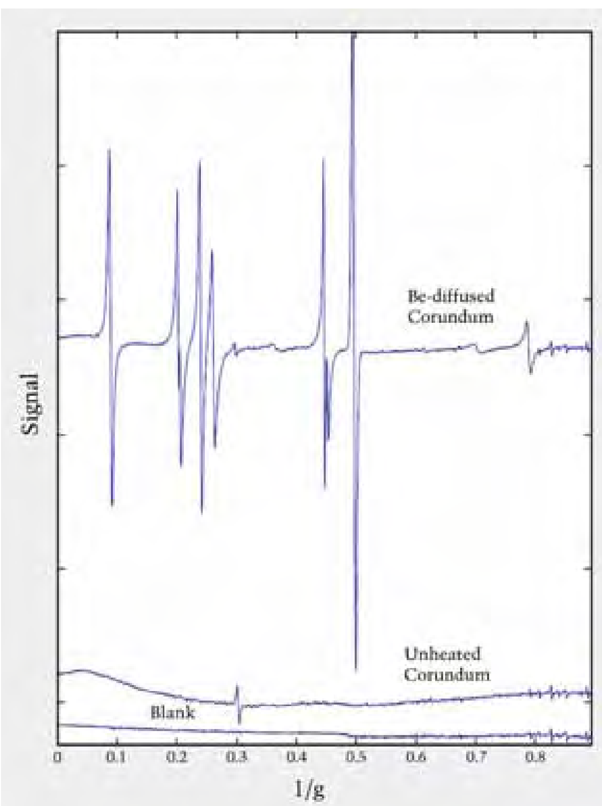
New Technologies Used to Identify Colored Stone Treatments

George R. Rossman

The detection of treatments in gem materials involves the application of a variety of complementary analytical methods that range from careful observation at low magnification to expensive and involved analyses with elaborate instruments. The need for the latter is driven by the increasing sophistication of treatment technology.

Significant advances have been made in the chemical analysis of minerals with the introduction of a variety of highly sensitive methods for elemental analysis. For example, researchers are scrutinizing several new instruments for their possible application to the detection of beryllium diffusion in corundum.

The EPR spectrum of a Be-diffused natural corundum (top) is very different from that of an untreated (control) sample of synthetic corundum. The term "g" is a calculated physical property that is proportional to the applied magnetic field strength. The graph plots the absorption caused by resonating electrons in paramagnetic centers as the magnetic field is varied.



Like laser ablation–inductively coupled plasma–mass spectroscopy (LA-ICP-MS), laser-induced breakdown spectroscopy (LIBS) provides rapid and comparatively inexpensive analysis of a wide range of elements, with many detected in the parts-per-million range. It is a quickly evolving technology that can give results within minutes from the time the sample is introduced into the instrument. Secondary ion mass spectroscopy (SIMS) likewise can determine a wide range of elements, with many in the parts-per-billion range. However, SIMS requires considerable sample and instrument preparation time, and the cost of the analysis is significantly higher than with LA-ICP-MS and especially LIBS. The application of these methods to gemological analysis has been reviewed by Abduriyim and Kitawaki (2006). If properly calibrated, SIMS can also determine the isotopic composition of major and minor components in solids. To date, this application has been primarily directed at origin studies, but it may be useful in the future for the detection of treatments, coatings, and synthetics.

Electron paramagnetic resonance (EPR) spectroscopy has existed for more than 50 years but has not found widespread application in gemology. A sample is placed in a high-frequency microwave field and subjected to an intense, variable magnetic field. Ions containing unpaired electrons will produce strong absorption of the microwaves at characteristic magnetic field strengths. EPR is an exquisitely sensitive technique for detecting certain components, such as those produced when ultra-high-temperature treatments are applied to gem minerals. The O^- ion that forms in beryllium-diffused corundum is a compelling method for identification (see figure). Beryllium-diffused corundum, in particular, could motivate improvements in the sample-size limitations (~3 mm) of many current instruments.

Advances in electron microscopes have also allowed improved detection of coatings and fillings. Resolutions in the 0.01 μm range are now routinely attained. Currently, these instruments are providing spectacular insight into such treatments as well as greatly improved imaging of natural inclusions and defects in stones.

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Dr. Rossman (grr@gps.caltech.edu) is a professor of mineralogy at the California Institute of Technology in Pasadena, California.

Identification Technologies for Diamond Treatments

Alan T. Collins

The major treatments used to improve the appearance of natural diamonds include laser drilling, typically followed by acid treatment, to remove black inclusions; the filling of large surface-reaching fractures with high-refractive-index glass; and color enhancement by various procedures. Two of the most important developments in the last decade are:

- A new type of laser drilling, the KM treatment (*Kiduah Meyuhad* means "special drill" in Hebrew), for removing inclusions (Horikawa, 2001). This procedure produces an internal, surface-reaching fracture that looks more like a "feather" than a traditional laser-induced channel, but still allows introduction of an acid to dissolve the inclusion.
- High-pressure, high-temperature (HPHT) processing, which causes dramatic changes in color (figure 1). Recently, the HPHT process has been combined with the older techniques of radiation and heat treatment to produce fancy pink-to-red specimens. Diamonds enhanced in this way by Lucent Diamonds Inc. (Wang et al., 2005) are illustrated in figure 2.

Of equal, if not greater, importance is the ability of HPHT processing to produce colorless or near-colorless stones from brown type IIa diamonds (see, e.g., Moses et al., 1999). This treatment also occasionally results in pink or (more rarely) blue specimens (Hall and Moses, 2000), which have absorption spectra that are similar to those of naturally colored diamonds.

Although most color enhancement of diamonds is done legitimately, and the process declared, some treated diamonds may be fraudulently described as having a natural color as they travel through different distribution channels. Therefore, it is vital that gem-testing laboratories have the expertise to recognize color-enhanced diamonds and that research into their characterization and identification continues to keep up with the new enhancement techniques as they are introduced.

All colored diamonds need to be examined carefully; furthermore, in principle, any colorless or near-colorless diamond is potentially a type IIa diamond that has been color-enhanced (from brown) by HPHT processing. Fortunately, it is quick and easy to determine whether a diamond is type IIa (by using the DiamondSure or a similar instrument), and the majority of diamonds (around 99%) are not, in fact, type IIa.

Dr. Collins (alan.collins@kcl.ac.uk) is professor of physics at King's College London.

Figure 1. Some brown type Ia diamonds, such as this 1.07 ct crystal fragment (left, before treatment), can be transformed to yellow to green with HPHT processing (right, after treatment). Photo by Elizabeth Schrader.

Visual inspection with a 10× loupe and an optical microscope (to detect drill holes and feathers produced by lasers, as well as the "flash effect" associated with glass-filled fractures [McClure and Kammerling, 1995]), together with optical absorption and luminescence spectroscopies, enables detection of most treated diamonds (some more readily than others). Visual evidence of graining, as well as graphitized cracks and inclusions, also give important clues that the diamond has been subjected to HPHT

Figure 2. The color in these pink-to-red diamonds was produced by a treatment that involves HPHT annealing, irradiation, and low-pressure annealing at relatively lower temperatures. Loose stones (0.15–0.33 ct) courtesy of Lucent Diamonds; necklace courtesy of Avirom Associates. Photo © Harold & Erica Van Pelt.

processing (Reinitz et al., 2000). However, despite the range of assessment techniques available, it is likely that a few diamonds will be encountered for which it is not possible to say with certainty whether the color is natural or enhanced (Collins, 2001). Recent research (Eaton-Magaña et al., 2006) indicates that the phosphorescent behavior of blue diamonds produced by HPHT processing is different from that of natural blue diamonds, and this observation may provide an additional analytical tool for examining certain stones. The KM laser treatment can often be verified by examining polishing marks on the diamond's surface by differential interference microscopy (Horikawa, 2001). These investigations and other ongoing research will hopefully address the challenges of the future.

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Identification of Synthetic Diamonds: Present Status and Future Developments

Christopher Welbourn

The subject of synthetic diamonds has received significant media attention over the last few years. Often, these goods are portrayed as being so perfect that it is virtually impossible to distinguish them from natural diamonds. The fact is, however, that the synthetic diamonds currently on the market can be readily identified. Even with projected developments in synthesis technology, it is likely that all synthetic diamonds produced in the foreseeable future will continue to be identifiable.

Present Status: Colored HPHT Synthetic Diamonds

The majority of commercially available synthetic diamonds are yellow in color and produced by high-pressure, high-temperature (HPHT) processes (see, e.g., Shigley et al., 2002). The yellow color is caused by isolated nitrogen impurities. Other colors may also be produced—namely, blue, green, and pink (Shigley et al., 2004a). These colors result either from the addition of boron to the synthesis capsule or from irradiation treatment conducted after synthesis.

Dr. Welbourn (C.Welbourn@warwick.ac.uk), formerly head of physics at the DTC Research Centre, is an associate fellow at the University of Warwick in Coventry, United Kingdom.

Striated orange fluorescence, seen in this DiamondView image, is characteristic of CVD synthetic diamond containing trace amounts of nitrogen. Courtesy of the DTC Research Centre.

HPHT synthetic diamonds have a characteristic cubo-octahedral morphology, frequently modified by dodecahedral and trapezohedral facets. The incorporation of impurities, in particular nitrogen and boron, is different for each type of growth sector, and this leads to distinctive color zoning and fluorescence patterns that demonstrate the characteristic morphology (Welbourn et al., 1996).

Future Developments: Colorless HPHT and CVD Synthetic Diamonds

For many years now, the Diamond Trading Company (DTC) Research Centre in the UK has been conducting a research program to address the kinds of synthetic diamond that may pose identification challenges in the future. To support this program, the DTC has commissioned a leading industrial synthetic diamond manufacturer, Element Six, to produce both HPHT and chemical vapor deposition (CVD) material aimed at probing potential weaknesses in existing identification strategies and enabling the development of new identification techniques.

Although several reports over the years have referred to the production of colorless to near-colorless synthetic diamonds, it does not appear that this material is generally available at present. This is probably due to the fact that it is significantly more difficult to produce good-quality synthetic diamonds when steps are taken to reduce nitrogen impurity levels. Nevertheless, research on colorless material from Element Six and other sources has shown that, although color zoning is absent, the characteristic morphology is still evident in patterns of fluorescence. These patterns are most conveniently observed by using the DiamondView instrument developed at the DTC Research Centre (Welbourn et al., 1996). Colorless to near-colorless HPHT synthetic diamonds have another easily observable characteristic, that of strong, long-lived phosphorescence following exposure to a UV lamp. Most colorless natural diamonds do not show phosphorescence.

Although some CVD synthetic diamonds have been made available for gemological study (see, e.g., Wang et al., 2003), no such material appears to be currently available for jewelry use in significant volumes.

Martineau et al. (2004) reported on CVD synthetic diamond produced by Element Six. This and other studies have shown that a common characteristic of CVD material is orange fluorescence (see figure). This fluorescence is due to nitrogen-vacancy defects. Although CVD synthetic diamonds are usually type II (i.e., relatively nitrogen-free), nitrogen is generally present in trace amounts in the CVD reactor unless strenuous efforts are made to exclude it. Therefore, it is also present in the growing diamond, since nitrogen tends to be readily incorporated. Nonetheless, CVD material of sufficiently high purity so as not to show orange fluorescence has been produced (again, see Martineau et al., 2004). DiamondView images of this kind of material essentially only show fluorescence from dislocations; however, the patterns of this fluorescence are quite different from those of natural type II diamonds.

Identification Strategies

Colored HPHT synthetic diamonds may be identified through observation of color zoning with a gemological microscope. Other helpful identification features are fluorescence behavior and, where present, inclusions (see, e.g., Shigley et al., 2004b).

Diamonds in the D–Z color range may be rapidly screened using the DiamondSure instrument, which is an automatic UV/visible spectrometer. Only those giving a "Refer" result (about 2% of the general diamond population) need to be investigated further. For stones in the D–J range, the HRD D-Screen instrument or the SSEF Diamond Spotter may also be used for screening. These instruments test for short-wave UV transmission. Referred stones may then be checked with a UV lamp: Strong, long-lived phosphorescence provides a good indication of an HPHT synthetic in this color range, whereas orange fluorescence may indicate a nitrogen-containing CVD synthetic diamond. Ultimately, referred stones should be sent to a gem testing laboratory where use of a DiamondView instrument, together with various types of spectroscopic measurement, should positively identify all synthetic diamonds, both HPHT and CVD.

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Identifying Treated and Synthetic Gems: The Dealer's Perspective

Robert E. Kane

In gem treatments and synthetics, there have been more developments in the last 10 years than in the previous 50 combined. Since the 1999 Symposium, we have seen, for example, the commercial availability of (1) HPHT-treated diamonds in a variety of colors, (2) various colors of faceted synthetic gem-quality diamonds, (3) beryllium-diffused corundum, (4) poor-quality opaque corundum that has been transformed into transparent red gems by filling fractures with high-lead-content glass, and (5) "diffusion ruby," which proved to be synthetic ruby overgrowth on natural corundum. It is critical that we identify and disclose these products if we are to maintain consumer confidence.

Although most of these treatments and synthetics are based on sophisticated technology, many can still be detected through precise gemological testing and observation. And when routine testing does not yield a definitive identification, major gemological laboratories can identify nearly all of them using advanced instrumentation. This presentation discusses approaches that members of the industry can take to deal with the constant influx of these new materials.

When examining a gem, the experienced gemologist systematically rules out the treatments and synthetics known for that particular stone. By running through a list of possibilities and how they are identified, one can identify the gem in question using standard observation and testing, or make an informed decision on a proper course of action, such as submitting the gemstone to an internationally respected gem laboratory for testing. The challenge is to recognize when the identification is beyond your knowledge level—*to know when you don't know*.

By not facing these difficult issues, and thus buying and selling "blindly," you open yourself and your company up to loss of reputation and to liability that could result in financial loss.

Gem Identity Assurance Program

One way to address these identification challenges is to develop a "gem identity assurance" program for your company based on gemological knowledge, trust in your suppliers, security through lab reports, and determining the level of risk that is acceptable in a given situation.

Mr. Kane (finegemsintl@msn.com) is president and CEO of Fine Gems International in Helena, Montana.

Gemological Knowledge. Decades of scientific research by groups such as De Beers, GIA, and others have provided practical solutions to identification problems created by the proliferation of treated and synthetic gems. You can—and should—take advantage of this information by (1) regularly reading the gemological journals; (2) attending seminars held during trade shows such as at Tucson, Las Vegas, Basel, Bangkok, and Hong Kong; (3) taking specialized training at laboratories such as SSEF and AGTA; and (4) availing yourself of resources such as the De Beers CD-ROM *Diamonds* and books on specific topics—for example, GIA's *Gems & Gemology in Review: Synthetic Diamonds*. There are also many educational programs available around the world to fit most needs.

There is no substitute for up-to-date gemological knowledge and solid experience. To this end, you should also consider purchasing your own gem-testing equipment, a portable lab, or—depending on your circumstances—a complete advanced testing laboratory.

Figure 1. Careful examination of this 8 ct sapphire with a darkfield binocular microscope and diffused lighting revealed subtle curved color zoning—proving that what appeared to be a magnificent natural gem was actually a flame-fusion or Verneuil synthetic sapphire. Photo by Robert Weldon, GIA.

Trust in Your Suppliers and Financial Recourse. It is very important to buy gems from a trusted and knowledgeable supplier—one who will refund your money if testing reveals that the gem is not what it was represented to be. Always demand full disclosure regarding treatments and synthetics in writing on the invoice—if the seller will not comply, then find a new supplier. Buy from companies that belong to organizations such as ICA (International Colored Gemstone Association), AGTA (American Gem Trade Association), AGS (American Gem Society), TGJTA (Thai Gem & Jewelry Traders Association), WFDB (World Federation of Diamond Bourses), and the like. Members of such organizations must adhere to rules of ethical behavior, and the organizations can and will issue sanctions if these rules are violated.

Security through Laboratory Reports. Establish a company policy whereby all gems over a certain monetary value, or certain kinds of gemstones, must have a report from an internationally recognized gem lab. On expensive gems, obtain reports from at least two different labs. This is particularly important when geographic locality reports are required (because these determinations are not an exact science, the second lab may indicate a different origin, in which case a third report is needed). Lab reports help protect you from future liability problems with your clients.

Risk Tolerance. Determine what level of risk is acceptable. Certainly, the buying and selling of a 1 ct purplish red diamond warrants an updated GIA lab report. Yet it may be reasonable to accept the word of your supplier (who knows the chain of custody and guarantees it in writing) when purchasing small amethysts, various colors of small sapphires, or parcels of emerald melee. Although you do run some risk that a mistake has been made, for most dealers the risk is manageable. Again, though, this depends on the specific situation. If a parcel of 2.0 mm yellow sapphires are going into an expensive piece of jewelry featuring 200 such stones, testing (or at least spot-testing) would be required to ensure accurate representation of the entire piece.

Buying and Testing Scenarios

Following are two examples of buying and testing situations.

Scenario 1: A Large Blue (Synthetic) Sapphire. A dealer is offered an 8 ct superbly cut, clean, intense blue sapphire—set in an antique mounting—for $10,000. However, it is not accompanied by a lab report. During very careful examination with a darkfield binocular microscope and diffused lighting, she sees subtle curved color zoning—proving that what appeared to be a magnificent natural gem was actually a flame-fusion or Verneuil synthetic sapphire. In 2005, a natural-color Sri Lankan sapphire of this size and apparent quality sold for $30,000; a comparable Burmese sapphire sold for $55,000. If it seems too good to be true, it probably is!

Figure 2. This 3+ ct "unheated" Mogok ruby contained evidence of clarity enhancement, which reduced the visibility of a surface-reaching fracture.

Scenario 2: A 3+ ct "Unheated" Mogok Ruby. One gem dealer offers another a 3+ ct ruby, accompanied by a report from a gem lab stating: "Burma (Myanmar), no indication of thermal treatment." Microscopic examination revealed inclusions characteristic of untreated Mogok rubies, such as unaltered rutile needles and small calcite crystals. It also revealed a small fracture extending from the crown facets toward the girdle. The second dealer's prospective buyer was willing to pay in excess of $100,000 for the stone, but wanted a report from a certain U.S. laboratory. That lab reported evidence of clarity enhancement—specifically, foreign material filling the surface-reaching fracture, which is typically done in an attempt to reduce the fracture's visibility. After the stone was soaked in acetone for several days (with the first dealer's permission), the filler was no longer present, causing the fracture to become more prominent. The client was no longer interested in the ruby, and the gem dealer lost the sale. As mentioned above, with high-value gems it is good to obtain reports from two different laboratories.

Navigating the Challenges Ahead

To maintain vitality and confidence in our industry, it is critical that we stay up to date on technological developments in gem synthesis, treatment, and identification. Learn what is in the market, how to identify it, and when to refer a gem to a recognized laboratory for advanced analytical testing. Buy from a trusted and experienced source. With expensive gems, this can be backed up by laboratory reports. The rapid advances in technology will inevitably bring challenges to the gem and jewelry industry—some will present positive opportunities, while many others will create daunting gem identification issues. Vigilance in pursuing knowledge will insure that our industry continues to flourish.