Never-before-made material similar to diamonds and ice

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Not since the use of germanium in the first transistor radios and the discovery of its crucial role in semiconductor research more than 50 years ago has the study of this element garnered so much attention.

This half-century rebound in popularity is thanks to a University of Houston scientist and his team's research into a first-time, low-density synthetic form of this chemical element. Led by Arnold Guloy, a UH chemistry professor, and a team of researchers from UH and the Max Planck Institute for Chemical Physics of Solids in Dresden, Germany, where Guloy is also a guest scientist, the findings are described in a paper titled "A Guest-free Germanium Clathrate" published in *Nature* magazine, a scientific journal for biological and physical sciences research.

The usual form of germanium has the same structure as a diamond, and this new form has a beautiful and unique "cage" structure. That is, it has a crystal structure with an open framework having empty cages or cavities. Additionally, this new solid form of germanium is less dense and has the uncommon property of ice in that it floats in its own liquid.

"There is a high interest in clathrate or open-framework semiconductors as a general class of high-tech materials," Guloy said. "These materials have lower densities and larger band gaps than the usual forms of semiconductors due to their rather open or 'porous' structures. Until our report, there was no scalable and high-yield preparative technique to produce these materials – particularly the silicon- and germanium-based clathrate semiconductors."

As an important semiconductor material, germanium has thousands of applications that range from use in fiber optics communication networks to infrared night vision systems. Anything that is computerized or uses radio waves uses semiconductors.

"The synthesis of this new form of germanium should allow for new avenues of research in the germanium semiconductor," said John Bear, dean of UH's College of Natural Sciences and Mathematics. "Clathrate semiconductors have significant technological potential because they exhibit a very wide variety of materials properties."

Silicon (which replaced germanium in transistor radios) and germanium form the most important semiconductors for electronic devices. However, their classical forms exhibit small and indirect band gaps that are not suitable for many possible optoelectronic applications that combine light and electronics technology. This new caged form of germanium will provide scientists useful information to design high-efficiency thermoelectrics, gain a better understanding of superconductivity in this class of materials and create more new materials based on Guloy's synthetic technique, as well as point to "the possibility of making silicon and carbon analogs that would be even more spectacular," he said.

"This breakthrough has resulted in a form of germanium with a low-density, open-caged structure and the potential to emit light," Guloy said. "Furthermore one cannot make this empty germanium clathrate or 'cage' compound by any other means. Our method is done at relatively mild temperatures – 300 degrees Celsius – and being a solution technique it can easily be scaled to prepare thin films and its other functional forms. We have created a low-density, metastable form of germanium that has lots of holes in it – a cage structure – and this has been predicted to have unusual thermoelectric and optoelectronic properties, such as the potential to emit light. All previously known compounds with clathrate structures have something in the cages to keep them from collapsing. It's amazing that our new germanium structure can be constructed even though its cages are empty."

"It is always novel and scientifically important to find a new form of an element that is not made naturally," Guloy said. "Since the material has never been made before, there is really no designed or direct application for it yet. The synthesis of this unusual material and the predicted properties open many possibilities. This is similar to the preparation of the buckyball in 1985, where researchers initially did not know what they were good for until they were made in bulk quantities that led to subsequent research, discovering many applications for the now-famous material."

Bear adds that this particular synthesis of germanium allows for the preparation of bulk material, and the scalability of the solution method offers excellent prospects of processing clathrate semiconductors.

Source: University of Houston

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