

normally binds with four other atoms or groups tetrahedrally to produce three-dimensional structures that have low energy requirements, making them stable, chemists used computational methods to predict that four groups around carbon molecules sometimes can lie in a plane. Several examples created in the laboratory confirmed this theory.

Von Ragué Schleyer and his research team in the Center for Computational Quantum Chemistry used computational techniques to investigate the possibility of hexacoordinate molecules with a carbon in the center of six-atom rings. As reported in the December 7 issue of *Science*, the researchers designed the boron and carbon compounds by fitting the atoms together in optimal ways, ensuring that all bond lengths were in the right ranges. They then checked their predicted planar hexacoordinate structures to verify their stability.

Open-Framework Material Consists of Cerium Oxyfluoride with CeO₆F₂ Dodecahedron

A research team from the Institute of Inorganic Synthesis at Yamanashi University, Japan, has synthesized an open framework material based on actinide oxyfluoride. As reported in the December 2000 issue of *Chemistry of Materials*, the researchers obtained cerium oxyfluoride by hydrothermal methods. The result is a compound with six dodecahedra of CeO₆F₂ linked in a basic structure forming an octahedral cage of Ce₆O₂₄F₁₂ interconnected by an O bridge, resulting in a channel structure with eight pore openings. The name given to the new cerium oxyfluoride is YU-1 (Yamanashi University) with the formula H_{25.5}(NH₄)_{10.5}Ce₉O₂₇F₁₈. As a precursor, a mixture was used of 1.0 Ce(SO₄)₂/0.5 H₃PO₄/1.5 H₂N(CH₂)₂NH₂/4.0 NH₄F/150 H₂O, which was heat treated at 160–180°C

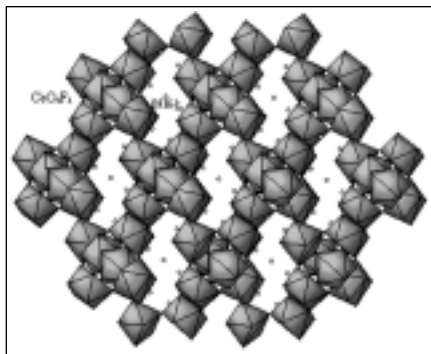


Figure: Framework of the cerium oxyfluoride YU-1 showing the hexagonal arrangement of the octahedral cages and locations of NH₄⁺ cations.

for several days. The crystalline product was washed and filtered with ethanol and deionized water and further dried.

Analysis on one of the crystals obtained shows that YU-1 belongs to the space group $R\bar{3}$, with the pore sizes and cages dictated by the distances between the centers of the corresponding oxygen and fluoride atoms. The octahedral cages formed by the six corner-sharing, cerium-centered CeO₆F₂ dodecahedra have a body diagonal of 5.8 Å and give rise to a framework structure with one three-dimensional channel systems. The channel systems connect opposite faces of the supercage and have elliptical eight-ring windows with O - - - O distance between 6.3 Å and 9.7 Å and F - - - F distance between 3.7 Å and 4.4 Å.

IULIA MUNTELE

Prism Coupling with Glass Spherical Microresonators Shows Optical Bistability

Optical whispering-gallery modes (WGMs) observed in microspheres are optical resonance modes that find useful applications as microspherical lasers. WGMs are widely applied in compact functional photonic devices. Some researchers are paying special attention to the fabrication method of these microspheres since it should produce a sphere with an optically smooth surface. A group of researchers from the Nagoya Institute of Technology has fabricated a prism-coupled glass microsphere containing Sm³⁺ ions and observed optical bistability of Sm³⁺ emission lines in WGMs. This pioneering experience introduces the possibility of the fabrication of all-photonic devices for optical computing using a spherical microresonator.

The investigators fabricated their microspheres starting from bulk glass of 70SiO₂-15B₂O₃-15Na₂O, as they explain in the January 15 issue of *Optics Letters*. They mixed the glass with Sm₂O₃ in a proportion of 2 mol%. From theoretical calculations, they found that this is the optimal concentration that gives the highest probability of spontaneous emission. The glass thus produced was crushed and reheated in a vertical electric furnace at 1200°C. During the free fall of the crushed glass, it remelted and acquired a spherical shape. Scanning electron microscopy observations confirmed that the microspheres formed had smooth surfaces.

Raman spectrophotometry was used to detect the emission bands in these microspheres, after excitation with a 488-nm Ar laser beam. The bulk material revealed emission bands from 550 nm to 670 nm of the ⁴G_{5/2}-⁶H_J (J = 5/2, 7/2, 9/2) transition

of Sm³⁺ ions. A spherical sample with a diameter of 23 μm exhibited several sharp resonance lines with a spacing of 3.90 nm. This value is consistent with results of 3.84 nm from calculations performed using Mie's theory.

Measurements from a microsphere previously immersed in distilled water revealed resonance lines with larger half width at half maximum (HWHM). This was caused by an increase in the roughness of the surface in the chemically unstable glass after water immersion.

Glass microspheres doped with Sm³⁺ ions exhibited optical bistability due to the prism coupling between the WGM and the pump beam. Prism coupling with these spherical microresonators decreases the threshold power for laser action in the resonance peak on the ⁴G_{5/2}-⁶H_{7/2} transition, and increases the capacity of the microspheres to store photon energy. This effect may be explained by a double resonance condition in an inverted V configuration of the three atomic levels, ⁴G_{5/2}, ⁶H_{7/2}, and ⁶H_{5/2}. These investigators plan to complete more detailed experiments to perform numerical analyses of their data.

SIARI S. SOSA

Pd Nanostructures Obtained inside Mesoporous Materials

A research team from the Department of Chemistry and School of Molecular Science—BK21 of the Korea Advanced Institute of Science and Technology (KAIST) has reported in the December 2000 issue of *Chemistry of Materials* the realization of arrays of palladium nanostructures inside cubic MCM-48 (a type of pure silica) and hexagonal mesoporous silica (SBA-15) by chemical vapor infiltration. The researchers obtained free-standing palladium nanostructures with precisely controlled shapes and sizes, opening the possibility to use the same approach for other metals and mesoporous materials that may be useful for catalytic, optoelectronic, and energy-storage applications. In this particular case, the Pd was used for its catalytic properties in H detection.

To obtain the ball-shaped Pd nanostructures, the researchers used granular MCM-48 and SBA-15 particles with pore diameters of approximately 3 nm and 9 nm, respectively, dried for 8 h at 400°C under dynamic vacuum and a Pd metalorganic precursor. The precursor was sublimated into the empty pores of the mesoporous materials (MCM-48 and SBA-15) under vacuum at 55°C, resulting in the formation of Pd(hfac)₂@MCM-48 and Pd(hfac)₂@SBA-15 composites (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate). The resulting composites were pyrolyzed at 150°C

under a flow of 10% H_2/F_2 to produce black powders of Pd@MCM-48 and Pd@SBA-15. X-ray diffraction and transmission electron microscopy (TEM) analysis show that the Pd is distributed locally inside the pores and does not block the channel entrances. The sizes of the ball-shaped Pd domains obtained have an average diameter of 35–40 nm. They are connected in a three-dimensional network, that is, the Pd domains fill the pores in the cubic matrix of MCM-48 with *la3d* symmetry. To verify that the Pd domains were free and the major product of the experiment, after the Pd@MCM-48 was treated with 20% HF to dissolve the silicate matrix, TEM analysis showed that “the Pd ball-shaped domains consist of three-dimensionally interconnected networks” whose shape and pores are “a replication of the MCM-48 template,” according to the article. Using the same method, Pd nanowires were obtained. SBA-15 was used as a template, resulting in 150-nm ellipsoidal domains with average diameters of 9 nm. This is almost the same as the diameter of the channel in the SBA-15 matrix.

IULIA MUNTELE

Low-Strain Warm Pressing of Multilayer Composites Yields Layers with Longer-Range Protection from Crack Deflection

To obtain a strong material with good crack-deflection properties, a delicate balancing act between a strong matrix material and a weak, crack-blunting second phase is required. In a study conducted by E.J. Winn and I.-W. Chen of the Department of Materials Science and Engineering at the University of Pennsylvania, crack-propagation mechanisms of zirconia-based composites containing an alumina second phase were examined. Despite the presence of a second phase, the samples demonstrated high bending strengths.

As reported in the December 2000 issue of the *Journal of the American Ceramics Society*, the two sample types used in the experiments had identical configurations. They were composed of 16 zirconia matrix layers, with 15 alumina (glue) interlayers. The matrix element was fabricated with zirconia slurries cast into strips of tape 100 μm thick. The interlayer glue consists of a porous alumina solution. A type of polymer known as AST, or alkali-soluble swellable thickener, was added to a mixture of alumina powder and acidic water (pH 4). While stirring, the pH of the mixture slowly changes to 9 with NaOH. The change in pH causes the AST to expand, adding volume but not weight. Subsequent sintering causes the AST to

disintegrate, leaving large pores behind. The layered samples were assembled by stacking 1.5 in. \times 1 in. \times 100 μm layers of zirconia tapes with a thin layer of glue between them.

The first sample was fabricated from the above formula and warm-pressed at 90°C to 20% of its true strain value. The second sample was prepared by pressing at the same temperature, but to 100% of its true strain value. Both samples were sintered for 30 min at 1350°C. Polished samples were subjected to the three-point bend test at 0.2 mm/min displacement. The mean strengths recorded for the two samples are 580 MPa and 540 MPa, respectively.

Examination of cross-sectional micrographs of the two samples suggests that through thickness, cracks were more likely to result from sample type 2. High strain from the press caused the interlayers to buckle and break apart. Thus, it is possible for cracks to “find paths through the material which never intersect a second-phase region,” as reported by the researchers. In sample type 1, the interlayers remained mostly straight and unaltered. This offered longer-range crack-deflection protection than found in the type 2 samples. In both cases, however, the chief mechanism of crack propagation was along the alumina/zirconia interface. These cracks ran perpendicular to the direction of applied stress, cleaving the interfaces.

These experiments supported the formation of composites with variable

crack-deflection proficiencies while only marginally compromising the strength of the bulk material.

JUNE LAU

Simulation Tool Demonstrates Double-Gate Transistor with 10-nm-Long Electrodes

Using a simulation tool called nanoMOS, engineers at Purdue University have shown that a double-gate transistor carries twice the electrical current and could work more than twice as fast as conventional devices. The research team led by Mark Lundstrom and Supriyo Datta, professors of electrical and computer engineering at Purdue, said that this type of transistor could keep Moore’s law in force until 2025 or beyond. This would give scientists time to develop technologies to replace integrated circuits made from silicon.

As described during the International Electron Devices Meeting, sponsored by the Institute of Electrical and Electronics Engineers in San Francisco on December 13, the electrodes known as gates are 10 nm long, rather than 100 nm as in conventional transistors.

The researchers have made nanoMOS available through the Purdue Nanotechnology Simulation Hub, or nanoHub. Lundstrom said that the nanoHub uses a network-computing platform that automatically enables computer users to run programs with conventional Web browsers. The nanoHub can be accessed at www.nanohub.purdue.edu. □

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