

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

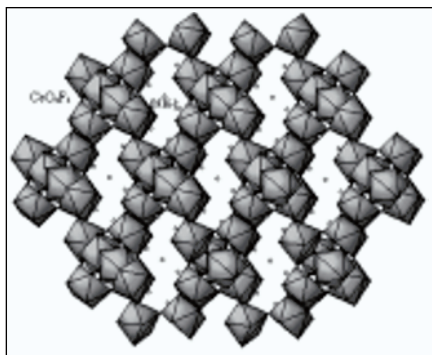


Figure: Framework of the cerium oxyfluoride YU-1 showing the hexagonal arrangement of the octahedral cages and locations of NH₄⁺ cations.

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