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NDT breaking the 10 carat barrier – world record synthetic diamonds investigated

Introduction

The first small manufactured industrial diamonds were produced in 1953 by the Swedish company ASEA but their accomplishment went unannounced. In 1970, General Electric (GE) produced synthetic diamond crystals using the HPHT method with a belt type of press and created a 0.78ct polished RBC colorless diamond. In the 1980's and 1990's Russians used their own technology ("BARS" and "TOROID" high pressure apparatus (HPA) with high pressure presses of up to 25 MN load) to grow industrial and crystals up to 2.00ct in polished size, mostly orange to yellow in colour. In the last 15 years, companies including **Lucent, Chatham, AOTC, Gemesis** (now **IIa Technologies**) and many other producers in China, Germany, India, Russia, Ukraine, USA and Taiwan have improved the technology yet again and used their expertise to successfully grow diamond crystals that cut to 1.00ct up to 2.00ct in size. This "next generation" of diamonds exhibited high clarities (VS and VVS) and colours (D-H), as well as new blue and pink colours (after irradiation). Other companies (ref. 2-3) including **Scio Diamonds, Washington Diamonds, Taidiam, PDC diamonds and Pure Grown Diamonds**(selling arm of IIa technologies) are also using a very different technology/process of Chemical Vapour Deposition (CVD) to produce laboratory-grown diamonds up to 3.00 ct in size (table 1).

Production Facility and Technology

The new world record for the largest laboratory-grown diamond crystal is 60ct and this gem was produced during the first week of July 2015 at the **New Diamond Technology (NDT)** facility in St. Petersburg (Russia) during an inspection by Branko Deljanin (CGL-GRS). In April 2015, NDT experimentally produced a 32.26ct colorless gem quality diamond crystal. From this stone, the largest lab-grown faceted diamond in the world has been cut. It is a 10.02ct faceted square emerald-cut synthetic diamond (Fig. 4a and Fig. 10). The NDT facility in St. Petersburg has over 50 HPHT presses (incl. 25MN load presses equipped with a high pressure apparatus (HPA) type "TOROID" and 50MN load presses type SK850 equipped with HPA type "Cubic", see Fig. 1 and Fig. 2a), producing 5,000ct of diamonds per month in collaboration with a modern cutting facility (Fig. 2b and Fig. 3a) where they process and polish the laboratory-grown diamonds. New Diamond Technology Ltd recently entered the synthetic diamond jewellery market after completing eight years of research and successful production of **type IIa** and **IIb** crystal plates for specific industrial applications (medical, synchrotron radiation and anvil design). NDT now uses much larger cubic type presses (the latest 850 series, Chinese made), and as a result many large stones can be produced in one run (16 colorless stones, 6-10 cts rough) in a cycle that takes 10 to 12 days on average.

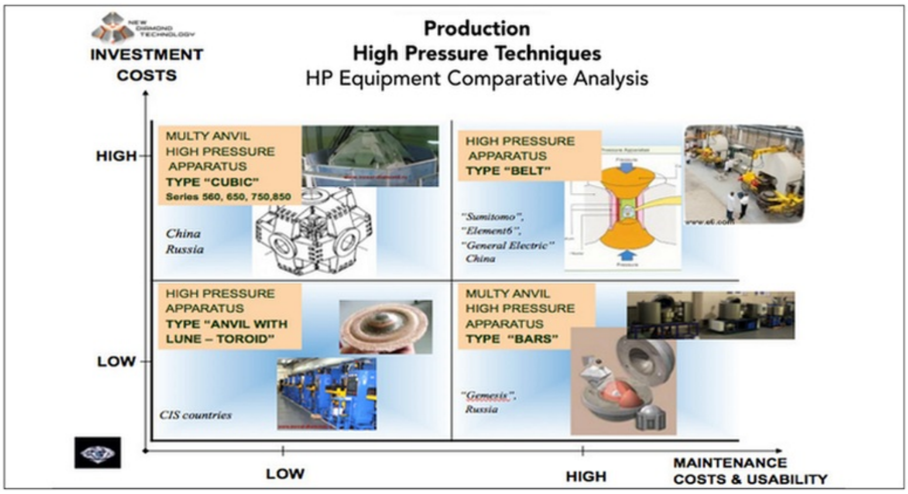

Fig. 1: The different types of equipment used for synthetic diamond production and analyses the production and maintenance costs. The largest cubic press is close to 1$M but it is still less expensive than BELT equipment. This has consequences for the future of the synthetic diamond production in terms of the numbers and sizes of produced synthetic diamonds. Courtesy of Dr. Andrey Katrusha and New Diamond Technology.

World synthetic diamond production volume from 2014-2017 is unlikely to be more than 2.5 million carats (white crystals) per year, and lab-grown diamonds currently represent only 2.5 – 3.0% of the natural diamond supply. This could change dramatically (double or triple) in the next 1 or 2 years if the Chinese manufacturers move their focus from the production of industrial diamond powder to growing single crystal diamonds and adapt their technologies to produce large crystals using cubic HPHT presses (Fig. 1).

Fig. 2a: View into the New Diamond Technology production factory in St. Petersburg (Russia). The facility comprises of over 30 cubic presses as well as a cutting factory (photo courtesy of NDT). Fig. 2b (inlay): Insight into the cutting factory during the inspection by CGL-GRS of the NDT facility in St. Petersburg. (From left Dr. Alexander Kolyadin, New Diamond Technology, Branko Deljanin, CGL-GRS Canada, and the manager of the polishing factory Volodya Dallakyan). Photo courtesy of NDT.

Material and Methods

Six of the largest crystals and polished colorless diamonds, including the record breaking 10.02ct (E VS1), 5.11ct (I, SI1) and 4.30ct (D, VS2) were tested at the M&A Gemological Instruments facility in Finland by M. Åström and B. Deljanin, and six other samples (including 2 blue lab-grown diamonds) were tested at the GRS laboratory in Hong Kong by M. Alesandri and Dr. A.Peretti. Both examinations used standard instruments and advanced spectrometers.

The instruments used at M&A Gemological Instruments facility were:

- GemmoRaman-532SG Raman/Photoluminescence spectrometer (536 – 765nm, 0.25nm resolution, TEC-cooled CCD)
- GemmoFtir fourier transform infrared spectrometer (tested with resolution 4cm -1 , range 500-7000cm -1)
- GemmoSphere UV-Vis-NIR spectrometer
- MAGI in-house built deep ultraviolet fluorescence excitation setup with 200nm, 258nm, 360nm and broadband UV- filtering

The instruments used at **GRS laboratory** in Hong Kong were:

- A custom-built UV-VIS-NIR instrument using a quadruple-channel Czerny-Turner spectrometer and two broadband light sources recorded the spectra in the wavelength range from 240 – 1100 nm. This apparatus enabled the detection at liquid-nitrogen temperature (LNT) of very weak absorptions with spectral resolution better than 0.2 nm.
- Photoluminescence (PL) of all samples was analyzed at LNT using a custom-built spectrometer working with 405 nm and 532 nm excitation lasers. PL measurements were performed in a wavelength range from 408 to 1100 nm range (UV-VIS-NIR and PL equipment assembled by Dr. Thomas Hainschwang, GGTL Laboratories).
- Infrared absorption spectra were recorded in the mid-IR range from 400 – 7800 cm^{-1} (resolution 4 cm^{-1}) at room temperature using a Perkin Elmer Spectrum Two FTIR spectrometer equipped with a ZnSe beam splitter.
- An ED-XRF instrument (FISCHERSCOPE XANDPP) was used to examine the trace elements within the diamonds.

Fig. 3a: NDT synthetic grown diamonds are synthesized and polished at their facility in St. Petersburg. In the picture is a 5.13 ct pear shaped lab-grown diamond on the polishing wheel at NDT in-house cutting factory. Photo by Branko Deljanin. Fig. 3b: icture shows a HPHT-grown cushion shaped diamond (4.30ct, D color, VS2) by NDT. Photo by NDT. Fig. 3c: Same HPHT grown diamond as in Fig. 3b, after exposure to pinpoint-light shows bluish orange luminescence and orange phosphorescence in darkened room. Photo by Mikko Åström.

Fig. 4a: The faceted 10.02ct (E, VS1) synthetic diamond by NDT is according to our knowledge the new world record for a gem-quality faceted synthetic diamond in terms of size.

Fig. 4b: Crystal 4.41ct colorless. Fig. 4c: Polished 1.73ct, D, VVS1.

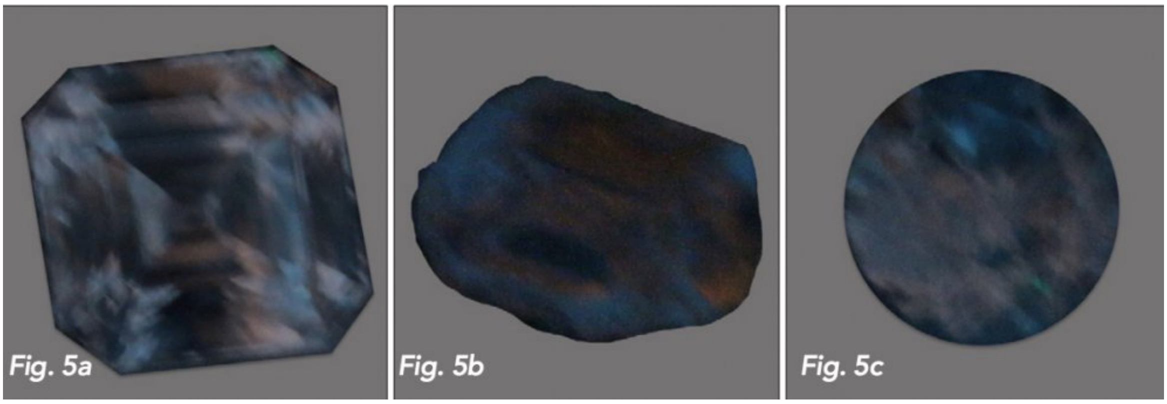

Fig. 5a-c: Photo of the same NDT diamonds as in Fig. 4a-c but under a UV light. The diamonds show a mixture of blue and orange phosphorescence in a darkened room after exposure to a strong UV light. Photo by Mikko Åström.

Examination with Microscope and Polarized Light

Most NDT-grown diamonds studied exhibit high (Fig. 4a) to medium (Fig. 3b) clarity (VVS1-SI1). Based on this clarity, for the majority of stones it is not possible to distinguish them from similarly colored natural diamonds by using just a loupe or microscope. Only a few lower clarity stones (especially crystals) had metallic inclusions that are typical for HPHT grown diamonds (Ref. 7). As expected, none of the samples exhibited any pattern when examined under cross polarized filters. This is likely due to a relatively short growth period (Ref. 6).

UV Fluorescence and Phosphorescence

As found with other HPHT-grown diamonds on the market, the SWUV (254nm) fluorescence of NDT-grown diamonds were greenish blue and stronger than LWUV (365nm) in half of the samples (Ref. 7). An interesting new feature discovered in approximately half of the samples is a weak-medium bluish orange fluorescence and phosphorescence (Fig. 3c and Fig. 5). This phenomena were not only present when excited by UV lamp but also when exposed to a strong pinpoint light (e.g. LED light). These samples were part of NDT's latest production.

Infrared Spectroscopy

All colorless lab-grown diamonds tested were type IIa with no presence of nitrogen and a small amount of boron (Fig. 6). Two blue lab-grown diamonds (Fig. 7a) were type IIb (Fig. 7b). They contained boron in higher amounts than found in natural type IIb blue diamonds (Ref. 5).

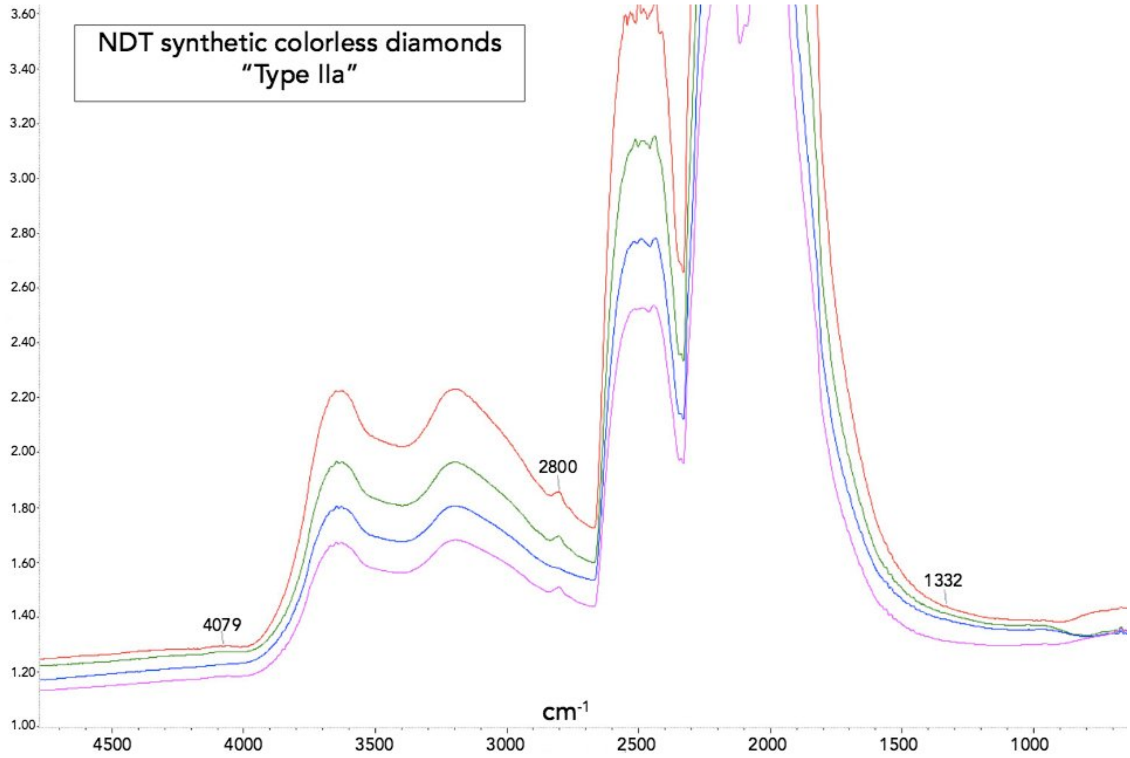

Fig. 6: Infrared spectra (absorbance) of 10.02ct E, VS1 (in red), 5.11ct I, SI1 (in blue), 4.30ct D, VS2 (in green) and 1.73ct D, VVS1 (in purple) that are type IIa (no nitrogen detected) with traces of boron (2800cm-1). (See Ref. 1, 2 and 3).

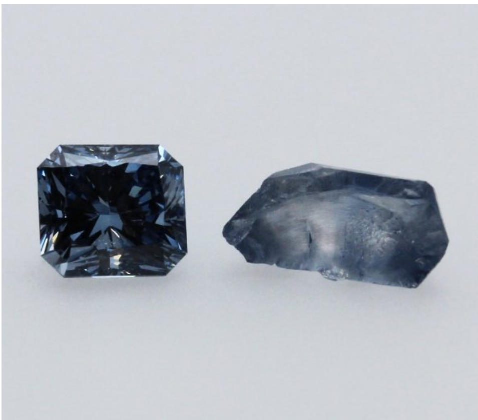

Fig. 7a: Two synthetic fancy blue diamonds, produced by HPHT (NDT). The left is a faceted synthetic of 0.56ct (VS2 clarity) and on the right a crystal of 0.67ct. Both are type IIb synthetic diamonds (both stones part of GRS reference collection). Photo by Matthias Alessandri.

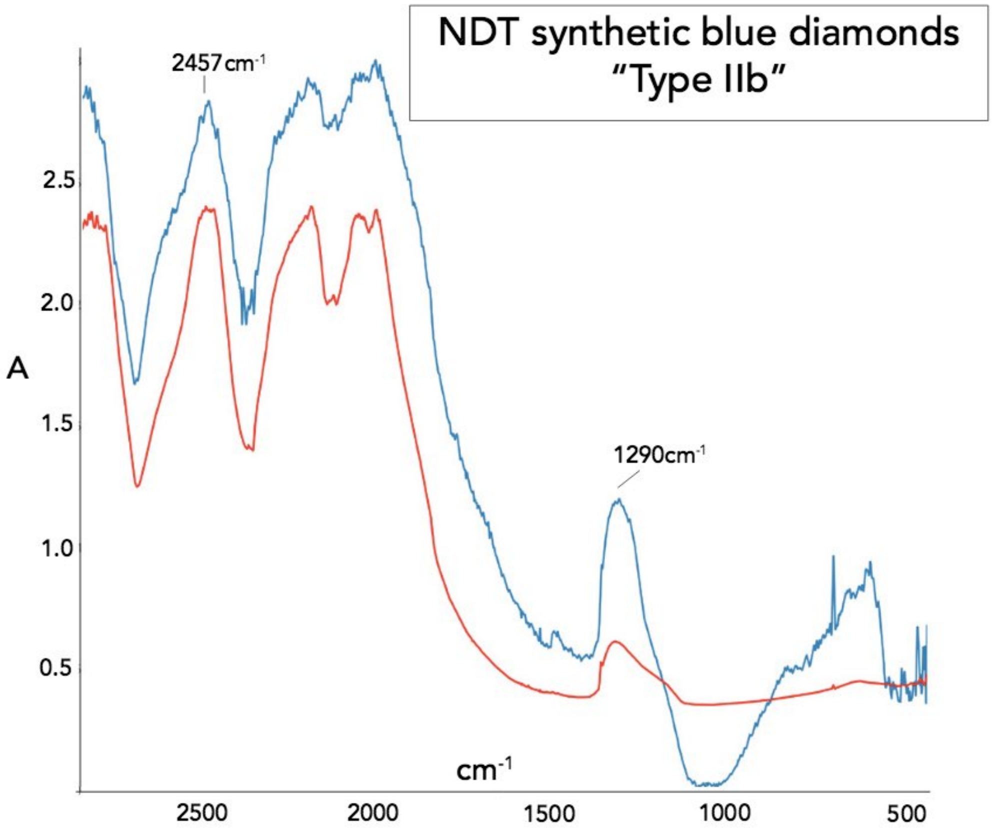

Fig. 7b: FTIR spectra (zoomed range 400 – 2800cm-1) of synthetic type IIb blue NDT-grown diamonds polished 0.561ct (in red) and rough 0.672ct (in blue). Boron related peaks at 2457cm-1 and 1290cm-1.

Photoluminescence Spectroscopy

Research tests at the GRS facility in Hong Kong confirmed preliminary results (Fig. 8a and Fig. 8b) by analysing additional 6 samples with repeated measurements and under various measuring conditions (no Ni-related peaks were found). All samples investigated by GRS remain in their reference collection for further investigation. Additional spectroscopic information was collected from these lab-grown diamonds, exhibiting unusual fluorescence and phosphorescence behaviour (Fig. 7b).

NV0 (575nm) and NV-(637nm) and Si-V0 (737nm) centres are present in approximately half of the samples. Si-V0 defect is found in CVD-grown diamonds and are extremely rare in natural diamonds and rare in HPHT-grown diamonds. Nickel was not detected in our samples and if is present, then it is probably present at low concentration below sensitivity of our PL spectrometers (using 405nm and 532nm lasers at GRS or 532nm laser at M&A Gemological Instruments). Further research is required to determine if NV centres (Fig. 8a) in NDT-grown diamonds are the result of additional HPHT treatment (used historically by other companies to improve the color of natural and synthetic diamonds) or is caused by some other phenomenon.

In our opinion, the orange color luminescence is most probably caused by NV centres, eventually in combination with other defects. This is most likely a characteristic of the very large stones and is caused by the long lasting growth period when stones were exposed to high pressures and temperatures.

ED-XRF spectroscopy

The only detected element in all samples was iron (Fe). Titanium (Ti) was only detected in samples where the seed is still exposed. We did not detect any manganese (Mn), cobalt (Co) or nickel (Ni) that are traditionally used as catalysts in the HPHT process. This can be explained because most of the samples tested were of high clarity (VS2 and better) and therefore without metallic inclusions.

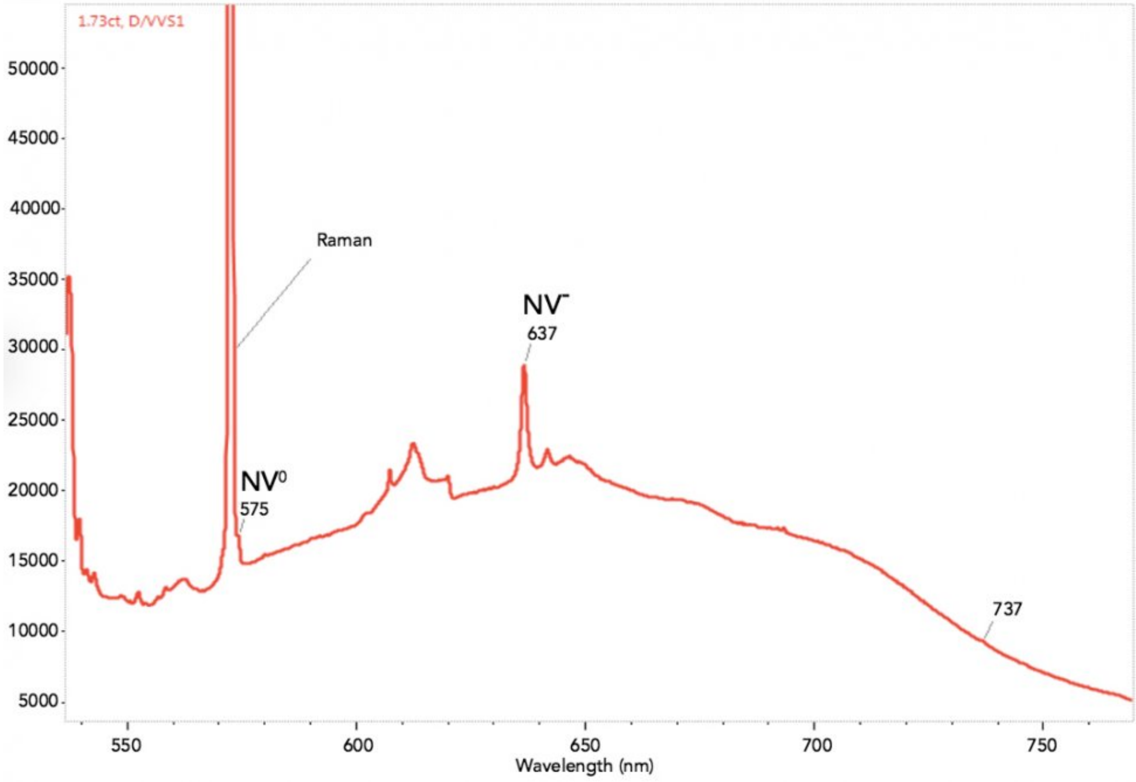

Fig. 8a: Photoluminescence spectra of a synthetic diamond from NDT (1.73ct) showing luminescence when excited with a 532nm laser by M&A Gemological Instruments (details in Fig. 8b) at liquid nitrogen temperatures. The NDT diamond shows a medium NV0 (575nm) and a strong NV- (637nm) center, most probably responsible for the orange luminescence. Note: Very small Si-V0 center at 737nm.

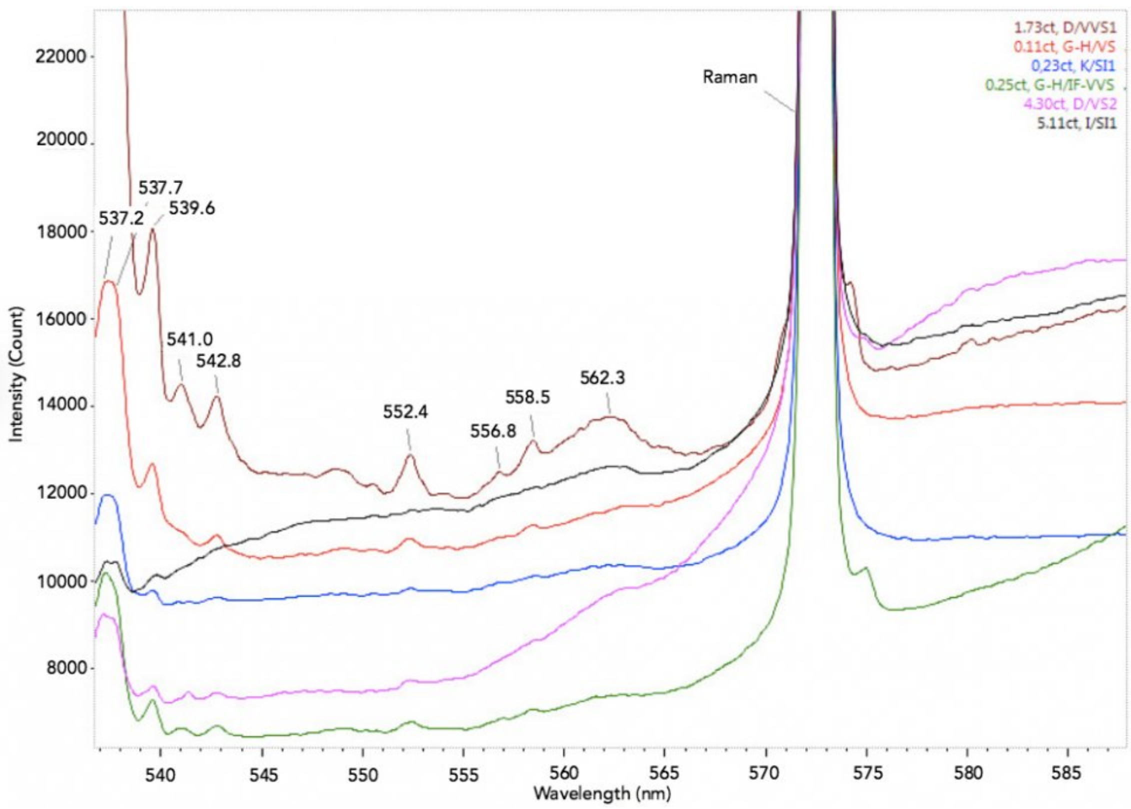

Fig. 8b: Photoluminescence spectra using same method as described in Fig. 8a (Ref. 4) showing 6 different NDT synthetic diamonds (note the intensity scale is strongly zoomed in comparison to Fig. 8a). There are many new defects of unknown origin from 537nm to 562nm that seem to be unique for NDT-grown diamonds.

Fig. 9: The faceted 10.02 ct gem-quality E color and VS1 synthetic diamond is featured here with CGL-GRS's Branko Deljanin. The dimensions are 12.49 x 12.43 x 7.37 mm. The clarity of VS1 and the color of E is combined with a very good polish and symmetry and an excellent cut (reminiscent of Assher cut). The NDT's "landmark" synthetic diamond is believed to be one of the largest of its kind in the world, and according to our best knowledge, sets the new world record for a faceted synthetic diamond of this quality. The stone was available at MGJ Conference 2015 in Athens (Greece). Photo by John Chapman.

Summary

Diamonds grown by New Diamond Technology (NDT) are the largest colorless synthetic diamonds reported to date (Fig. 10), with weights up to 60ct crystals and 10.02 ct faceted (Fig. 9). Most samples are of high color grades (colorless and near-colorless, D-J) and high to medium clarity, but may contain metallic inclusions formed from metal/catalyst. Natural and CVD synthetic diamonds show strong Ia or weak IIa birefringence patterns as they are more heavily strained than HPHT synthetic diamonds. HPHT synthetic diamonds do not show birefringence under cross polarized filters (Ref. 6 and 7). Our colorless samples were type IIa with some boron (weak type IIb) or blue with high B content. Their natural counterparts, colorless type IIa diamonds are highly transparent and considered the worlds most valuable diamonds, usually appearing in large sizes (5ct – 100ct+) and in high colors (D-E) and clarities (IF-VVS). They are also known as type "Golconda" diamonds because legendary the "best" stones are historically believed to originate from the Golconda province in India. All synthetic diamonds fluoresced and phosphoresced blue under SWUV light. In addition, half of them showed orange color when exposed to a UV lamp, with stronger responses to short-wave than long-wave excitation and lasting phosphorescence. Natural diamonds show a stronger reaction (usually blue) under LWUV than SWUV light. Phosphorescence in natural diamonds is very rare and almost exclusively found in type IIb and Chameleon diamonds, but without blue/orange colour. Therefore the synthetic diamonds can be distinguished based on their phosphorescence, particularly from their natural type IIa counterparts.

Photoluminescence spectra revealed NV centres and in combination with other defects could be responsible for orange luminescence. Boron impurities are responsible for the blue phosphorescence in HPHT-grown diamonds but further research is needed to determine what is causing the orange phosphorescence. The exact nature of the phosphorescence processes is still not fully understood, but likely involves complex steps of charge carrier trapping and de-trapping (Ref. 5). Orange phosphorescence could come from the recombination at donor-acceptor pair. In case of NDT-grown diamonds with orange phosphorescence, the donor may be the NV center or some others. Further research is underway to also understand role of boron and other impurities present.

Using a combination of standard gemological and spectroscopic tests, it is possible to identify all New Diamond Technology (NDT) colorless and blue HPHT-grown diamonds. Gem-quality synthetic diamonds from NDT can therefore be distinguished from natural diamonds of similar quality.

One of the authors (BD) has had the opportunity to study HPHT-grown and CVD-grown samples from all producers of gem-quality synthetic diamonds in the last 15 years and this is first time that HPHT-grown diamonds are exhibiting an orange luminescence (usually a characteristic of CVD-grown colorless diamonds) under SWUV light. The most surprising phenomena is, that even visible pinpoint light triggers this orange reaction. This specific type of fluorescence/ phosphorescence offers the possibility for a straightforward and simple "screening test" for most larger diamonds created by NDT (Russia).

Acknowledgements

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We also appreciate that the producers of synthetic diamonds **New Diamond Technologies** (Russia), **Taidiam** (Taiwan) and **Volldstaedt** (Germany) participated in a round table discussion on synthetic diamonds and shared the information on technology of growing diamonds and identification techniques with other labs and conference delegates. A special thanks goes to **Nikolai Khikhinashvili** (NDT) who brought the largest 10.02ct lab-grow diamond to MGJ Conference 2015 and organized the visit to the facility in Russia, as well as to **Dr. Alexander Kolyadin** (NDT) for useful technical information and providing samples for this study. We appreciate the help of **Bill Vermeulen**, CGL-GRS Canada for editing the article. Many thanks to **John Chapman** for his assistance and contribution in photography. This report would not have been possible with out the scientific input from **Dr. Andrey Katrusha**, project research advisor for New Diamond Technology (NDT).

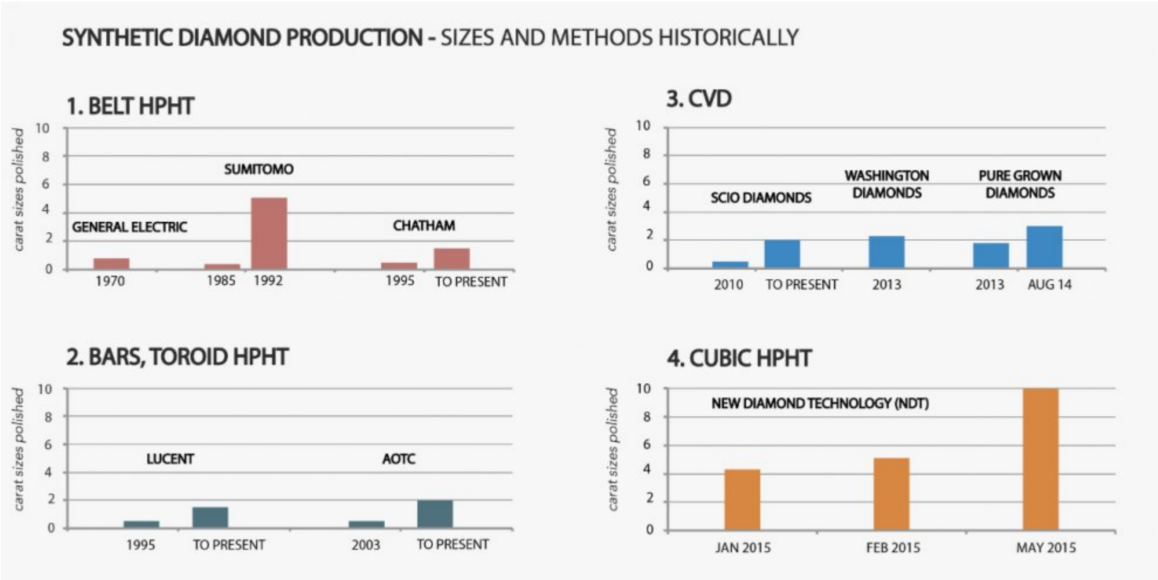

Fig. 10: The bar diagrams illustrate the evolution of synthetic diamond production of different methods and companies in time. The maximum size for a commercially relevant faceted diamond of gem quality produced is shown. As it can be seen, the preferred methods changed in time. The Belt HPHT method is used initially (with record 34.80ct crystal by De Beers not shown, but 5.09ct crystal from Sumitomo shown), followed by BARS and Toroid HPHT, CVD and finally by Cubic HPHT method. Cubic HPHT produced the largest faceted synthetic diamonds so far. Various companies are involved in the production of synthetic diamonds world-wide (details see table 1). The critical boundary of over 10ct faceted gem quality diamond is expected to be broken again soon (see text).

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