Rare-Earth-Doped Bromide Materials Display Lasing Activity at Near-Infrared Transitions

Long-wavelength infrared light sources are important for a variety of applications, including remote sensing, night vision, and medical diagnosis. However, almost all solid-state materials that exhibit lasing at these wavelengths are easily damaged by moisture, making them difficult to use outside of the laboratory. Now, K. Rademaker, S.A. Payne, and W.F. Krupke of Lawrence Livermore National Laboratory; E. Heumann and G. Huber of Universität Hamburg, L.I. Isaenko of the Russian Academy of Sciences; and A. Burger of Fisk University have achieved lasing at near-infrared wavelengths in moisture-resistant, Nd^{3+}-doped KPb_2Br_5 (KPB) and $RbPb_2Br_5$ (RPB) crystals. The results, reported in the April 1 issue of *Optics Letters* (p. 729), suggest that these media may be able to support long-wavelength infrared lasing and be usable in the field.

Rademaker and colleagues grew single KPB and RPB crystals from a stoichiometric mixture using the Bridgman technique. Since the key limitation for solid-state long-wavelength infrared laser media is nonradiative decay from the lasing levels due to multiphonon interactions, the researchers anticipated that the greater mass of Br compared to Cl would reduce the phonon energy relative to previously studied KPb_2Cl_5 crystals and allow lasing from previously unusable high-angular-momentum levels. Under optical excitation at 0.75 μm, the samples displayed strong emission peaks at 1.18 μm, 1.07 μm, and 0.97 μm, indicating that the conjecture was correct. The researchers were able to generate laser activity at 1.07 μm in flat, uncoated samples of both Nd:KPB and Nd:RPB and at 1.18 μm and 0.97 μm in Nd:RPB, using a 10 ns pulsed optical parametric oscillator as a pump source.

These results show that moisture-resistant, rare-earth-doped alkali lead halide compounds may be the solution for robust long-infrared-wavelength sources. Although Rademaker and colleagues were able to demonstrate lasing only in pulsed operation, they speculate that a higher concentration of the Nd dopant might enhance cross-relaxation of population from the lower lasing levels and allow for continuous-wave operation.

COLIN MCCORMICK

Protein-Based Thermoplastic Elastomers Biochemically Synthesized

Genetic engineering methods can now be used to prepare multiblock protein copolymers. It is well known that synthetic multiblock copolymers can form biphasic materials that exhibit, to varying degrees, the mechanical and chemical properties of the constituent blocks. Property tuning can be effected by controlling interphase mixing of incompatible blocks. Interphase mixing, in turn, depends on the range of microstructures accessible to the blocks, which is much larger for systems comprising large, well-defined blocks. Recently, researchers at Emory University and the Georgia Institute of Technology demonstrated that, by synthesizing large multiblock protein copolymers, material microstructure at both the nanoscale and mesoscale can be systematically modified in a manner that was previously unfeasible.

As reported in the January 25 issue of *Macromolecules* (p. 345; DOI: 10.1021/ma0491199), K. Nagapudi of the Emory University School of Medicine and the Georgia Institute of Technology, E.L. Chaikof of the Emory University School of Medicine, V.P. Conticello of Emory University, and co-researchers used a recombinant DNA technique to synthesize a new class of protein **BAB** triblock copolymers, whose respective blocks exhibit distinct elastomeric (**A**) and plastic (**B**) mechanical properties analogous to synthetic thermoplastic elastomers, where

$$\mathbf{A} = \text{VPGVG}[(\text{VPGVG})_2\text{VPGEG}(\text{VPGVG})_2]_{48}\text{VPGVG and}$$

$$\mathbf{B} = \text{VPAVG}[(\text{IPAVG})_4(\text{VPAVG})]_{16}\text{IPAVG}$$

Knowing from previous research that elastin-mimetic proteins display an inverse temperature profile for self-assembly, the researchers chose the sequence of the hydrophilic elastomeric A block so that its transition temperature (T_c) is substantially higher than 37°C (physiological temperature) and the sequence of the hydrophobic plastic **B** block so that its T_c is close to room temperature. When casting films, the researchers observed that their triblock copolymer protein reversibly self-assembled from concentrated aqueous solution at a temperature above the **B** block's T_c to form a network of plastic microdomains dispersed in a continuous elastomeric phase composed of the **A** blocks. The researchers said that the ability of the **B** blocks to form virtual cross-links and to maintain plastic deformation behavior in the absence of chemical or radiation cross-linking was completely unanticipated. Through rational choice of film processing conditions that control mesoscale and nanoscale structure, the researchers observed increases in the Young's modulus of more than three orders of magnitude (0.03–35 MPa) and fivefold increases in elongation to break (250–1300%).

In order to investigate the effect of processing conditions on drug-release properties, the researchers measured the release rates of a model amphiphilic drug from the protein triblock copolymer. For identical drug-loading conditions, the research team observed a diffusion coefficient in a water-cast film that was 30 times larger than that in a film cast from tetrafluoroethylene.

The researchers said that their novel class of protein polymer illustrates important new design principles for protein-based materials with unique microstructures and properties. In addition, they anticipate that "protein-based thermoplastic elastomers will find applications as novel scaffolds for tissue engineering and as new biomaterials for controlled drug release and cell encapsulation."

STEVEN TROHALAKI

Si_3N_4 Nanobelts Grown by Pyrolysis of Polyureasilazane with Iron Catalyst

Silicon nitride is known for its robust thermal and mechanical properties as well as its wide-bandgap electronic band structure, in which mid-gap energy levels can be introduced with dopants to tailor its electronic and optical properties. One-dimensional Si_3N_4 nanostructures may make it possible to engineer devices that take advantage of electron confinement effects for use in high-temperature environments. One example of such structures is the Si_3N_4 nanobelt synthesized by W. Yang of Tsinghua University, L. Zhang of the Chinese Academy of Sciences, H. Ji of Peking University, L. An of the University

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of Central Florida, and their co-workers. As reported in the February issue of the *Journal of the American Ceramic Society* (p. 466, DOI: 10.1111/j.1551-2916.2005.00069.x), these nanostructures with rectangular cross sections and triangular tips result from high-temperature pyrolysis of polyureasilazane in the presence of an $FeCl_2$ catalyst and N_2 vapor.

A powder precursor formed by curing the polyureasilazane and ball-milling it with the catalyst material was annealed at 1450ºC, yielding nanobelts 50–100 nm thick, 400–1000 nm wide, and ranging in length from hundreds of microns to several millimeters. Energy-dispersive spectrum analysis confirmed that the nanobelts consisted only of Si and N. High-resolution transmission electron microscopy revealed that the belts were perfectly crystalline α-Si_3N_4 with both [011] and [100] growth directions. Investigation of the structure using x-ray diffraction verified the presence of α-Si_3N_4, and a broad underlying diffraction peak was interpreted to come from an amorphous precursor that remained under the nanobelts.

The researchers suggest a solid–liquid–gas–solid growth mechanism for the nanobelts. As the amorphous Si-C-N precursor is heated with the Fe catalyst, a Si-Fe-C liquid eutectic forms and becomes supersaturated with Si and C. The supersaturated liquid reacts with N_2 vapor to form stable Si_3N_4 precipitates, which then grow into the nanowires. To account for the rectangular cross sections, the researchers propose that after the Si_3N_4 nucleates within the liquid droplets, the precipitate grows anisotropically due to the nature of the nitride crystal structure. Once the base of the triangular precipitate is the same dimension as the eutectic drop, the width ceases to increase but growth continues along the axial direction. Since other studies have shown that round nanowires can be grown in similar materials systems but at lower temperatures, Yang and co-workers are currently examining a hypothesis that the lower solubility of Si in the eutectic phase at lower temperatures results in smaller droplets, which in turn limits anisotropic growth of the nitride precipitates.

AMANDA GIERMANN

Doped PMMA Used For 3D Multilayered Optical Memory

As reported in the April 1 issue of *Optics Letters* (p. 774), H. Jiu and co-workers at the University of Science and Technology of China use a femtosecond-pulsed infrared laser to sequentially create eight layers of voids, with diameters less than a micrometer, within a block of doped poly(methyl methacrylate) (PMMA). Their result joins a body of research that uses pulsed lasers to controllably form voids within dielectric and polymer materials. This activity has been prompted mainly by the allure of applications in microfabrication and high-density optical storage.

As a dopant, the researchers chose an easily synthesized rare-earth complex, $Sm(DBM)_3Phen$, which is highly soluble in PMMA. Compared with pure PMMA, the doped polymer has a lower optical memory threshold, which is due to the strong absorption of DBM (dibenzoylmethane) at 400 nm. A high and uniform concentration of dopant compounds resulted in stability and reproducibility during the subsequent laser etching process.

The group members use a Ti:sapphire laser operating at 800 nm (in the infrared region) to create the embedded voids. Because the polymer is largely transparent at this wavelength, single photons penetrate easily to the desired void depth, tens of micrometers within the sample. Once inside the doped PMMA, the laser beam is focused, and multiphoton absorption then excites a micro-explosion that causes controlled damage to a tiny volume. Each pulse changes one region, or binary data bit, within the material. Electron spin resonance spectra of the sample, taken before and after the laser-induced damage, confirm the photodegradation of PMMA.

Jiu and co-workers then read out these bits, both serially by observing the fluorescence of the structurally altered cavities under illumination by a 514.5 nm argon laser, and also in parallel by imaging the region with a CCD coupled to an optical microscope. Fluorescence in the void regions is strongly enhanced, which the researchers attribute to defects introduced by the scission of bonds of PMMA.

"With our validation of how voids can be arranged and then also detected within this storage medium at room temperature," said co-researcher Qijin Zhang, "we have demonstrated the basic parts of a 3D, multilayered, read-only optical memory system."

RICHARD LOUIE

Anthracene Derivatives Used to Form *n*- and *p*-Type OFETs

Organic semiconductors have been widely studied from the viewpoints of their fundamental optoelectronic properties and their potential applications in organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), and photovoltaic cells. Novel *p*- and *n*-type organic semiconductors can be produced by introducing electron-accepting or electron-donating groups as terminal groups into a common core unit (e.g., thiophene oligomers). When the core units consist of acene, pentacene is known to exhibit the highest mobility (μ = 3.0 cm^2/V s) among OFETs. However, poor solubility in common organic solvents and instability in air makes pentacene difficult to modify. S. Ando of the Tokyo Institute of Technology, E. Fujiwara of the Institute for Molecular Science, Y. Inoue of NHK Science and Technical Research Laboratories, and their colleagues have reported anthracene as a preferred candidate over pentacene for its better solubility. The researchers prepared two new anthracene derivatives as semiconductors for FETs to prove the effect of terminal groups on charge transport. The research team believes this is to be the first *n*-type performance of anthracene derivatives.

As reported in the March 22 issue of *Chemistry of Materials* (p. 1261; DOI: 10.1021/cm0478632), thiophene rings (**1**) and 4-trifluormethylphenyl rings (**2**) are used as terminal groups for electron-donating and electron-accepting parts, respectively, in an anthracene unit to produce derivatives for *p*- and *n*-type transistor materials. The researchers constructed OFETs using these derivatives and demonstrated their performances as *p*- and *n*-type semiconductors. OFETs were fabricated on SiO_2/Si substrates using a top-contact geometry with gold source and drain contacts deposited on the organics. According to the research team, the absorption data reveal that the HOMO–LUMO gap for **1** is 2.85 eV and 2.68 eV for **2**. Through analysis, the researchers demonstrated that FETs with the derivatives **1** and **2** have been constructed with electron and hole mobilities on the order of 10^{-3} cm^2/V s. X-ray diffraction, they said, reveals high lamellar ordering and crystallinity for **1** and disorder for **2**. Atomic force microscopy shows a small grain size for **1** and a large grain size for **2**, which have important implications for transport. The researchers conclude that the terminal substituents near the gate electrode have a great effect in determining the polarity of FET characteristics.

VIVEK RANJAN

Nanopipettes and Nanoparticles Enable Detection of Single DNA Molecules

Progress in DNA detection methods may lead to new ultrafast DNA sequencing methods, which are essential for the development of new lab-on-a-chip technologies. In the February issue of *Nano-Letters* (p. 403; DOI: 10.1021/nl0480464), M. Karhanek and colleagues from the