Naval research laboratory takes a close look at unique diamonds

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The Wittelsbach-Graff diamond (31.06 ct, left) and the Hope diamond (45.52 ct, right) apparently were not cut from the same crystal, even though they share several similarities, such as strong red phosphorescence (bottom). Credit: Chip Clark, Smithsonian

The song says that "diamonds are a girl's best friend," but scientists at the Naval Research Laboratory are finding that diamonds are a researcher's best friend too.

NRL, which has been involved in pioneering work involving chemical vapor deposition of diamond and the use of diamond materials in advanced technologies relevant to the Department of Defense since 1987, has recently undertaken some new projects in diamond research. In collaboration with the Smithsonian Institution Museum of Natural History, NRL researchers have begun studying unique and historic natural colored diamonds to understand and characterize the defects/impurities, which cause the color. Many of the properties of diamond necessary for technology are impacted by defects and impurities present in the lattice. NRL has been complementing its studies of these defects and impurities in chemical vapor deposition diamond materials with its studies of natural diamonds at the Smithsonian.

Since late 2005, a team of NRL researchers led by Dr. James Butler of the Chemistry Division, has been examining unusual natural colored diamonds available to the Smithsonian. These included many of the diamonds in the Smithsonian Collection, such at the "Hope" and the "Blue Heart," as well as a collection of 240 fancy colored diamonds in the Aurora Butterfly collection on loan to the Smithsonian.

During 2005, NRL researchers James Butler, Sally Magana (NRC), Jaime Freitas and Paul Klein worked with the Smithsonian, Penn State University, and Ocean Optics to study the optical emission properties of the Hope Diamond. This work, "Using Phosphorescence as a Fingerprint for the Hope and Other Blue Diamonds", was published in *Geology*, 36, 83-86 (2008). Most recently, in 2010, NRL has been working with the Smithsonian and the Gemological Institute of America (GIA) to study another famous blue diamond, the Wittelsbach-Graff diamond. Both the Hope and the Wittelsbach-Graff diamonds are believed to have originated from the same region in India in the 17th century, have similar blue color and nearly identical red/orange phosphorescence when excited by ultra-violet light. Hence, it has been speculated that they might have originated from the same stone. The Wittelsbach-Graff diamond was last seen in public in 1958; then in 2008 Laurence Graff, a diamond dealer, bought it at auction for 16.4 million GBP. Graff had the stone cut and repolished, reducing it from a 35.5 carat stone to a 31 carat stone, compared to the Hope diamond which is 45.52 carats.

The research team studying the Wittelsbach-Graff diamond used a variety of spectroscopic and microscopic analyzes to determine the extreme similarity of the gems, but also observed distinct differences in the dislocation and strain microstructure which suggests that the gems probably did not originate from the same rough stone.

The Wittelsbach-Graff is on display at the Museum of Natural History from February to August 2010 along with the Hope Diamond. This work continues the ongoing collaboration between NRL scientists and the Museum of Natural History on the Hope diamond and other blue diamonds at the Smithsonian which has examined the phosphorescence (due to donor-acceptor recombination), the boron concentration using secondary ion mass spectroscopy, and soon to be published work on the spectroscopic and structural properties of a collection of pink diamonds.

Another aspect of NRL's diamond research collaboration with the Smithsonian involves an interdisciplinary effort to study rare pink diamonds. Many natural pink diamonds derive their color from colored bands or lamellae in an otherwise colorless diamond. Led by Jeff Post, Eloďse Gaillou, and Tim Rose of the Smithsonian Museum of Natural History; NRL researchers James Butler (Chemistry Division), Rhonda Stroud and Nabil Bassim (Materials Science and Technology Division); along with Alexander Zaitsev, CUNY; and Marc Fries, JPL/Cal Tech studied a suite of natural pink diamonds. The research team used a variety of spectroscopic and microanalytical tools to study the structure, defects, and impurities in and around the colored lamellae.

Pink diamonds are extremely rare, on a par with blue diamonds in rarity and value. But unlike most blue diamonds where the color is caused by an impurity atom, boron, pink diamonds seem to derive their color from structural, or a combination of structural and impurity related defects.

While the research team has not identified the exact structure of the defects causing the pink color, they have determined that it is contained in narrow colored lamellae in an otherwise clear matrix of diamond. Using a focused ion beam microscope, NRL researchers extracted cross-sections of the pink lamella for detailed examination in a transmission electron microscope (TEM). TEM examination of the lattice structure, combined with spectroscopic analysis, suggest that the lamellae are the result of plastic deformation, which occurred while the diamond was still in the earth's mantle and before it was transported to the surface in ancient volcanic eruptions. They will continue their studies to characterize a suite of rare pink diamonds to see if they can fully identify the nature and cause of the defects which cause the pink color. "The pink lamella are twin domains, with atoms arranged to mirror almost exactly those of the surrounding clear diamond. The real question is, what subtle shift in the atomic arrangement makes the twins pink but leaves the nearly identical sibling colorless? The sub-angstrom imaging capabilities of the latest generation of electron microscopes should tell us the answer," says Stroud.

"Understanding these unique colored natural diamonds provides knowledge useful to both technologists and gemologists," Butler explains. "A better understanding of these defects and impurities (dopants) allow us to tailor the materials properties of diamond materials: from electrically insulating to semiconducting; from optically transparent to a variety of colors; or to provide the isolated quantum states for quantum cryptography or quantum computing."

Provided by Naval Research Laboratory

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