

### Single Gallium Nanoparticle Displays Optical Phase-Change Memory

Memory devices based on phase changes have the potential to supplant electronic memories due to their greatly reduced size and power consumption. In addition, crystalline-to-crystalline transitions exhibited in polymorphic systems may provide higher base logic than current binary systems. It has been previously demonstrated that single Ga nanoparticles exhibit light-induced structural phase changes with different dielectric properties. Recently, B.F. Soares, F. Jonsson, and N.I. Zheludev from the Optoelectronics Research Centre, University of Southampton, United Kingdom, have demonstrated that a single Ga nanoparticle undergoing light-induced phase changes acts as an all-optical, rewritable, quaternary memory element (i. e., a memory element with four stable logic states).

As reported in the April 13 issue of *Physical Review Letters* (DOI:10.1103/PhysRevLett.98.153905), the researchers used the atomic beam from an effusion cell and a light-assisted deposition technique to grow an 80-nm Ga nanoparticle at the 30-nm aperture of the tip of a gold-coated tapered fiber, which was kept at 80 K. The nanoparticle was then connected to an external fiberoptic and placed in a cryostat. The four observed memory states, referred to as 0, 1, 2, and 3, correspond to three different crystal structures and the Ga liquid. The researchers first activated the transitions to the four states sequentially by heating the nanoparticle slowly from 100 K to 160 K. Switching nonsequentially between the nanoparticle's four states, that is, writing information to the nanoparticle, was achieved with single laser pulses while sampling the nanoparticle's reflectivity with pump-probe lasers, operating at a much lower intensity than the write laser, corresponds to reading the information. The researchers switched between different logical states in a controlled manner, thereby demonstrating the memory functionality. Moreover, higher order logical functionality was shown by switching directly from the ground state to any targeted higher state. For example, at 120 K, switching from state 0 to state 1 was accomplished with a 1.5 pJ pulse of 1- $\mu$ s duration while a 4.85 pJ pulse of 1- $\mu$ s duration switched 0 to 3. After exposure to the optical pulses, the nanoparticle remained in state 3 even after the ambient temperature was reduced to 100 K. Returning to the 0 state required a temperature of 100 K and turning off the read lasers.

The researchers said that "with quaternary memory functionality, one nanoparticle is capable of storing an estimated 0.2 Tb

in<sup>-2</sup>, compared to 0.015 Tb in<sup>-2</sup> in Blu-ray DVDs, and requires about one-tenth of the energy required to write single bits of information using current state-of-the-art methods. These figures demonstrate the potential for single nanoparticles to provide memory functionality in future highly integrated nanophotonic devices, operating at very low power levels."

STEVEN TROHALAKI

### Ferroelectric Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> Nanoparticles Synthesized at Low Temperatures

Ferroelectric materials like the lanthanide-doped bismuth titanates (Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>) may be used in nonvolatile memory, sensors, and actuators. Typically, Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>-based materials are synthesized by a solid-state reaction of Bi<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub>. Calcination temperatures in excess of 800°C are then required to achieve the perovskite Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> phase, often resulting in unwanted grain growth and coarsening. P. Prakash, A. Garg, M.K. Roy, and H.C. Verma of the Indian Institute of Technology, Kanpur, India have developed a chemical method to make stoichiometric neodymium-doped bismuth titanate nanoparticles. As reported in the April issue of the *Journal of the American Ceramic Society* (p. 1295; DOI: 10.1111/j.1551-2916.2007.01539.x), crystalline, stoichiometric Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> was realized at ~ 550°C, nearly 300°C lower than conventional techniques.

Nanoparticles of Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> were made by a chemical route. First, the bismuth (Bi) and neodymium (Nd) precursors were dissolved in citric acid. Ethylene amine was used to stabilize the solution. Next, acetyl-acetone-stabilized titanium isopropoxide was mixed with the Bi/Nd solution. Excess Bi (10%) was added to the solution to overcome Bi loss during heat treatment. The sol was then dried at 110°C, first while stirring on a hot plate until the sol thickened and then in an ultrasonic bath. The dried powder was then calcined for 1 h in air at various temperatures ranging over 200–700°C.

Based on their x-ray diffraction and thermal analysis results, the researchers said that the crystallization of Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> is a two-step process: first, formation of a nonferroelectric Bi<sub>2</sub>Ti<sub>3</sub>O<sub>7</sub> phase at ~310°C followed by formation of ferroelectric Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles with perovskite structure at temperatures at ~500°C. According to their transmission electron microscopy results, the average particle size for the sample calcined at 550°C and 600°C is ~50–60 nm. Capacitance versus temperature measurements of the as-prepared samples confirm that the

nonferroelectric-to-ferroelectric transition is ~610°C. The researchers said that the key to the reduced crystallization temperatures of ferroelectric Bi<sub>3.5</sub>Nd<sub>0.5</sub>Ti<sub>3</sub>O<sub>12</sub> nanoparticles is the vigorous stirring and ultrasonication during drying, preventing gel formation, which, if formed, inhibits proper mixing of the precursors leading to higher crystallization temperatures and larger sized particles.

JEREMIAH T. ABIADÉ

### Nanosized Pt Particles in Pt-CeO<sub>2</sub>/Carbon Black Composite Anode Improve Performance of Direct Methanol Fuel Cell

Anodes of commercially produced direct methanol fuel cells (DMFCs) are synthesized from an expensive platinum (Pt) and ruthenium (Ru) alloy with limited availability of raw materials for large-scale production. One alternative currently under development is to use a Pt-cerium oxide (CeO<sub>2</sub>) composite supported on carbon black (CB), but research to date has reported lower performance than the standard Pt-Ru/C anode. T. Mori, M. Takahashi, F. Ye, and A. Vinu from the Fuel Cell Materials Center in Japan, in collaboration with H. Kobayashi from Saitama University and J. Drennan from the University of Queensland, have overcome this disadvantage by using nanometer-sized Pt particles to synthesize a Pt-CeO<sub>2</sub>/CB anode, improving its performance beyond existing formulations and the standard Pt-Ru/C anode.

As reported in the April issue of the *Journal of the American Ceramic Society* (p. 1291; DOI:10.1111/j.1551-2916.2006.01483.x), the research team based the fabrication process of this material on precipitation and co-impregnation methods, resulting in a Pt-CeO<sub>2</sub>/CB anode with a uniform distribution of Pt particles of 7–8 nm in size. The same technique was used to synthesize the Pt-Ru/C anode, giving a Pt-Ru particle size of 4 nm.

Using cyclic voltammetry and chronoamperometry, the researchers measured potential, current density and electrochemical activity. The peak current density of Pt-CeO<sub>2</sub>/CB was 1.9 times higher than that of Pt-Ru/C, and current density was consistently higher over the range of temperatures measured. The onset potential of the Pt-CeO<sub>2</sub>/CB anode, measured at a current density of 0.02 mA/cm<sup>2</sup>, was lower by ~10% than that of the Pt-Ru/C anode. The activation energy of the Pt-CeO<sub>2</sub>/CB anode was half that of the Pt-Ru/C anode. The relationship of current density to potential revealed to the researchers that the controlling mechanism for the anodic reaction on the Pt-Ru/C anode is the sur-

face reaction of H<sub>2</sub>O on Ru, and for the Pt-CeO<sub>2</sub>/CB anode is the diffusion of the active species on the Pt-CeO<sub>2</sub> particles. These findings led the research team to infer that using nanosized CeO<sub>2</sub> particles has the potential to increase the performance of the Pt-CeO<sub>2</sub>/CB anode even more, making it possible to reduce the amount of Pt needed in the electrode.

SIARI S. SOSA

### Bioactive Glass Scaffolds with Hierarchical Pore Networks Fabricated

Mesoscopic bioactive glasses have been reported to have excellent bone-forming bioactivities, but are ineffective as tissue scaffolds. The pore dimensions are too small to promote cell seeding and migration necessary for tissue regeneration. Researchers from Korea Institute of Machinery & Materials (KIMM) addressed these concerns in the March 16 issue of *Chemical Communications* (DOI: 10.1039/b702103h). H.-S. Yun and co-workers at KIMM reported on the design and fabri-

cation of three-dimensional bioactive glass scaffolds with hierarchical pore networks and bone-tissue regeneration capabilities.

The fabrication protocol is a combination of sol-gel synthesis, polymer templating, and rapid prototyping using a robotic deposition mechanism. A virtual 3D scaffold architecture was generated by computer-aided design and interpreted by the robotic deposition device for fabrication using a gel paste. In addition to inorganic precursors, the gel paste uses a triblock copolymer (EO<sub>100</sub>PO<sub>65</sub>EO<sub>100</sub> (F127)) as a mesostructure directing agent and methyl cellulose (MC) as a macrostructure directing agent and binder. Extrusion of the gel paste onto a heated (60–100°C) substrate yields a stable gel structure following quick solvent evaporation and solidification of MC. The size, thickness, pore dimensions, and number of stacking layers in the scaffold can be easily manipulated by computer control. After aging for 24 h at 40°C, calcination of the organic-inorganic hybrid removes

the polymer template. As a result, 3D pore networks with hierarchically giant (>100 μm), macro- (10 μm < d<sub>pore</sub> < 100 μm), and mesopores are generated in the scaffold. No apparent structural deformation was observed after calcination although there was an ~35% decrease in scaffold size.

*In vitro* bioactivity of the 3D porous scaffolds were tested in simulated body fluid (SBF) at 37°C. Formation of hydroxyl apatite on the porous surface was monitored by acquiring and comparing scanning electron microscopy images before and after interaction with SBF. Within 24 hours, formation of biomimetic hydroxyl apatite confirmed excellent bone-forming bioactive capabilities *in vitro*.

Although this simple and reproducible synthetic method was directed toward biomimetic applications, the researchers said that it could be very easily adapted for various hierarchical porous structures with potential applications in optics, sensing, and catalysis.

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