted-pore structures in the material. The researchers indicated the potential for using this technique for the fabrication of "display devices, 2D photonic crystals, and ordered open-pores structures" that could be used as "templates for nonspherical aggregates of colloidal particles."

LARKEN E. EULISS

### Nanofiber Alumina Enhances Osteoblast Function for Orthopedic Implants

Some key questions in biomaterials address the bonding of bone to implant surfaces for dental and orthopedic applications. In their study on osteoblast function on anisotropic nanoparticulate compounds, researchers from Purdue Univer-

sity and Argonide Corporation (Sanford, Fla.), led by Thomas J. Webster of the Department of Biomedical Engineering at Purdue, found that osteoblast function and consequently bone formation on the implant depend strongly on the topology of the implant's surface and the morphology of crystallites. They said that the shape and size of the nanophase implant particles are consistent with the dimensions of hydroxyapatite particles of natural bone. In general, the researchers identify three factors that promote enhanced osteoblast response: chemical composition, crystalline phase, and topography.

As reported on November 5 in the online edition of the *Journal of Biomedical Materials Research Part A* (to appear in print in the December 15 issue), Webster, Rachel L. Price at Purdue, and their colleagues analyzed the osteoblast function depending on the degree of nanometer surface roughness of alumina substrates. The alumina-based materials were chosen for their high osteoblast activity as compared with titanium and etched glass. The researchers used conventional spherical ( $\alpha$ -Al<sub>2</sub>O<sub>3</sub> spheres, 167 nm), nanophase spherical ( $\delta$ -Al<sub>2</sub>O<sub>3</sub> spheres, 23 nm), and nanofiber (boehmite fibers 2–4 nm diameter by more than 50 nm long) alumina compounds.

The researchers found that cell adhe-

sion and proliferation results are statistically greater on nanofiber alumina as compared with other compounds. More important, calcium deposition by bone cells significantly increases on both nanoparticulate alumina substrates. They analyzed the influence of the three factors on osteoblast function. The study of the first factor shows that proteins absorb differently on materials with dissimilar chemical composition; the study of the second factor, that the transition alumina ( $\delta$ - and boehmite phases) may promote an increased cell response compared to the more crystalline alumina phase ( $\alpha$ ); and the study of the third factor, that a decrease in the grain size to nanometer dimensions translates to an increase in osteoblast function. The researchers demonstrated that nanofiber alumina may offer the potential to ensure sufficient bone ingrowth and therefore to make orthopedic implants more stable.

The researchers concluded that "with knowledge of the influence that chemistry, phase, size, and nanoparticle aspect ratio have on osteoblast function, an ideal material for orthopedic/dental applications may be designed."

EKATERINA A. LITVINOVA

### Ferromagnetic Ordering of Pure Organic Compound Occurs Below 1.6 K

Contrary to Heisenberg's proposition that bulk ferromagnetic ordering could only appear in systems with heavy atoms, recent synthesis and characterization of several organic ferromagnets has been reported. Such systems are mainly based on sulfur- or nitrogen-containing organic radicals. A group of researchers from Cambridge University, in cooperation with scientists

from CSIC–Universidad de Zaragoza (Spain), CNRS (France), Bunkyo-ku, Japan, and the University of Cardiff (United Kingdom) has discovered a thiazyl-based neutral organic compound that undergoes ferromagnetic ordering below 1.6 K.

As reported in the November 3 issue of *Angewandte Chemie*, Jeremy M. Rawson of Cambridge and colleagues have synthesized and described magnetic properties of the thiazyl-based radical,  $p$ -O<sub>2</sub>NC<sub>6</sub>F<sub>4</sub>CNSSN•. The radical was obtained by consequent reaction of  $p$ -O<sub>2</sub>NC<sub>6</sub>F<sub>4</sub>CN with Li[N(SiMe<sub>3</sub>)<sub>2</sub>] and SCl<sub>2</sub> in Et<sub>2</sub>O solution.

Upon determination of the crystal structure of the radical, the researchers were able to explain the ferromagnetic behavior of the substance. They described the crystal structure as chains of molecules linked through electrostatic S<sup>δ+</sup>...O<sup>δ-</sup> interactions in the (110) plane with the planes related by means of a 4<sub>1</sub> screw axis along the  $c$ -axis. In this case, the molecules form four symmetry-equivalent intermolecular S...N contacts 3.681 Å in length.

The researchers provided detailed magnetic measurements at low temperatures and showed that the compound exhibits Curie–Weiss behavior down to 10 K, while at the temperatures below 1.6 K, it begins to order ferromagnetically. Furthermore, the research team observed magnetic anisotropy in magnetization values along and perpendicular to the [001] axis of a single crystal. Based on crystal structure and previous studies of ferromagnetic properties of analogue thiazyl molecular magnets, the research team concluded that ferromagnetic interactions in the compound are referred to the nearly orthogonal nature of the singly occupied molecular orbitals on neighboring molecules.

ANDREI A. ELISEEV

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### News of MRS Members/Materials Researchers

**Annelise Barron**, of the Materials Research Center in Northwestern University, Illinois, was promoted to associate professor with tenure this fall.

**Jean Blachère**, associate professor emeritus at the University of Pittsburgh, has received the **Albert Victor Bleininger Memorial Award** from the Pittsburgh section of the American Ceramic Society in recognition of his leadership in the ceramics field.

**Lynn Boatner** of Oak Ridge National Laboratory received the **2003 American Association for Crystal Growth Award** in recognition of his "novel research in the area of crystal growth that has advanced the application of single-crystalline materials and enhanced the appreciation of crys-

tals both scientifically and aesthetically."

**Gail J. Brown**, principal research physicist in the U.S. Air Force Research Laboratory at Wright-Patterson Air Force Base in Ohio, has received the **Air Force Basic Research Award** for cutting-edge research on superlattice materials for next-generation infrared sensing. The award also recognizes Brown for exemplary leadership in coordinating the research project from computational modeling and growth of the superlattice materials to initial device testing of the new materials' system.

**James Wai-Jeung Chan** of the Chemical Engineering and Materials Science Department at the University of California, Davis, received the **2003 Zuhair A. Munir Award**

**for Best Doctoral Dissertation** from the UC–Davis College of Engineering for his research on "Confocal Laser Spectroscopy of Glasses Modified by Ultrashort Laser Pulses for Waveguide Fabrication" under the mentorship of Subhash Risbud.

**Bai Chunli**, vice president of the Chinese Academy of Sciences, has been elected vice president of the Asia Pacific Academy of Materials, a nongovernmental institution aimed at promoting free exchanges of research and development in the field of materials research through international cooperation.

**Thomas F. George** has been appointed chancellor of the University of Missouri—St. Louis, effective September 1, 2003. Before coming to UM—St. Louis, George