conjugating nanoparticles with biomolecules opens up new possibilities for making functional electronic devices using biomaterial systems."

STEVEN TROHALAKI

Germanium Nanocrystals Embedded in Glass Exhibit Large Melting-Point Hysteresis

J.W. Ager III, Q. Xu, D.C. Chrzan, and E.E. Haller of Lawrence Berkeley National Laboratory (LBNL) and the University of California, Berkeley, P. Kluth of the Australian National University, and their colleagues have discovered that nanocrystals of germanium embedded in silica glass do not melt until the temperature rises almost 200 K above the melting temperature of germanium in bulk. These melted nanocrystals have to be cooled more than 200 K below the bulk melting point before they resolidify. Haller explains that beyond broad scientific interest, the properties of germanium nanoparticles embedded in amorphous silicon dioxide matrices have promising applications.

"Germanium nanocrystals in silica have the ability to accept charge and hold it stably for long periods, a property which can be used in improved computer memory systems. Moreover, germanium dioxide mixed with silicon dioxide offers particular advantages for forming optical fibers for long-distance communication."

To exploit these properties means understanding the melting/freezing transition of Ge under a variety of conditions. The researchers embedded nanoparticles averaging 2.5 nm in diameter in silica. As they reported in the October 13, 2006, issue of *Physical Review Letters* (155701; DOI: 10.1103/PhysRevLett.97.155701), the researchers made silica glass samples 500 nm thick by oxidizing pure silicon wafers in steam. They implanted germanium ions in the amorphous silica and then annealed the sample at 900°C to form nanocrystals. The transparent glass allowed characterization of the embedded nanocrystals by Raman spectroscopy. The glass was also readily etched away for examination of the nanocrystals with an atomic force microscope.

Heating and cooling of the samples were performed *in situ* in a transmission electron microscope. By thinning the samples to less than 300 nm, the researchers could observe the electron diffraction rings produced by the crystal lattices of the embedded particles. When the particles began to melt, the diffraction rings weakened and vanished, allowing precise measurement of the temperature at which the embedded particles melted. As the temperature was lowered again, the appearance of the diffraction rings signaled resolidification.

For most materials, interface energies between solid and vapor—for example, a bar of gold in air—favor the formation of a liquid surface layer as the temperature increases, which continues to grow until the entire object is melted; this liquid layer forms more readily at lower temperatures as the proportion of surface to volume increases. Haller notes that "if you make free-standing nanoparticles of gold small enough, they melt at room temperature."

Embedded nanocrystals occasionally behave differently, however. Superheating has been observed in the case of nanocrystals embedded in a crystalline matrix, for example, nanoparticles of lead embedded in an aluminum matrix. This is attributed to the lattice structures of the two crystals "locking up," suppressing the vibration of the nanoparticles' surface atoms that would lead to melting. But Ge nanocrystals in silica glass are a different matter: the glass matrix has no lattice structure to lock with the surface of the germanium crystal. Ager said that "because there was no lattice structure in the matrix, we had naively expected the germanium crystals to behave more like freestanding nanoparticles—that is, we expected the melting temperature to be much less than in bulk germanium. Instead, to our surprise, germanium nanocrystals in glass had to be superheated to melt."

That was only the first surprise. In bulk materials, the interface energy between solid and vapor, which allows the transition from solid to liquid at the melting temperature, creates a roadblock in the opposite direction, an energy barrier to freezing.

"It always costs energy to form a surface," said Chrzan. "In the bulk, in fact, it's possible to supercool many materials and maintain them in a liquid state well above their normal freezing/melting point. In order to freeze, a material must overcome that slight energy barrier so as to form a critical solid nucleus."

In the case of Ge nanocrystals embedded in glass, the same large interface energy barrier that leads to superheating before the solid crystal can melt means the melted inclusions must be supercooled before they freeze.

"While these results were unexpected," Chrzan said, "it turns out they can be explained in a straightforward way. We modified the traditional theory of nucleation developed by David Turnbull in the 1950s. Even though in our system, the ratio of surface to volume is far greater than in the bulk materials Turnbull was working with—and even though, instead of a solid–vapor interface, we are working with a solid–glass interface—we saw that we could apply his theory in this new regime."

Chrzan said, "Typically in bulk materials, surface premelting means there's no need for nucleation before melting occurs. But in our case, the large proportional surface area of the germanium nanoparticles, plus the interface energy of the solid–glass interface, creates a calculable nucleation barrier in both directions."

As the nanoparticle heats up, a liquid nucleus, its lens shape partly determined by the confining spherical cavity in the glass, must achieve a critical size before it can spread and entirely melt the nanocrystal. Conversely, as the temperature drops, a solid nucleus forms and starts to grow from the surface of the liquid sphere—a nucleus that will eventually cause the entire nanometer-sized liquid globule to freeze into a solid crystal. The Turnbull theory as modified by Chrzan predicted the temperatures at which both events would occur.

"Melting and freezing points for materials in bulk have been well understood for a long time," said Haller, "but whenever an embedded nanoparticle's melting point goes up instead of down, it requires an explanation. With our observations of germanium in amorphous silica and the application of a classical thermodynamic theory that successfully explains and predicts these observations, we've made a good start on a general explanation of what have until now been regarded as anomalous events." □