

then compared with transmission spectra results generated using a finite-element method. The agreement between the plane-wave method and finite-element calculations was very good.

Results from this experiment showed that 12-fold symmetry structures had bandgaps that are nearly independent of propagation direction. As these tilings increase in complexity, so do their number of symmetry elements, rendering them more isotropic.

JUNE LAU

Pulse-Generation Limited to Five Optical Cycles Using Negatively Chirped Optical Parametric Oscillator

Researchers at the University of St. Andrews in the United Kingdom have demonstrated the feasibility of using optical parametric oscillators (OPOs) with chirped grating crystals to produce mid-infrared pulses with a bandwidth as narrow as five optical cycles. In the July 15 issue of *Optics Letters*, T. Beddard, M. Ebrahimzadeh, T.D. Reid, and W. Sibbett report that crystals of aperiodically poled lithium niobate (APPLN) effectively recompressed dispersion-broadened laser pulses of known frequency, resulting in the bandwidth restriction. The recompression is due to the chirped grating period of the crystals.

A 1-mm-long APPLN crystal with eight different linearly chirped gratings was used in the study. The least-chirped grating had a uniform period of 22.96 μm , while the most-chirped had a period ranging from 21.89 μm to 23.55 μm . The average grating period was constant throughout the series, and the crystal was studied in both positively and negatively chirped orientations. When the crystal was pumped collinearly by a Ti:sapphire laser, the OPO generated nearly transform-limited 53-fs-duration pulses at a center wavelength of 3 μm in the best-case scenario. This optimum output (approximately five optical cycles at FWHM intensity) was found to correspond to a negatively chirped grating with periods from 22.00 μm to 23.54 μm . Pulses emanating from the positively chirped OPO orientation were consistently broader. The development of numerical models to explain the observations is planned.

TIM PALUCKA

Sol-Gel Coating Improves Structural Stability of LiCoO₂ Cathodes during Electrochemical Cycling

A team of researchers from Samsung SDI Company and Seoul National Univer-

sity has greatly improved the structural stability of LiCoO₂ cathodes by sol-gel coating LiCoO₂ powders with SnO₂. The coated materials were heat-treated to 400°C or 500°C and retained 87% and 84% of their initial capacities after 47 cycles between voltages of 4.4 V and 2.75 V. This was attributed to a nonuniform Sn distribution throughout the particles and the resulting suppression of the monoclinic-to-hexagonal phase transition commonly observed in uncoated materials upon cycling.

Lithium transition-metal oxides are used as cathode materials for lithium-ion cells. The most stable among the α -NaFeO₂ structure types is Li_{1-x}CoO₂.

According to the scientists, "Li_{1-x}CoO₂ cycling stability is excellent over the limited composition range $0 < x < 0.5$, but the stability rapidly deteriorates for $x > 0.5$." They attribute this behavior to the occurrence of a monoclinic-to-hexagonal phase transition upon cycling at $x \sim 0.5$, which is accompanied by a large decrease in the *c*-axis dimension, while the *a*-axis length remains almost unchanged. The resulting differential stress leads to fracture of the oxide material. Efforts to improve the cycling stability of lithium cobalt oxide electrodes by partial substitution of Al or Mg on the Co site were unsuccessful, despite the fact that the change in *c*-axis dimensions was much smaller than in undoped materials. This influenced the researchers to use an alternate approach. They said that surface doping with metal oxides can sometimes suppress phase transitions.

Their procedure started with a 10- μm Li_{1-x}CoO₂ powder prepared by a solid-state method. As reported in the August issue of *Electrochemical and Solid-State Letters*, the grains were then subjected to sol-gel coating in a solution of tin(IV) ethylhexanoisopropoxide in isopropanol and subsequently dried at 150°C. Parts of this coated sample were heated to 400, 500, and 600°C, respectively. X-ray diffraction (XRD) patterns confirmed that a single phase with the α -NaFeO₂ structure was formed in all samples. Lattice-constant analysis proved that the SnO₂ was present as an amorphous surface layer in the 150°C material, whereas changes in the lattice constants of the samples treated at higher temperatures implied the formation of a LiCo_{1-x}Sn_xO₂ solid-solution phase. Electron microprobe analysis showed increasing migration of the Sn atoms into the grains with increasing heating temperature, and the 600°C material exhibited a homogenous distribution throughout the grains. Upon cycling, the materials with a nonuniform Sn distribution (e.g., the 400°C and 500°C samples)

had lower initial capacities than uncoated LiCoO₂, but retained 87% and 84% of it after 47 cycles as stated earlier, whereas the uncoated and 600°C samples showed only 49% of their initial capacity after the same number of cycles. Cyclic voltammograms revealed that the 400°C and 500°C samples did not undergo the monoclinic-to-hexagonal phase transition that was observed between 4.15 V and 4.2 V for the 150°C and 600°C materials. *Ex situ* XRD experiments showed that this phase transition induced cation disorder in the oxides by the exchange of Li and Co between their respective sites.

The researchers concluded, "The higher Sn concentrations at the particle surfaces prevent the phase transition from the monoclinic to the hexagonal phase."

CORA LIND

Host-Directed Polar Order Observed in Organic Molecular Crystals

Polar order in organic inclusion compounds is normally the result of direct head-to-tail contact between the guest molecules and is not affected by the host lattice. Another type of organic inclusion compound that exhibits polar order as a result of guest-host interactions has been discovered by graduate student Jennifer Swift and Prof. Michael Ward at the Department of Chemical Engineering and Materials Science at the University of Minnesota. The host structure consists of hydrogen-bonded guanidinium-ion "sheets" connected by perpendicular 4,4'-biphenyldisulfonate (BPDS) ion "pillars." The guest molecules are trapped in pores whose boundaries are defined by the guanidinium sheets on the top and bottom and the BPDS pillars on the sides. Molecular crystals exhibiting polar order were prepared using 4-nitroxylene, 1-nitro-, 1-iodo-, and 1-cyanonaphthalene (NX, NN, IN, and CN, respectively) as guest species.

As reported in the August issue of *Chemistry of Materials*, the inclusion compounds were synthesized in nearly quantitative yield by preparing a methanol solution of equimolar guanidine hydrochloride and 4,4'-biphenyldisulfonic acid along with excess guest, and allowing the solvent to slowly evaporate at room temperature. Real-time, *in situ* atomic force microscopy studies showed that the crystal forms by means of layer-by-layer growth.

The scientists assert that the high degree of polar order exhibited by the guest molecules is the result of ion-dipole interactions between the host guanidinium ions in the bottom sheet of each layer and the guest C-X (X = NO₂, I, CN) group dipoles during

crystal growth. This assertion is supported by short ion-dipole distances in the product crystal, as well as the observation that the degree of polar order in the crystal varied directly with the magnitude of the dipole moment of the guest.

The scientists said that the polar order of the bulk crystal cannot be the result of guest-to-guest interactions because of the large separation between the guests brought about by the host structure. The guest dipoles are further separated by the tilting of the BPDS pillars and guest dipoles relative to the crystallographic *c*-axis of the crystal. This tilting is the result of the distortion of guanidinium sheets during crystal growth to accommodate the guest molecules. The value of the tilt angle is the same for all pillars and guests in a single layer of the crystal, but is reversed in adjacent layers, which serves to further separate the guest dipoles. In addition to the physical separation of the guests, the charged guanidinium sheets also act as a dielectric screen for dipole-dipole interactions between guests in adjacent layers. Additional evidence for the absence of guest dipole-dipole interactions comes from molecular modeling, which shows that guest dipole-dipole interactions favor a different guest-dipole configuration than the one observed in the product crystal.

GREGORY KHITROV

Electrodeposition Found as a Versatile Tool in the Preparation of Magnetic Nanostructures

In an effort to investigate the suitability of electrodeposition for the controlled preparation of high-quality structures on an atomic scale, Yukimi Jyoko of Fukui National College of Technology in Japan and Walther Schwarzacher of the University of Bristol studied the growth of magnetic Co/Pt and CoNi/Pt nanostructures, as reported in the August issue of *Electrochemical and Solid-State Letters*. The obtained multilayered nanostructures exhibit perpendicular magnetic anisotropy and a large magnetic coercivity. The codeposition of Ni, as well as the deposition overpotential, has a significant influence on the film properties.

SBIR Update

Ion Optics (Waltham, Massachusetts) has been awarded a Phase II Small Business Innovation Research (SBIR) contract from the National Science Foundation to develop a lab-quality water-vapor sensor, built on a single integrated circuit using micro-electromechanical systems (MEMS) technology.

Magnetic multilayered nanostructures have received considerable attention since the discovery of perpendicular magnetic anisotropy, the magneto-optical Kerr effect, and giant magnetoresistance in metallic multilayers. New magnetic nanostructures have potential for application in high-density magneto-optical recording media or magnetoresistive sensor devices. "Most magnetic nanostructures have been fabricated by sputtering or molecular-beam epitaxy," said Schwarzacher, lecturer of physics. "Electrodeposition, however, may be more promising for all practical purposes, given the efficiency and simplicity of the required equipment."

Recently, he and Jyoko's group at Fukui proved that there is compositional modulation across successive layers in a Co/Pt nanometer-multilayered structure grown on a Pt(111) substrate by electrodeposition under potential control. The present work investigates the role that codeposition of Ni plays on the films' properties.

The researchers grew multilayered Co/Pt and CoNi/Pt thin films on Pt(111) and Cu(111) single-crystal substrates by alternating deposition from a CoSO_4 - and NiSO_4 -containing electrolyte and a H_2PtCl_6 electrolyte under potential control. For comparison, alloy films were also prepared by electrodeposition under potential control from a single electrolyte of all three precursors. The CoNi/Pt films crystallized in a fcc structure, while the Co/Pt films or alloy films showed a mixture of fcc Co, hcp Co, and Co stacking faults. X-ray diffraction superlattice profiles confirmed that the CoNi/Pt films exhibit well-defined interfaces between successive layers with compositional modulation on the nanometer-length scale, while the Co/Pt films do not contain pure Pt layers, but a compositionally modulated multilayer structure with graded transitions between a PtCo alloy and Co. "The microstructure and magnetic properties of electrodeposited Co/Pt multilayers depend strongly on the deposition overpotential and the growth mechanism," said Jyoko. The fcc Co/Pt films showed perpendicular magnetic anisotropy and large magnetic coercivity values. With decreasing thickness of the Co layers, remanent perpendicular magnetization was observed. The CoNi/Pt films exhibited even larger coercivities, up to 1.5 kOe. "This suggests the presence of a non-ferromagnetic or weakly ferromagnetic Pt-rich phase localized at grain boundaries or segregated grains in the CoNi/Pt nanostructure, which would pin domain-wall motion and also inhibit exchange interactions among grains," according to the researchers' report. This could occur by means of a place exchange between pas-

sive hydroxide adsorbates, $\text{Ni}(\text{OH})_{2\text{ad}}$ and $\text{Pt}(\text{OH})_{2\text{ad}}$, in the adsorbed intermediate.

The researchers believe that electrodeposition is a promising path for the preparation of magnetic multilayered nanostructures. As the properties of the films depend strongly on the multilayer growth mechanism, the researchers concluded that further studies on the growth kinetics and mechanism are necessary to achieve improved structural and magnetic qualities in the electrodeposited nanostructures.

CORA LIND

Cobalt Impurities Cause Nonlinear Current-Voltage Behavior in Niobium-Doped SrTiO_3 Bicrystals

Studies of the interfacial phenomena occurring at grain boundaries in polycrystalline electroceramic components have attributed nonlinearity in current-voltage (*I-V*) behavior to two sources: the degree of coherency of the grain boundary and the formation of additional interface states (such as double Schottky barriers). In the June issue of the *Journal of the American Ceramic Society*, researchers Takahisa Yamamoto, Katsuro Hayashi, Yuichi Ikuhara, and Taketo Sakuma of the University of Tokyo reported the formation of potential barriers in highly coherent bicrystals due only to impurities at the boundary, thus supporting the additional-interface-states theory.

Four niobium-doped SrTiO_3 single crystals of dimensions $10\text{ mm} \times 10\text{ mm} \times 3\text{ mm}$ were polished to a mirror state along the chosen {001} contact planes (corresponding to the $10\text{ mm} \times 10\text{ mm}$ faces). Metallic cobalt was evaporated onto the contact plane of one of the crystals to provide a controlled concentration of impurities in one sample (the "cobalt-evaporated" sample); the other contact surfaces remained clean. Bicrystals were then fabricated by carefully aligning and hot-pressing pairs of the single crystals at 1400°C for 10 h under 0.4 MPa pressure in air. After cooling, 1-mm-thick plates were machined from the samples perpendicular to the grain boundaries for current-voltage testing, high-resolution transmission electron microscopy (HRTEM), and energy-dispersive spectroscopy (EDS).

Selected-area diffraction patterns produced by HRTEM show highly coherent boundaries in both samples, with no secondary amorphous phases present in the cobalt-evaporated sample. EDS analysis of the cobalt-evaporated sample clearly demonstrates that the cobalt is dissolved and distributed in the grain boundary, allowing the observed coherency to