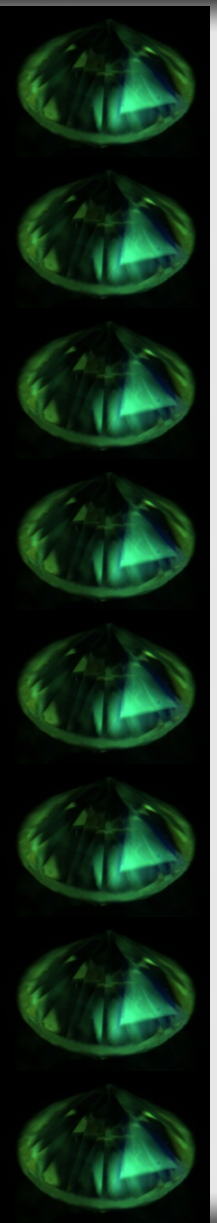

The Challenge of Identifying Recent Generations of Melee-Sized Synthetic Diamonds

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Gemology Workshop, University of Geneva, 2014

Growth Methods of Synthetic Gem Diamonds

1) HPHT (High Pressure High Temperature) growth:

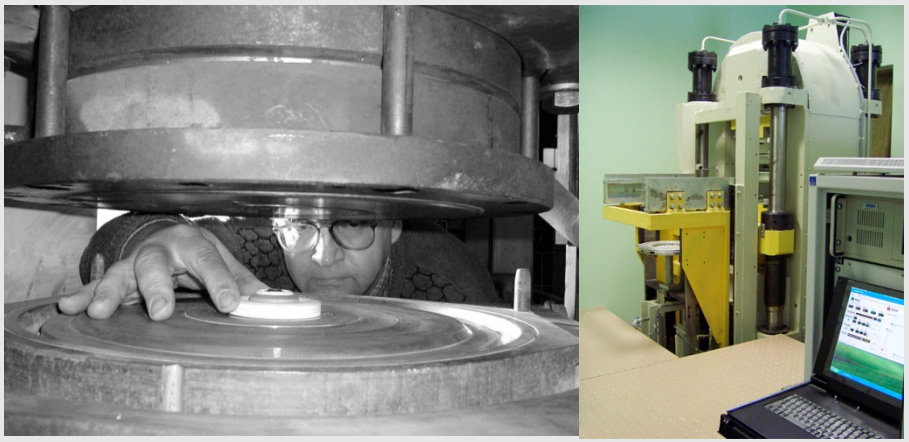
Growth in HPHT Press under conditions of 1300 – 1800°C and 50 to 70 kBar; first successful growth in 1953 by Asea - today ABB -, Sweden

2) CVD (Chemical Vapor Deposition):

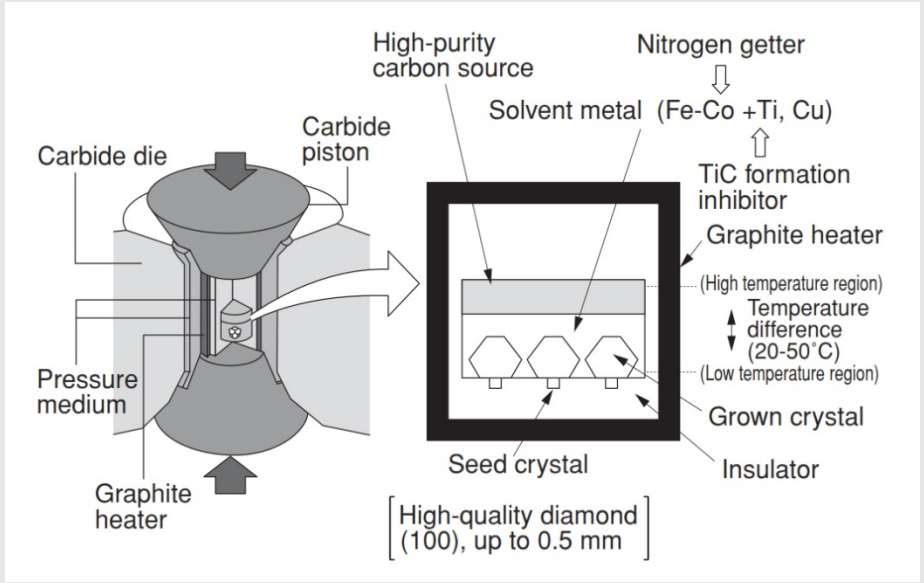
Growth using a CVD reactor, at 700 to 1000°C at 10-200 Torr; first successful growth 1952 by the Union Carbide Corporation, USA

HPHT Growth

- Seed used for growth of large crystals
- Catalyst used for efficient growth, in commercial growth usually FeCo or FeNi since they have a low melting point
- Getter metals (e.g. Al, Ti, Zr) for „N free" diamonds
- Temperature gradient method

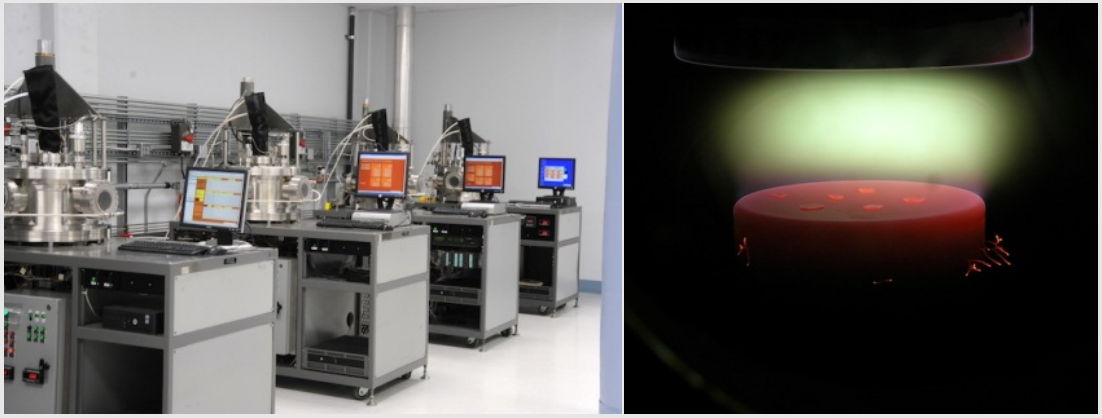


Toroid press

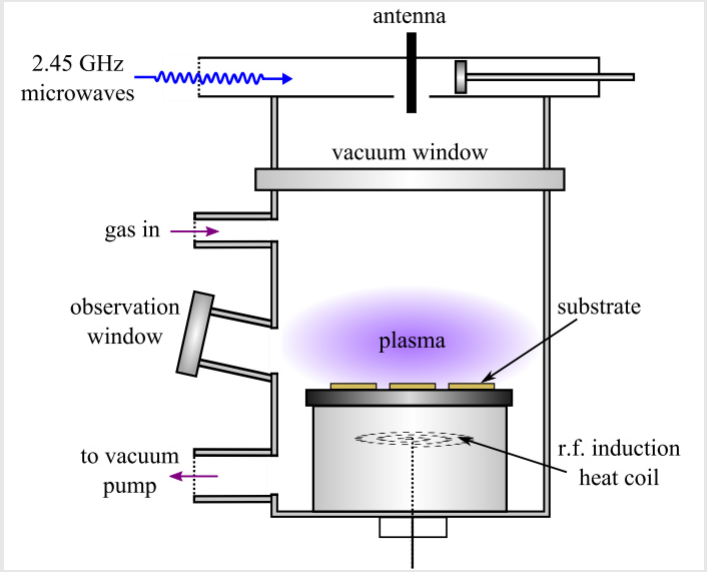


CVD Growth

- Diamond substrate (seed crystal) used for growth of large single crystals
- Diamond is deposed on seed when a precursor gas, typically CH_4, is passed through a plasma at 10-200 Torr and 700 -1000°C.
- When silicon wafer is used as seed → polycrystalline diamond



CVD reactors (left) and growth of diamond on seed plates (right) © Scio Diamonds

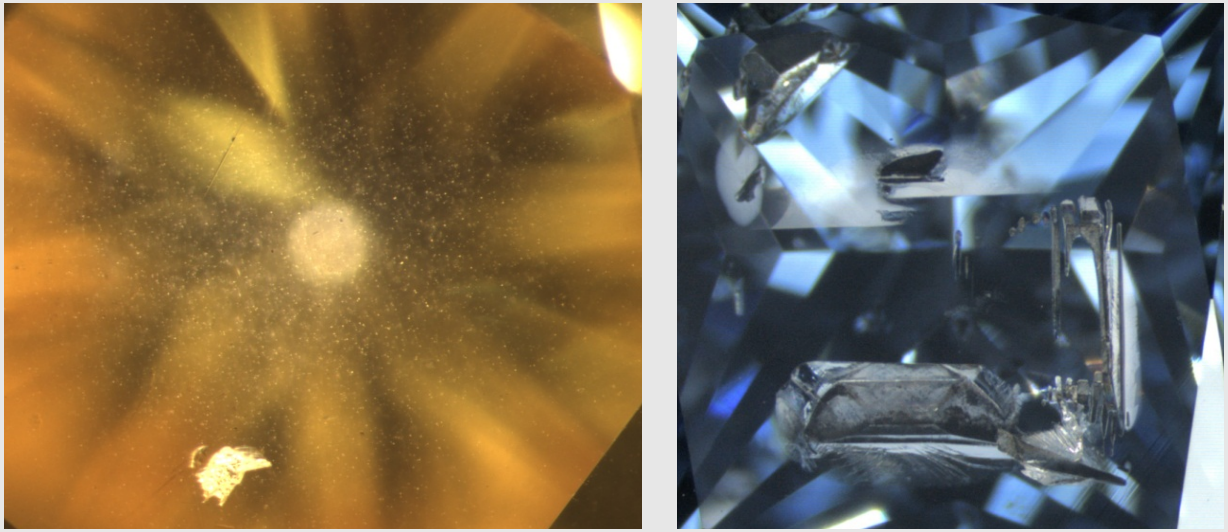


Characteristics of HPHT Grown Synthetic Diamonds

- HPHT synthetic crystals typically cubo-octahedral habit; as-grown «colorless», yellow to orange and blue, treated green and pink to red.
- Natural crystals typically octahedral or cuboid growth; practically all colors of the rainbow known in nature.

Characteristics of HPHT Grown Synthetic Diamonds

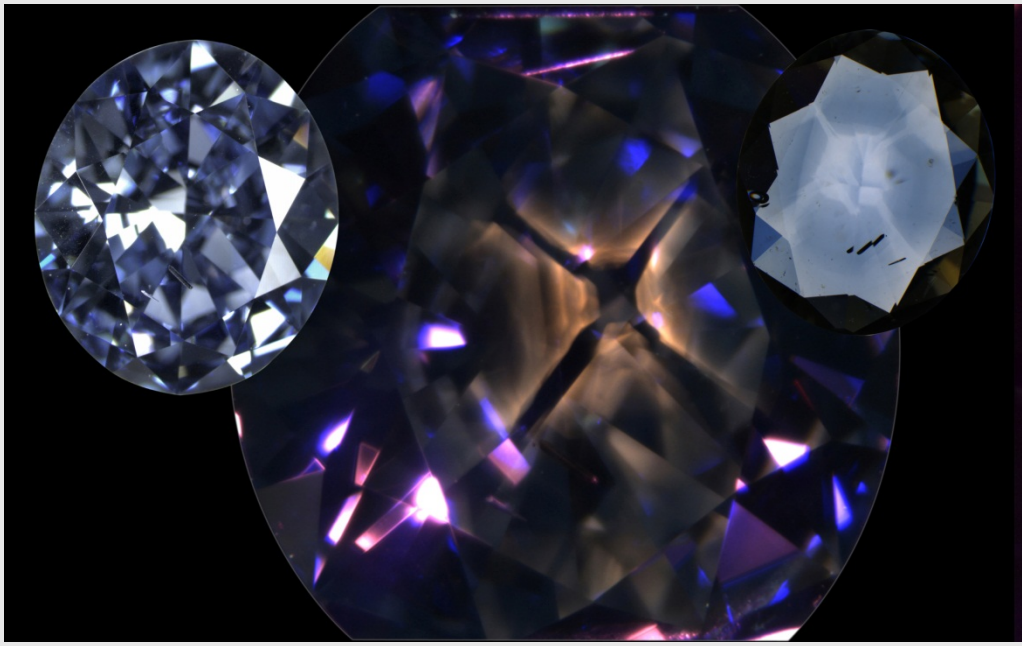
- Inclusions: generally pinpoints and/or metallic residues from the metallic catalyst

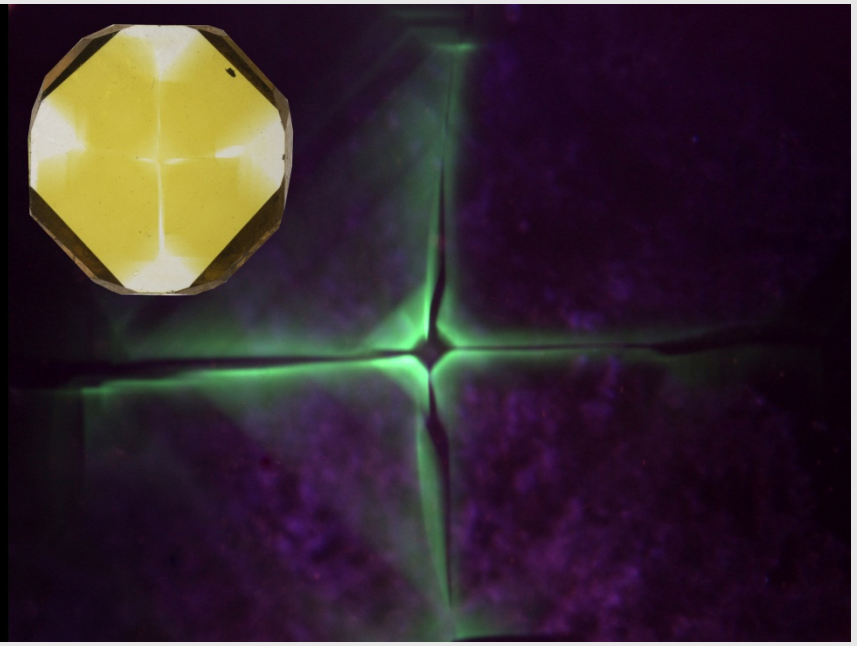


Pinpoint inclusions (left) and metalic resides (right) in synthetic diamond.

Characteristics of HPHT Grown Synthetic Diamonds

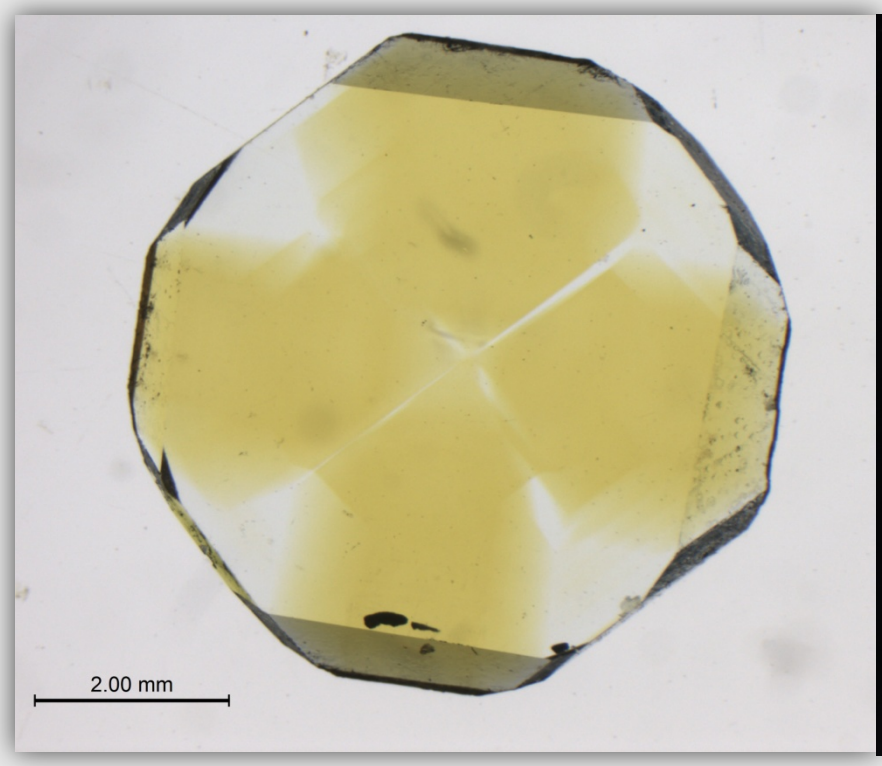
- HPHT synthetics show often distinct sector zoning separating the different growth sectors, typically cube and octahedral
- Typical sector-distributed luminescence in type I and type IIb synthetic diamond; IIa diamonds show it weaker, but generally exhibit phosphorescence (low boron content)

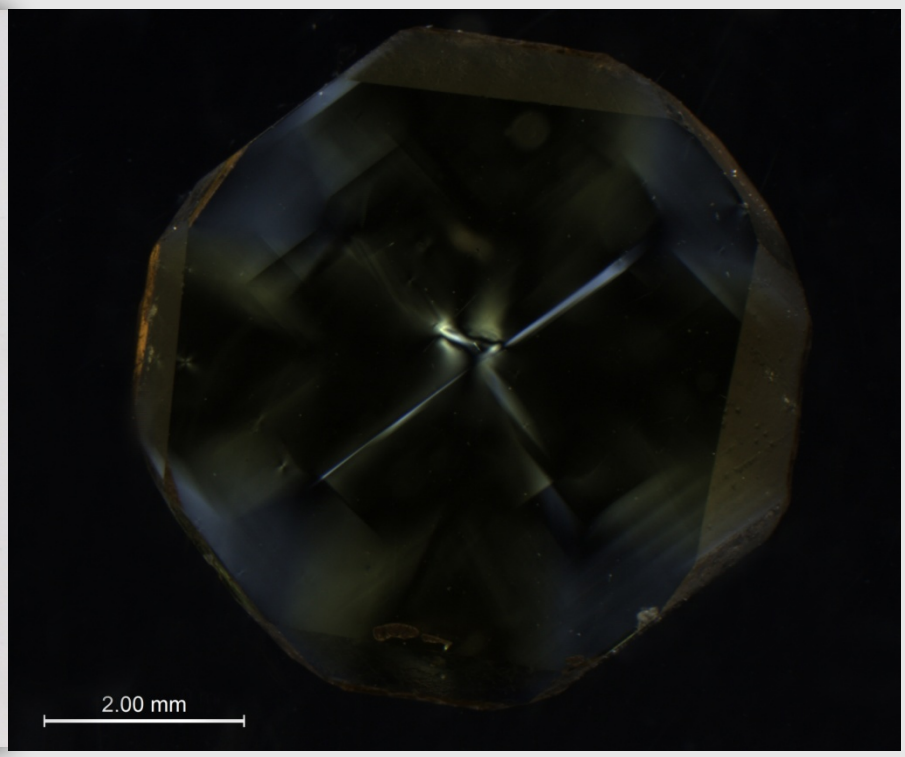




Characteristics of HPHT Grown Synthetic Diamonds

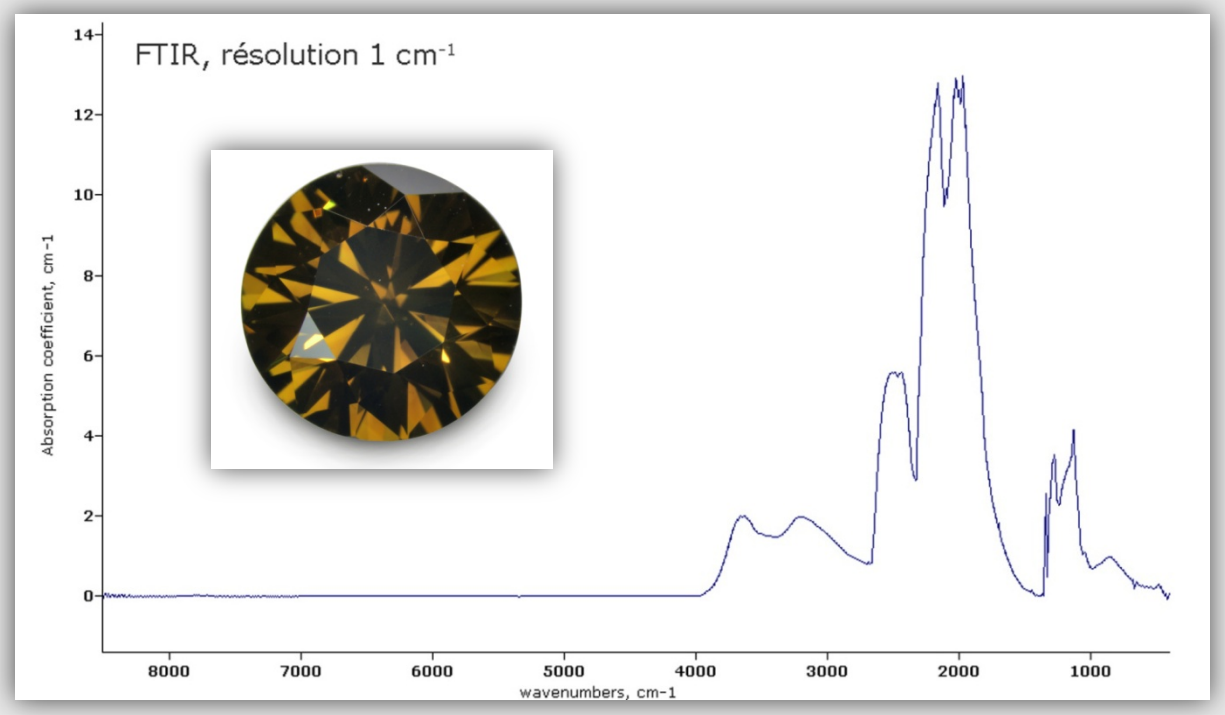
- HPHT synthetic crystals often show very little or no strain when viewed under crossed polarizing filters; strain is usually limited to growth sector induced strain.





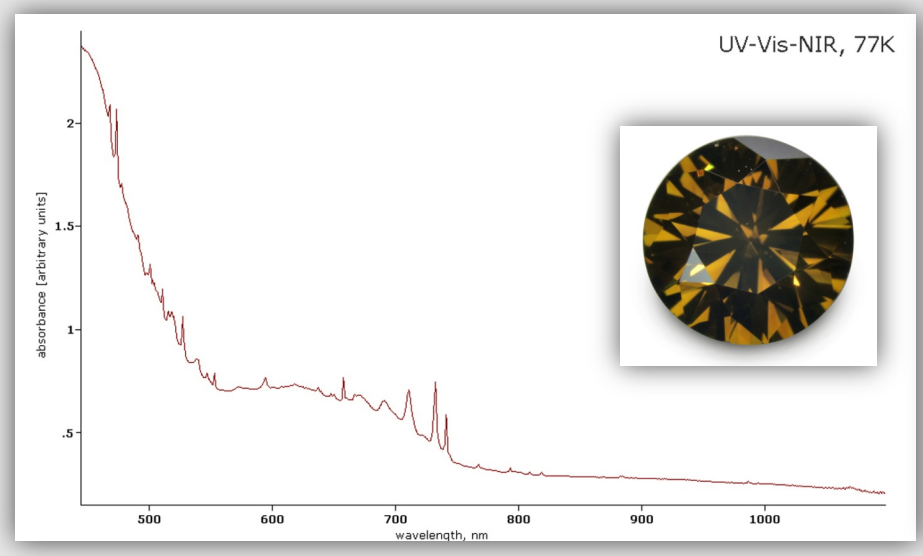
Spectroscopic Properties of HPHT Grown Synthetic Diamonds

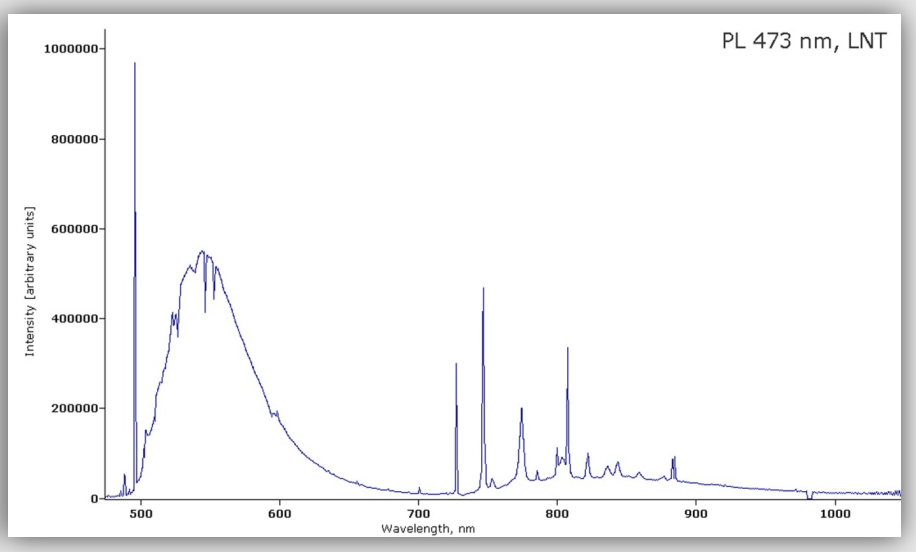
- As-grown HPHT synthetic incorporate nitrogen mainly in form of C centers and minor A centers → yellow color
- By the use of a „getter" → type IIa → „colorless"
- By boron doping → type IIb → blue



Spectroscopic Properties of HPHT Grown Synthetic Diamonds

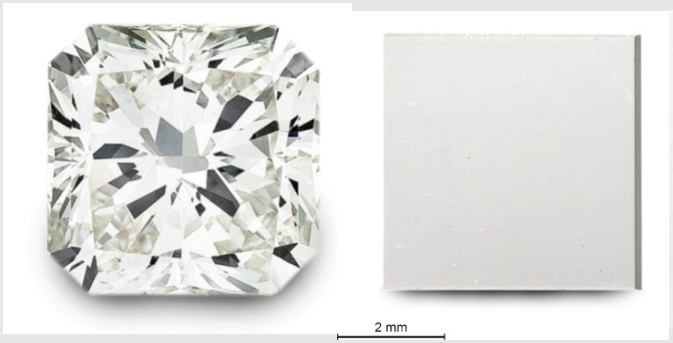
- Fe-Ni HPHT synthetic often exhibit some Ni related defects that can be detected either by UV-Vis-NIR or photoluminescence spectroscopy





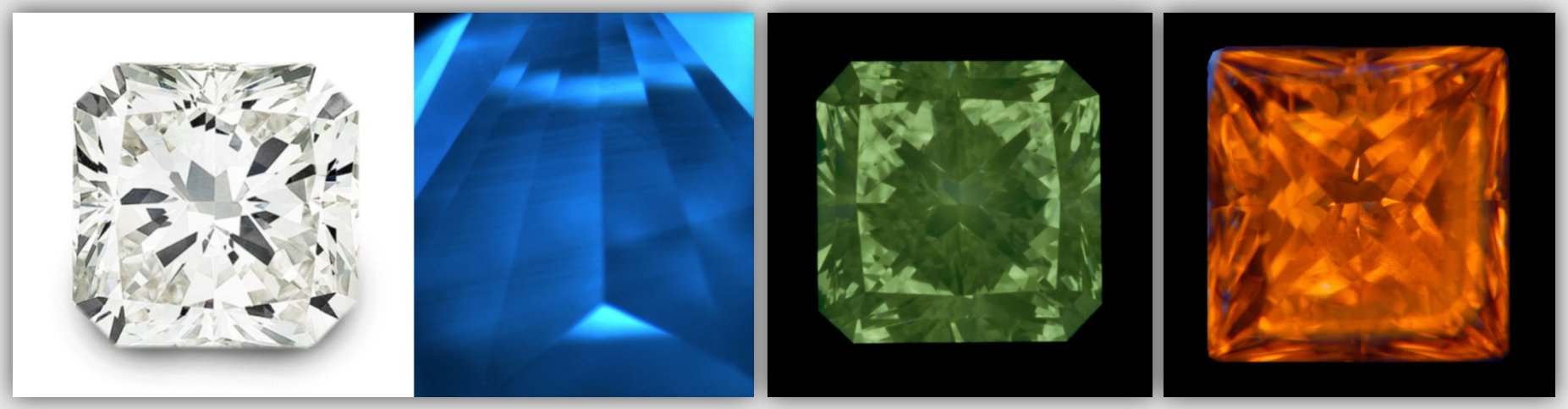
Characteristics of CVD Grown Synthetic Diamonds

- CVD synthetic crystals have typically very dominant cube faces.
- They are type IIa («N free» per FTIR), as grown «colorless» to brown, faster growth rates cause browner colors. Green or pink via treatment.
- HPHT treatment used to eliminate the brown coloration.
- Commercially available HPHT treated good are generally F to J color and IF to VS clarity. Inclusions are pinpoints or fissures.



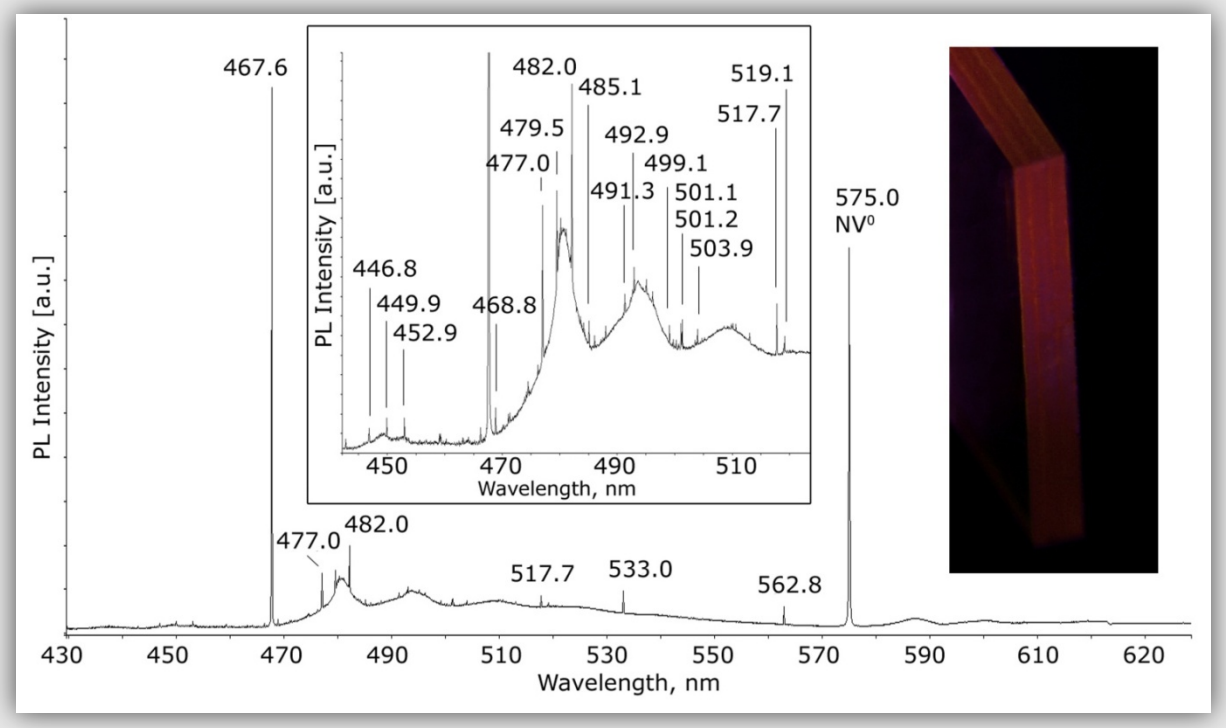
Characteristics of CVD Grown Synthetic Diamonds

- As-grown CVD exhibits NV center related orange to red PL
- HPHT treated CVD exhibits green to blue PL under LW and green PL under SW, with strong green phosphorescence.



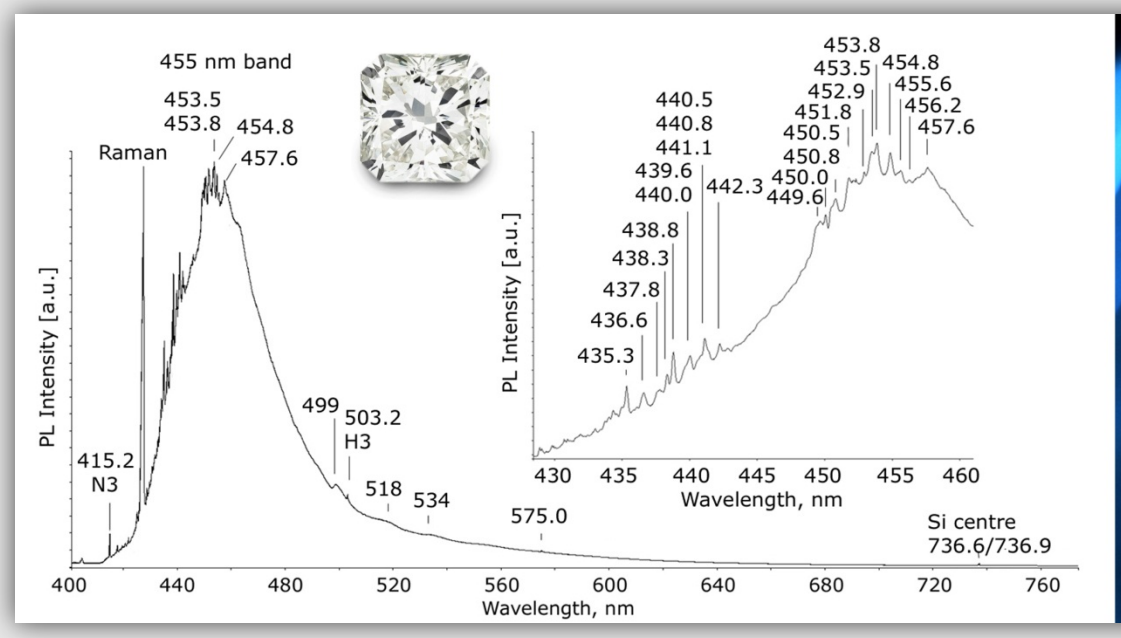
Spectroscopic Properties of as-grown CVD Synthetic Diamonds

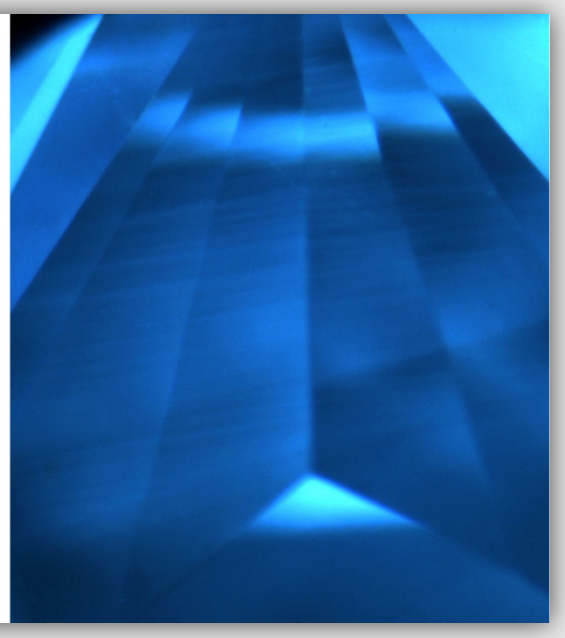
- As-grown CVD diamonds exhibit orange to red PL caused by the NV centers. Such samples can have very complex PL spectra with a large amount of extremely sharp emissions (FWHM as narrow as 0.05 nm).



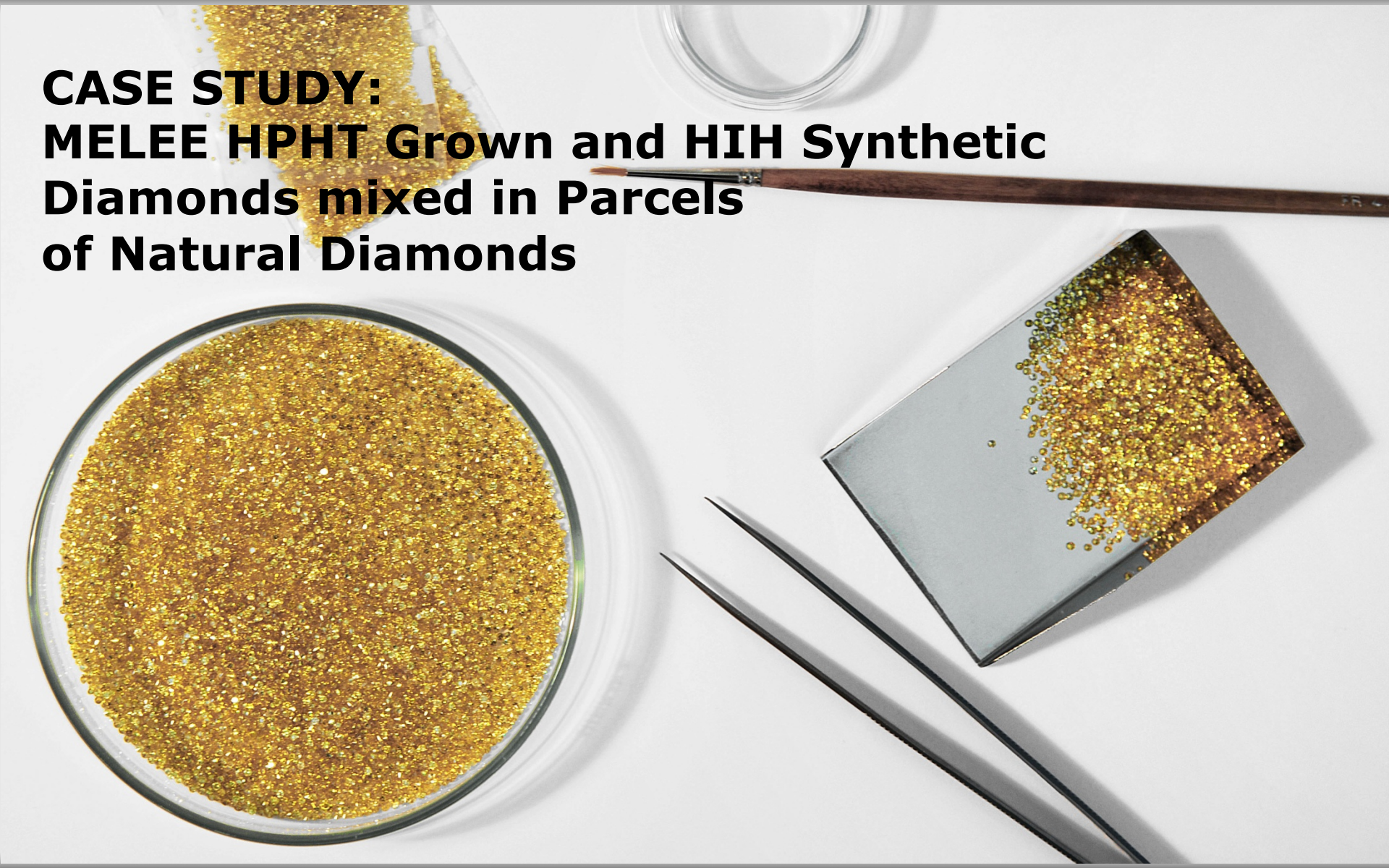
Spectroscopic Properties of HPHT treated CVD Grown Synthetic Diamonds

- Luminescence changes from NV center related to a broad band emission at approx. 455 nm (greenish blue).
- NV and H3 centers are present, but minor.
- Si center usually detected.





CASE STUDY:
MELEE HPHT Grown and HIH Synthetic Diamonds mixed in Parcels of Natural Diamonds



MELEE HPHT Grown Synthetic Diamonds

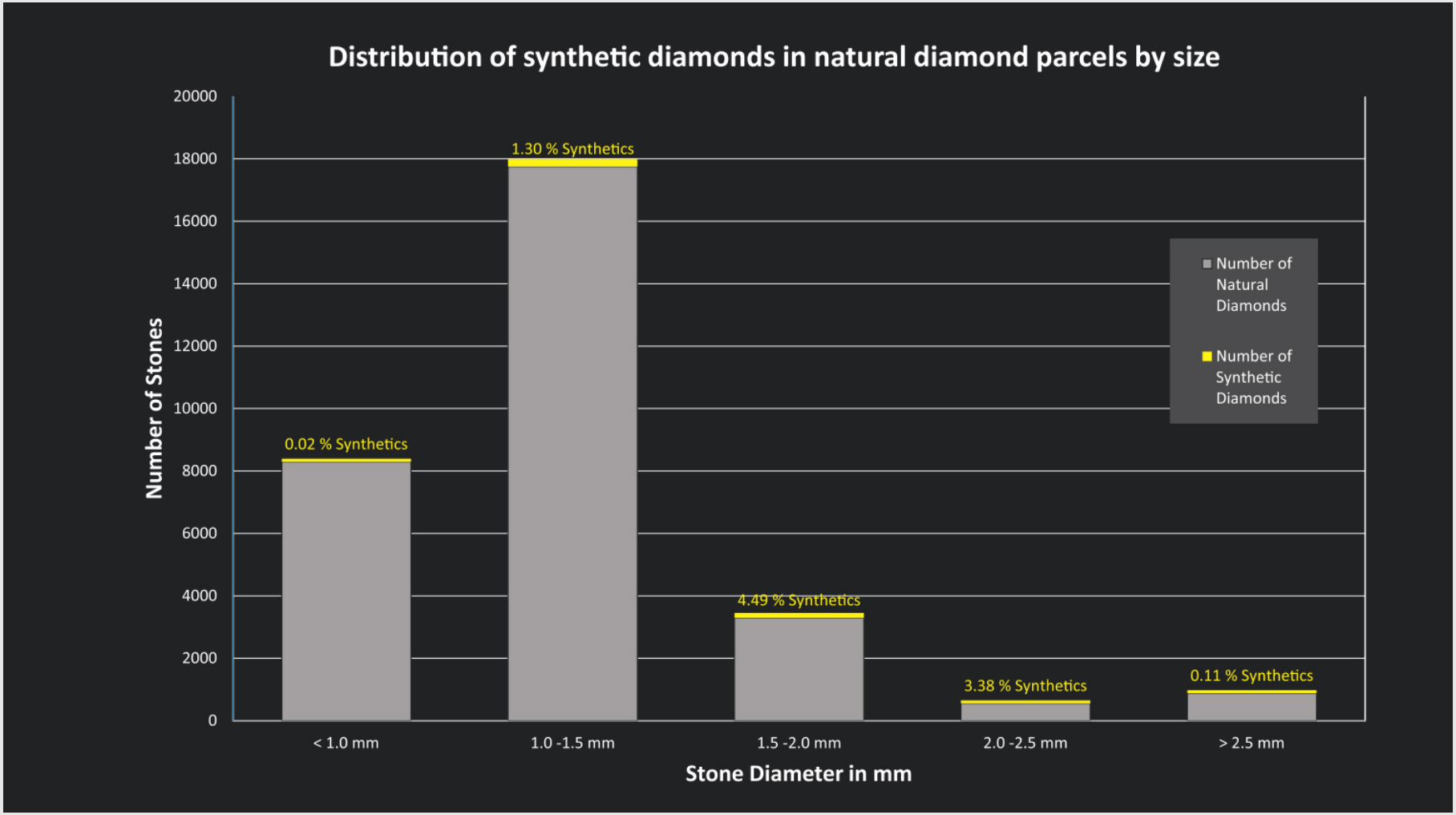
- Synthetic yellow Diamonds of <3.7 mm (Melee) are found mixed within parcels of natural diamonds

- In ALL parcels of „vivid yellow" melee analyzed from 2010 to 2012 we have found synthetic diamonds in variable percentages

- Even in parcels of fancy light yellow to fancy yellow we found synthetic diamonds

- Testing procedure highly complex and specialized

MELEE HPHT Grown Synthetic Diamonds

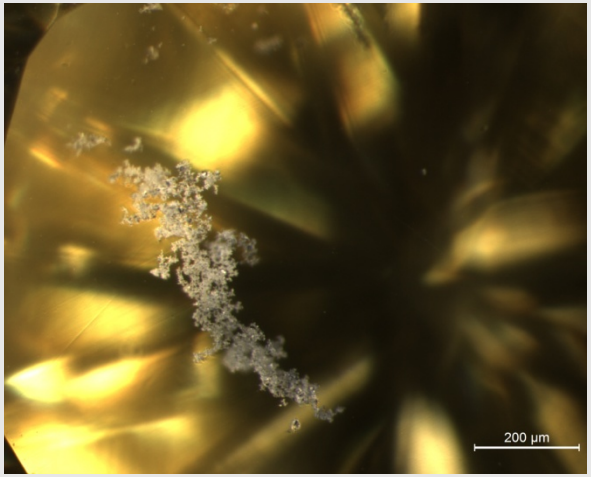


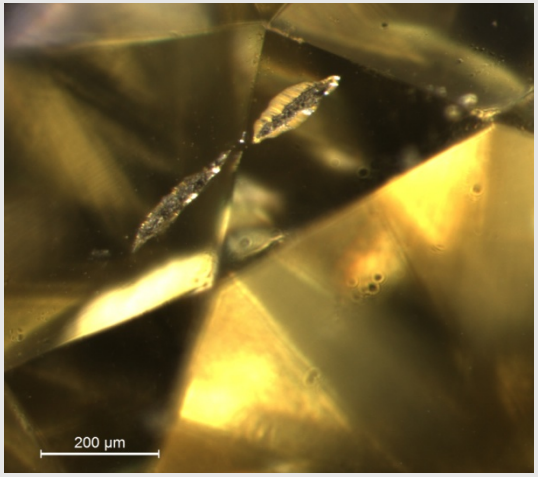
MELEE HPHT Grown Synthetic Diamonds

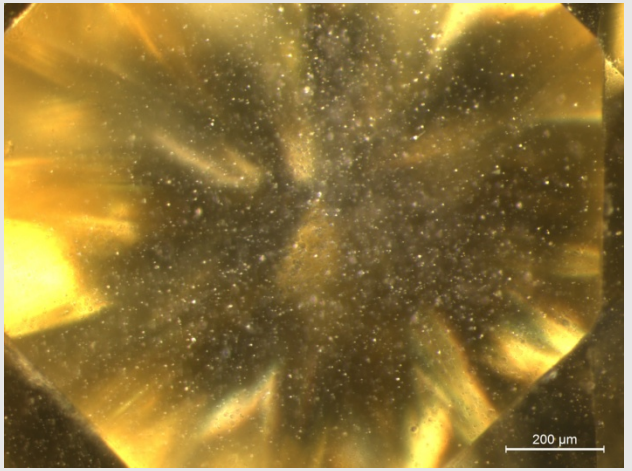
- Usually RBC intense to vivid yellow, mostly found in sizes 1.5 to 2.5 mm, mostly high clarities (VVS to VS)

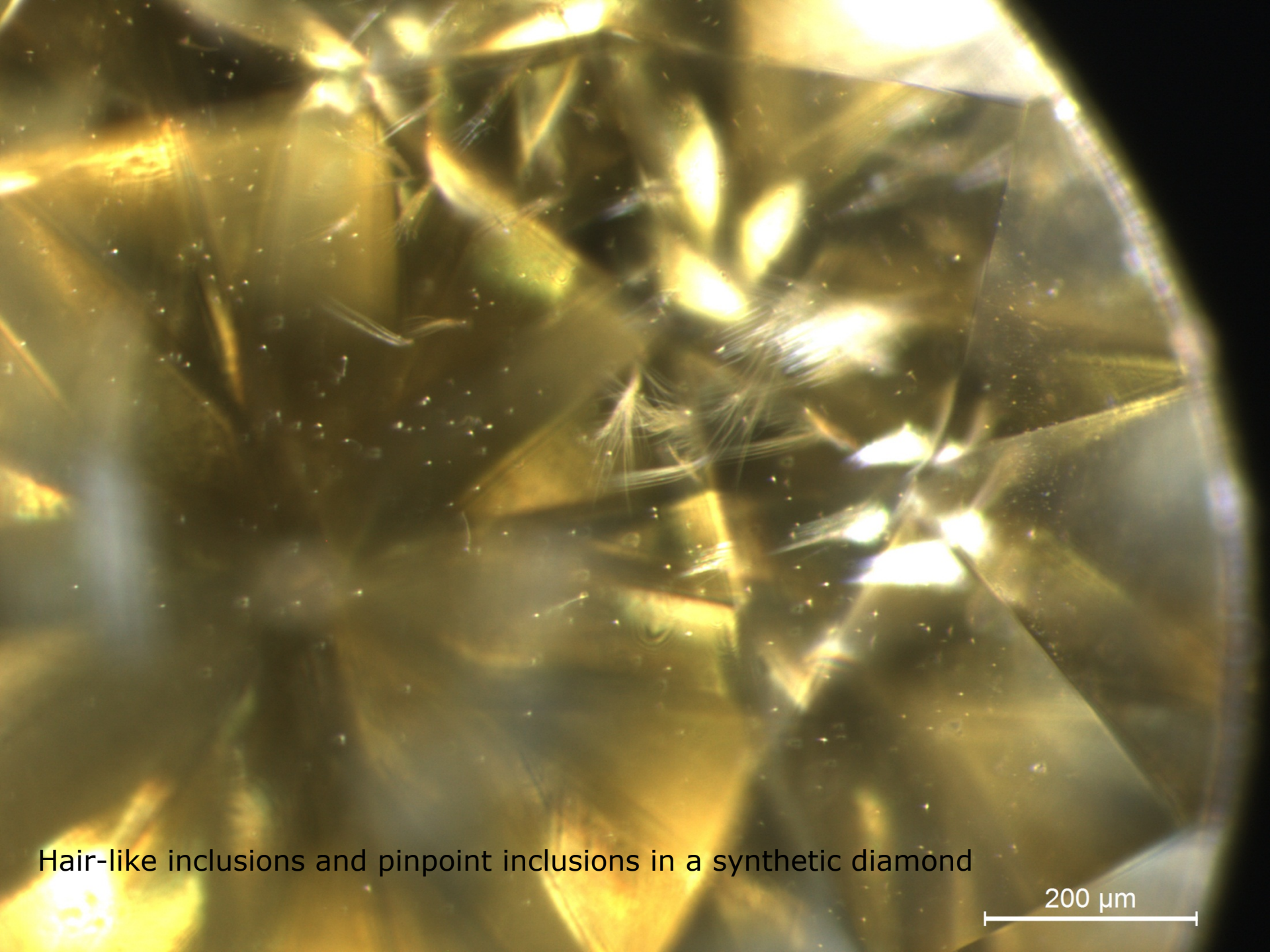
MELEE HPHT Grown Synthetic Diamonds

- Frequently tiny pinpoint inclusions, sometimes denser clouds
- Very rarely metallic inclusions
- Ash or snow-like appearing inclusions can occur
- Very rarely hair-like inclusions were observed





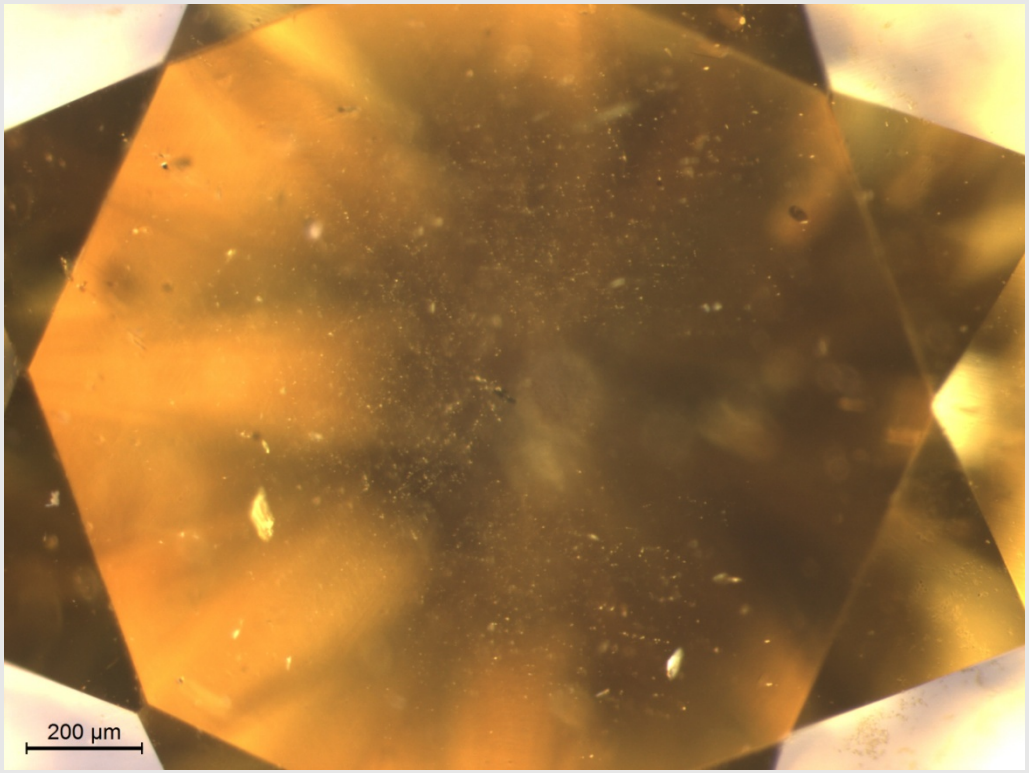


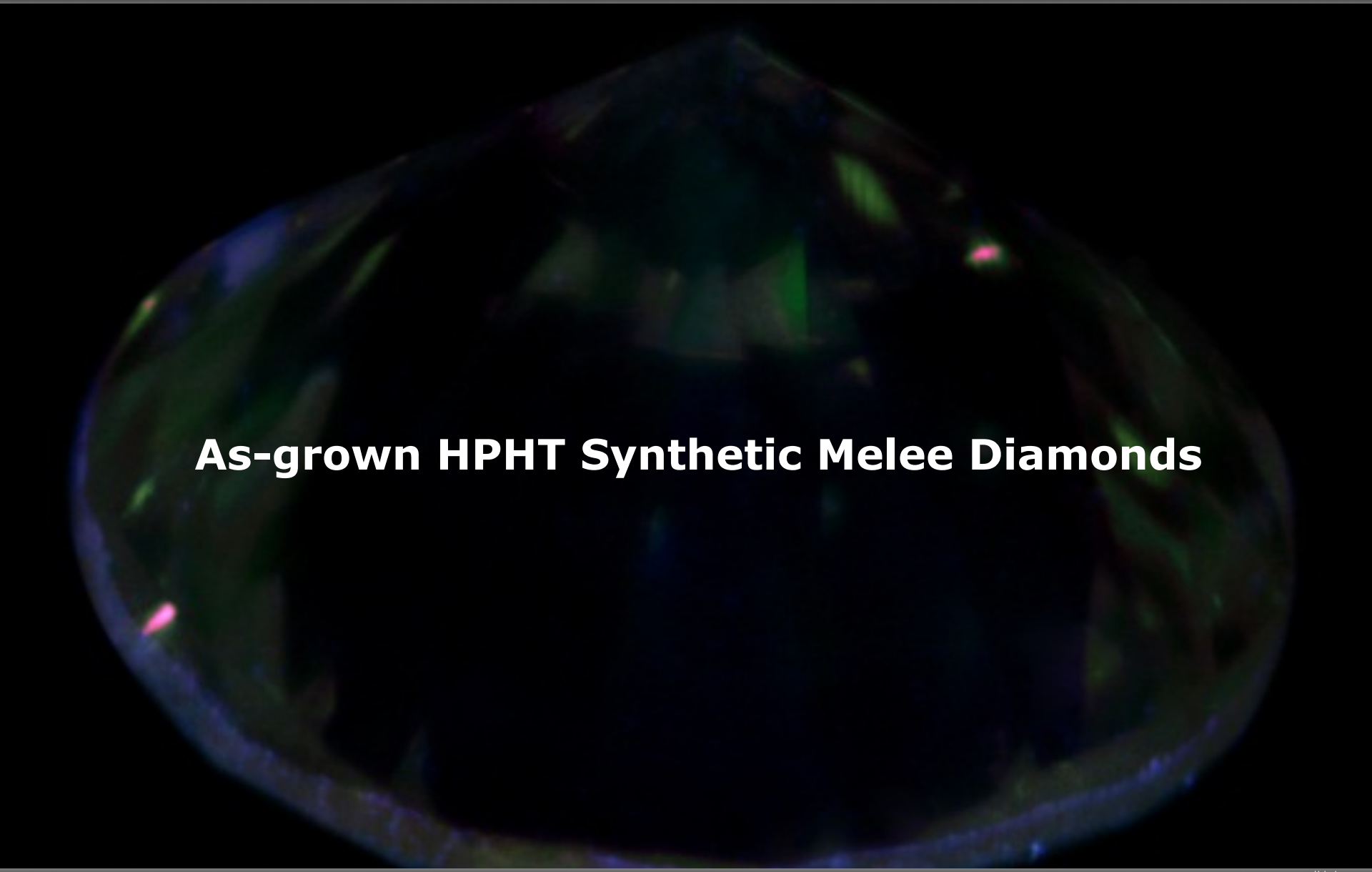


Hair-like inclusions and pinpoint inclusions in a synthetic diamond

„Natural Counterpart“

- Natural diamonds, especially type Ib and mixed type IaA/Ib diamonds do almost always contain pinpoint inclusions, that may appear very similar to the ones in synthetics

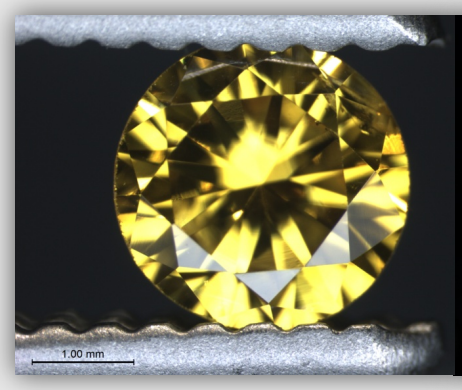




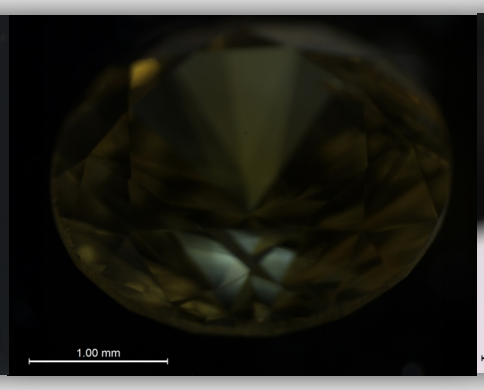
As-grown HPHT Synthetic Melee Diamonds

As-Grown MELEE HPHT Synthetic Diamonds

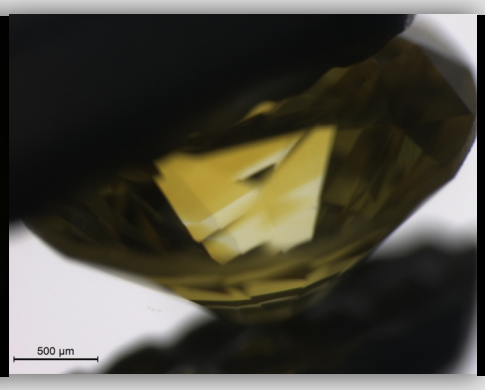
- Color zoning is frequent but not prominent, and sectors are often not clearly distinguishable.
- Strain under polarizing filters is often practically absent, and if present then only sector-dependant.
- Luminescence is usually extremely weak green.



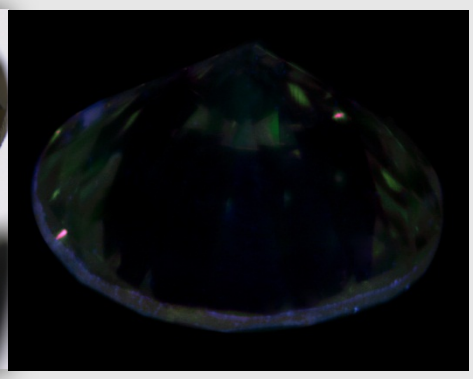
Refleced light



Crossed polarizers



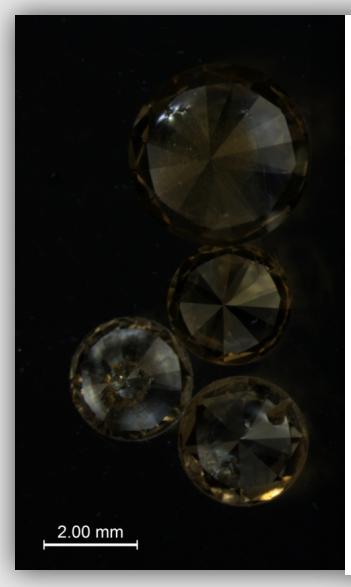
Immersion



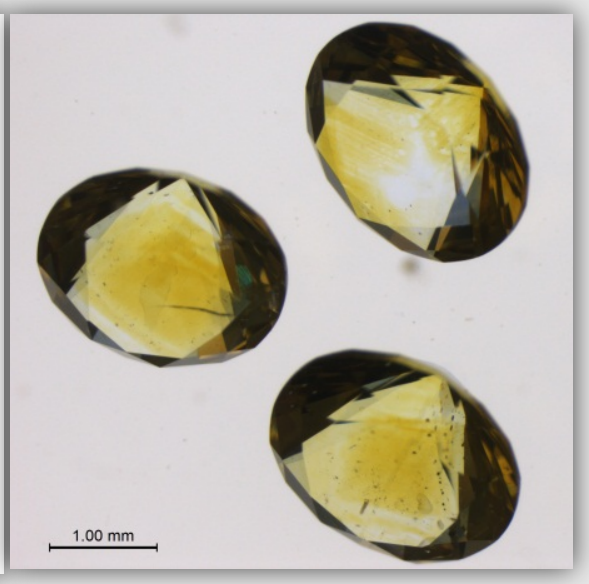
Luminescence

„Natural Counterpart“

- The color zoning and strain in mixed type IaA>Ib diamonds is sometimes very similar to synthetic diamonds (cross-like sector dependant strain or even nearly no strain, inhomogenous color). Luminescence can be very faint green.



Crossed polarizers

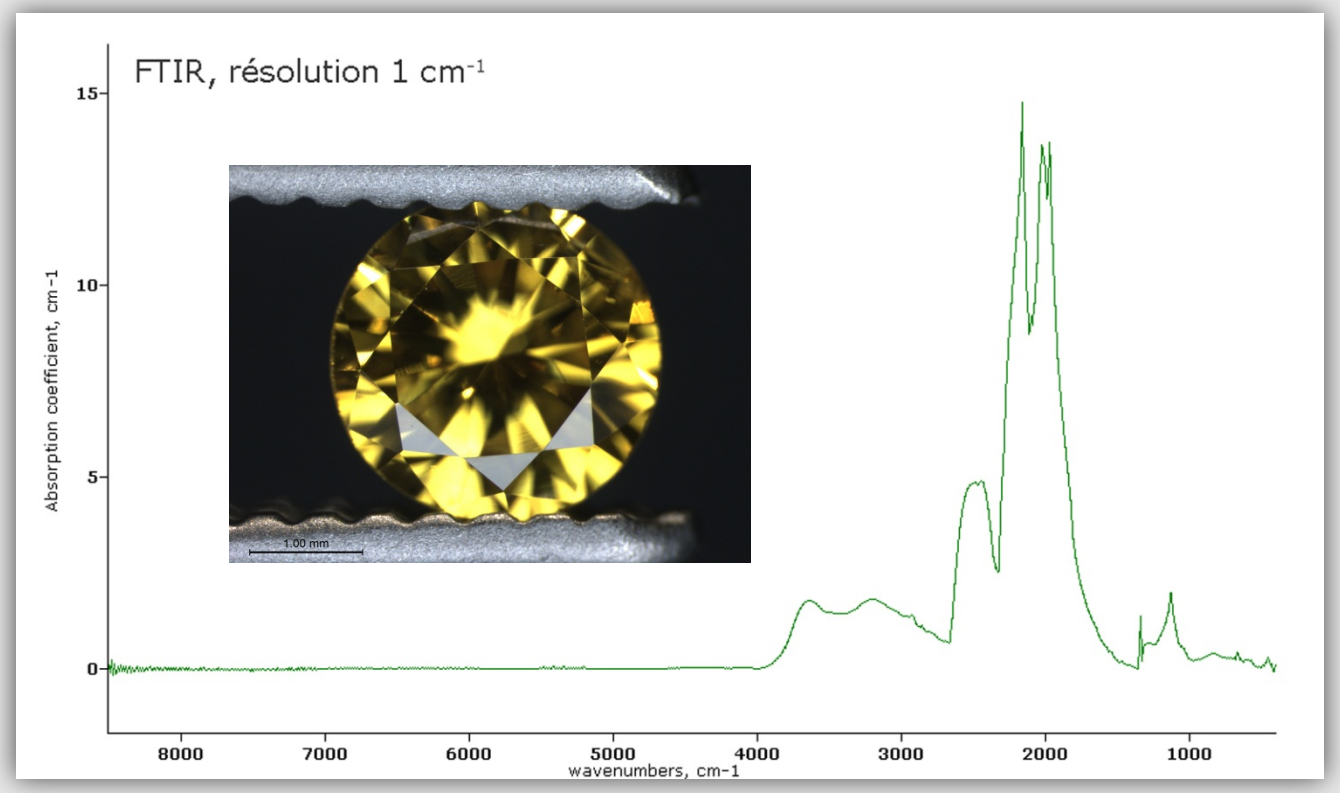


Immersion

Luminescence

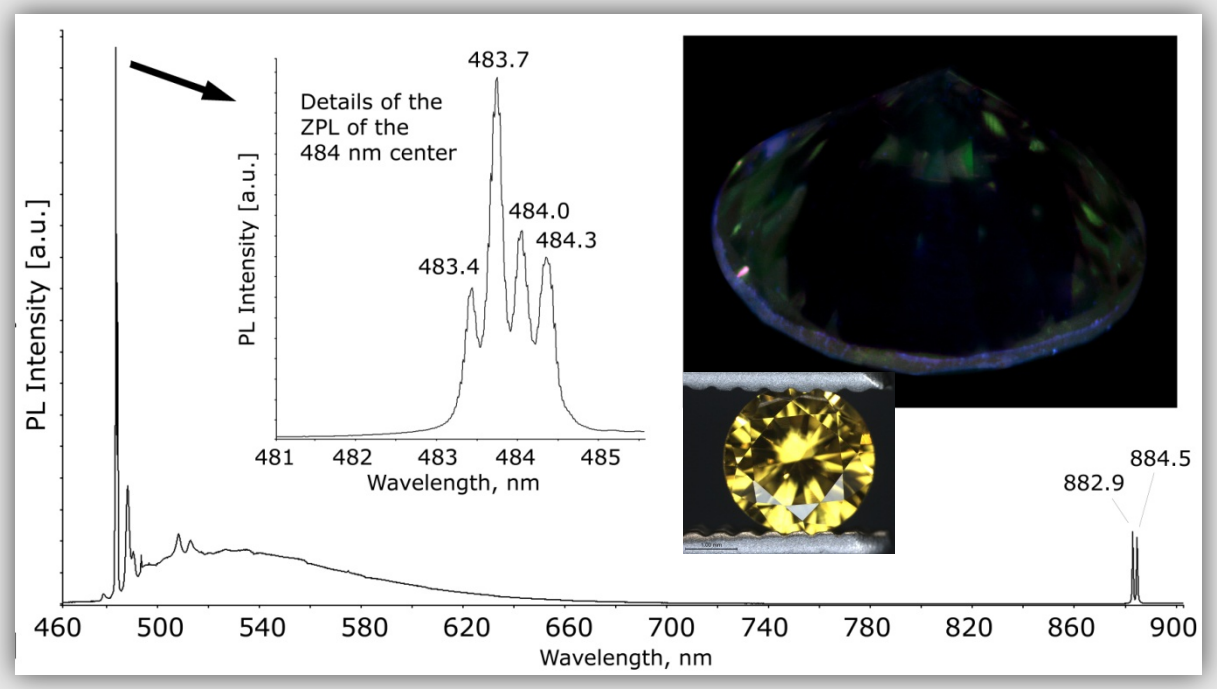
As-Grown MELEE HPHT Synthetic Diamonds

- As-grown HPHT synthetic melee diamonds are very often nearly pure or pure type Ib (extremely rare in nature).



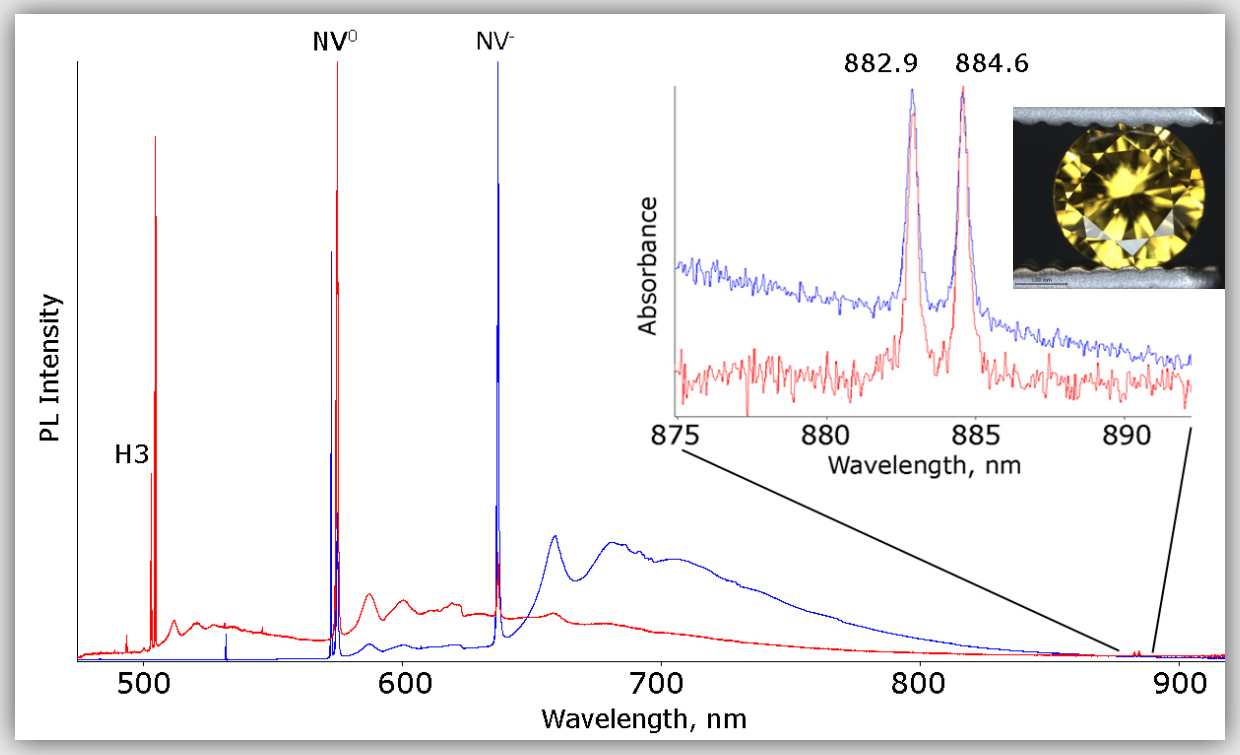
As-Grown MELEE HPHT Synthetic Diamonds

- The PL of as-grown diamonds is often very weak and visible as a very faint green glow from the Ni-related 484 nm center under intense UV excitation

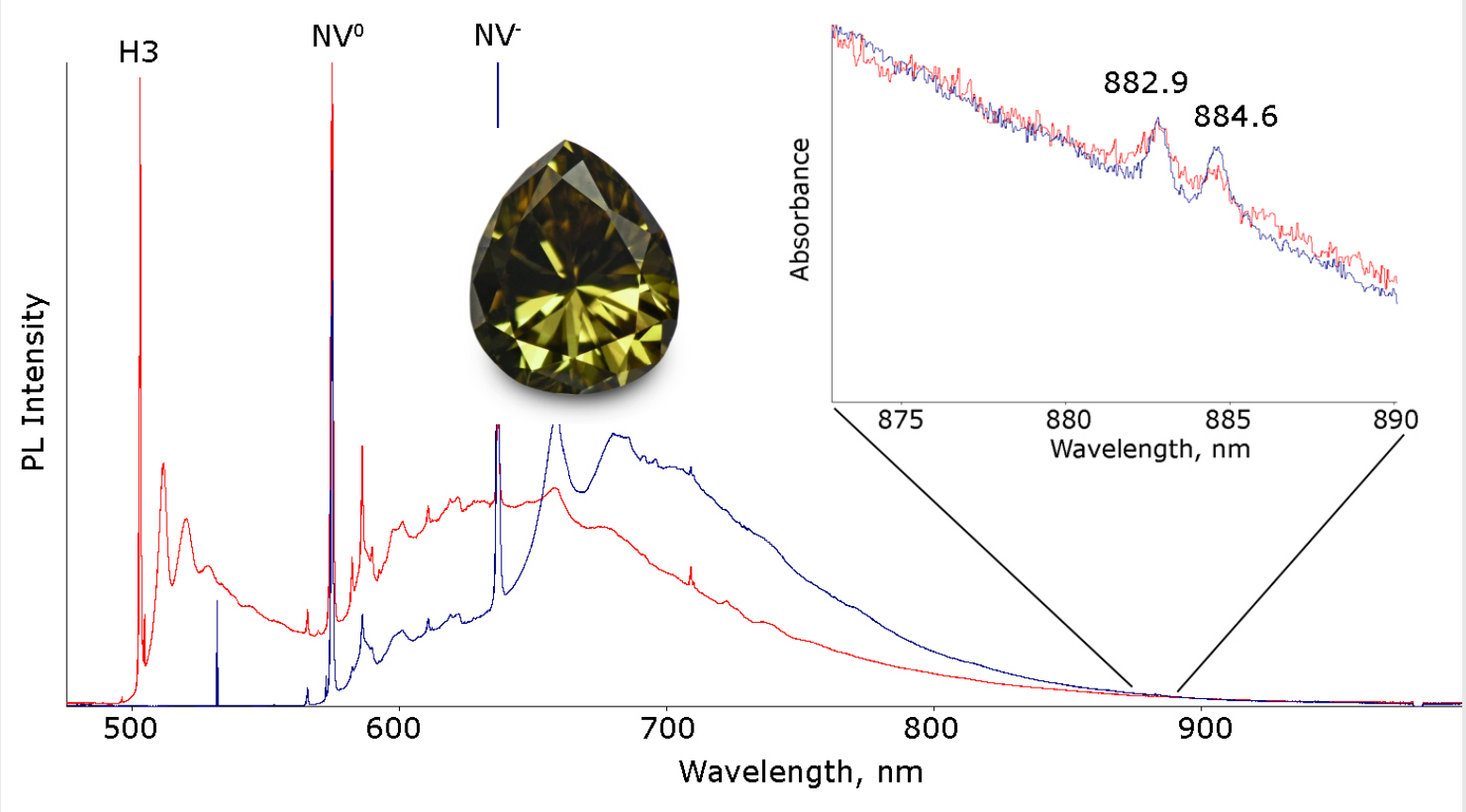


As-Grown MELEE HPHT Synthetic Diamonds

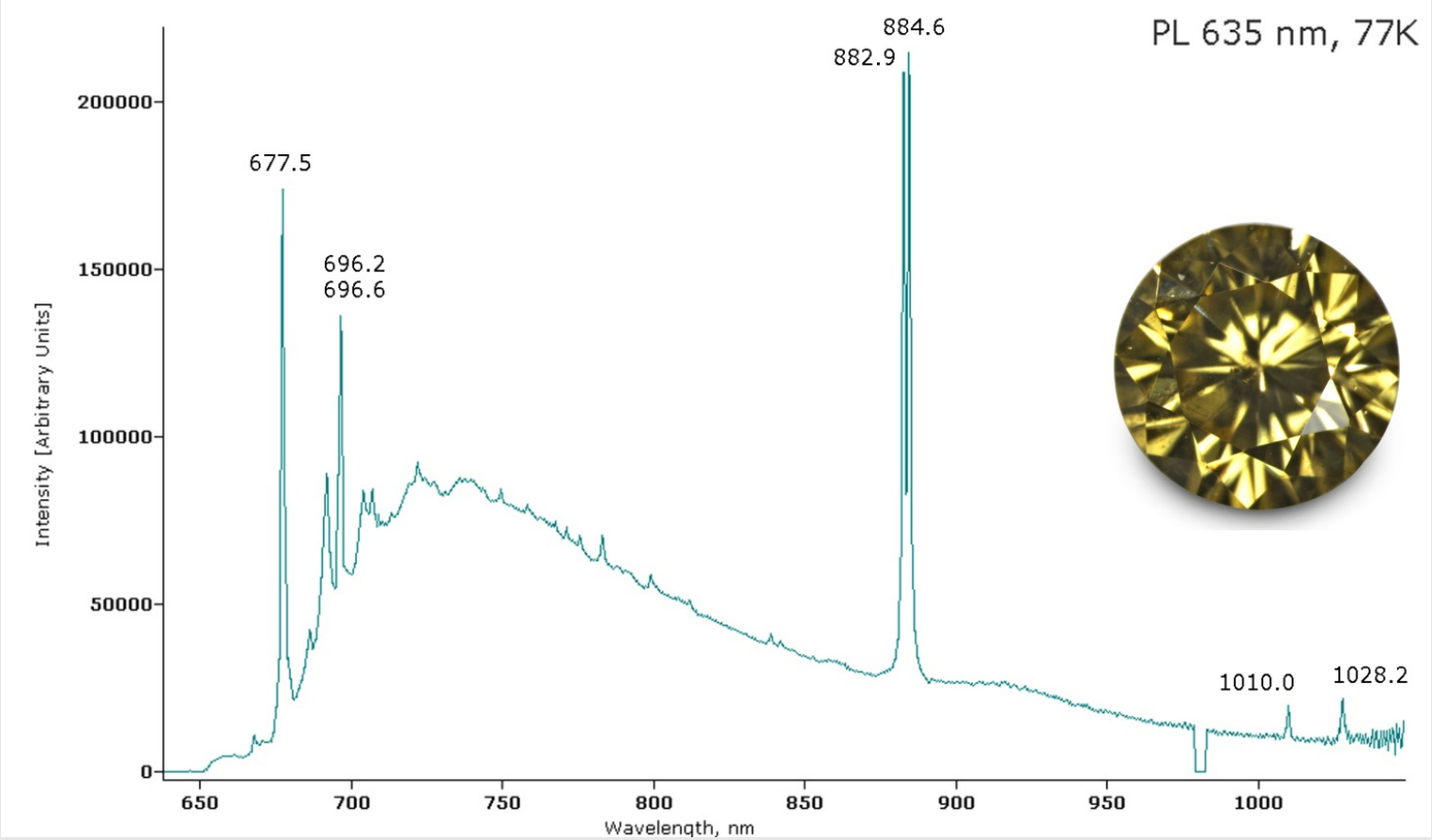
- Using 473 and 532 nm excitation many of these diamonds either show no characteristic defects or weak Ni-related 882.9/884.6 nm doublet.

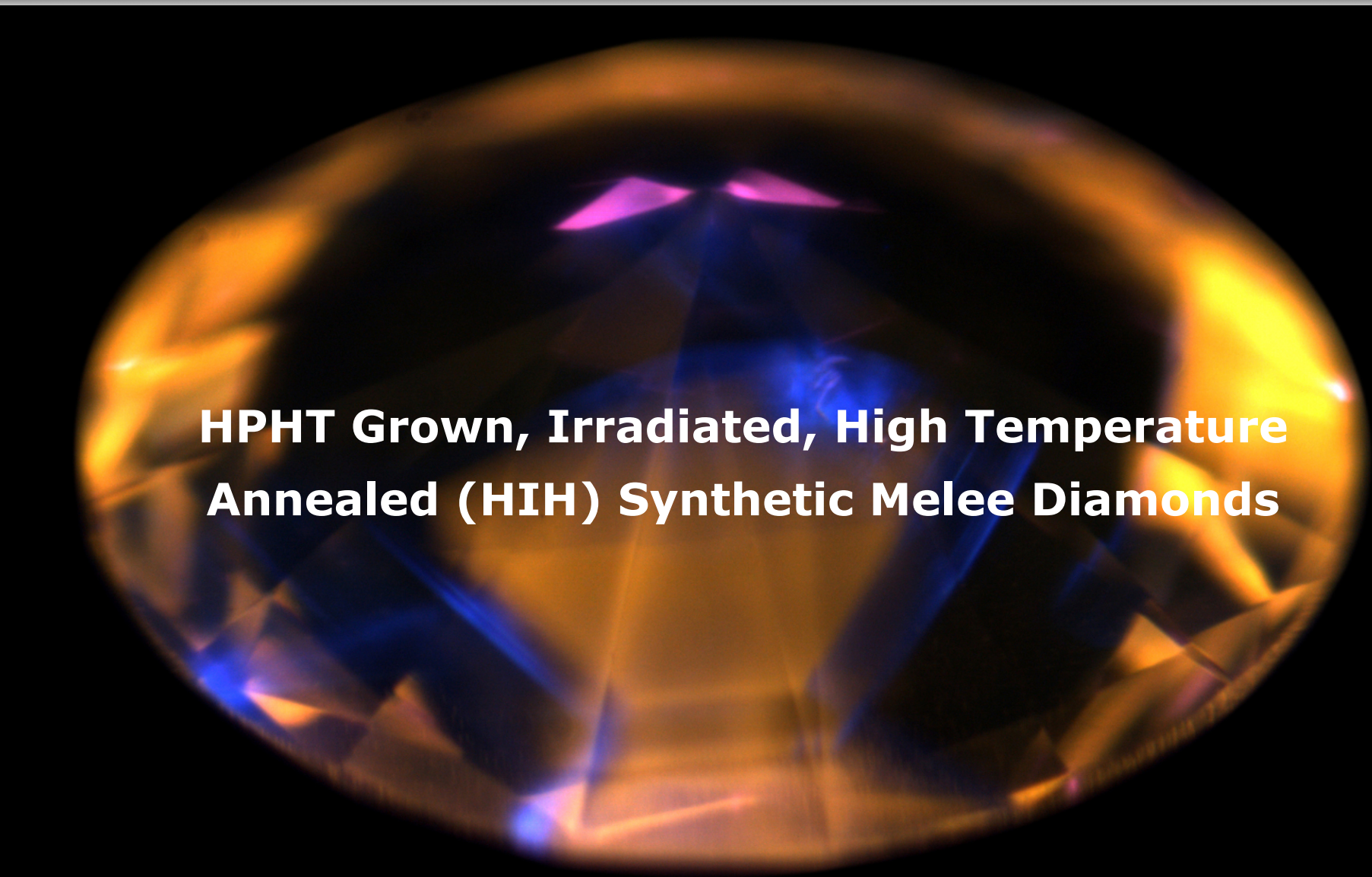


„Natural Counterpart“



„Natural Counterpart“

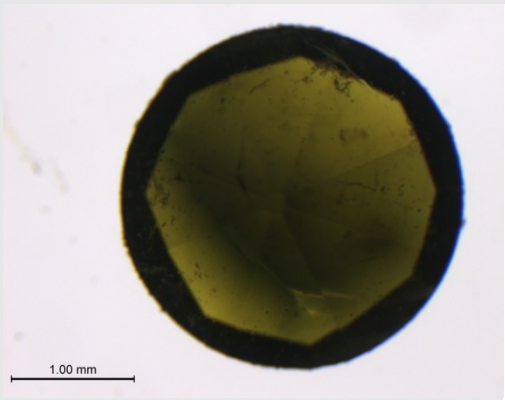


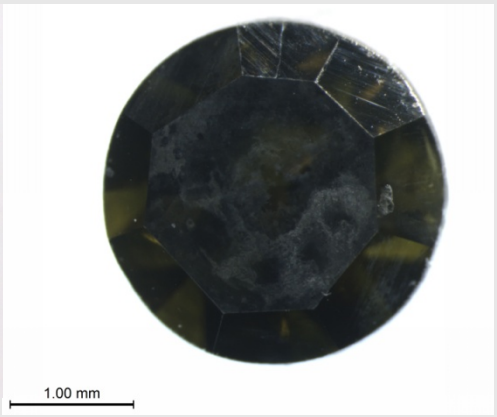


HPHT Grown, Irradiated, High Temperature Annealed (HIH) Synthetic Melee Diamonds

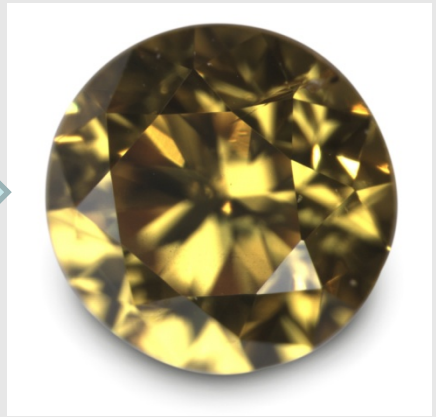
MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds

- Brownish or overly dark synthetics are treated by irradiation and HT or HPHT in order to lighten color.
  (HPHT-Irradiation-HT → HIH)

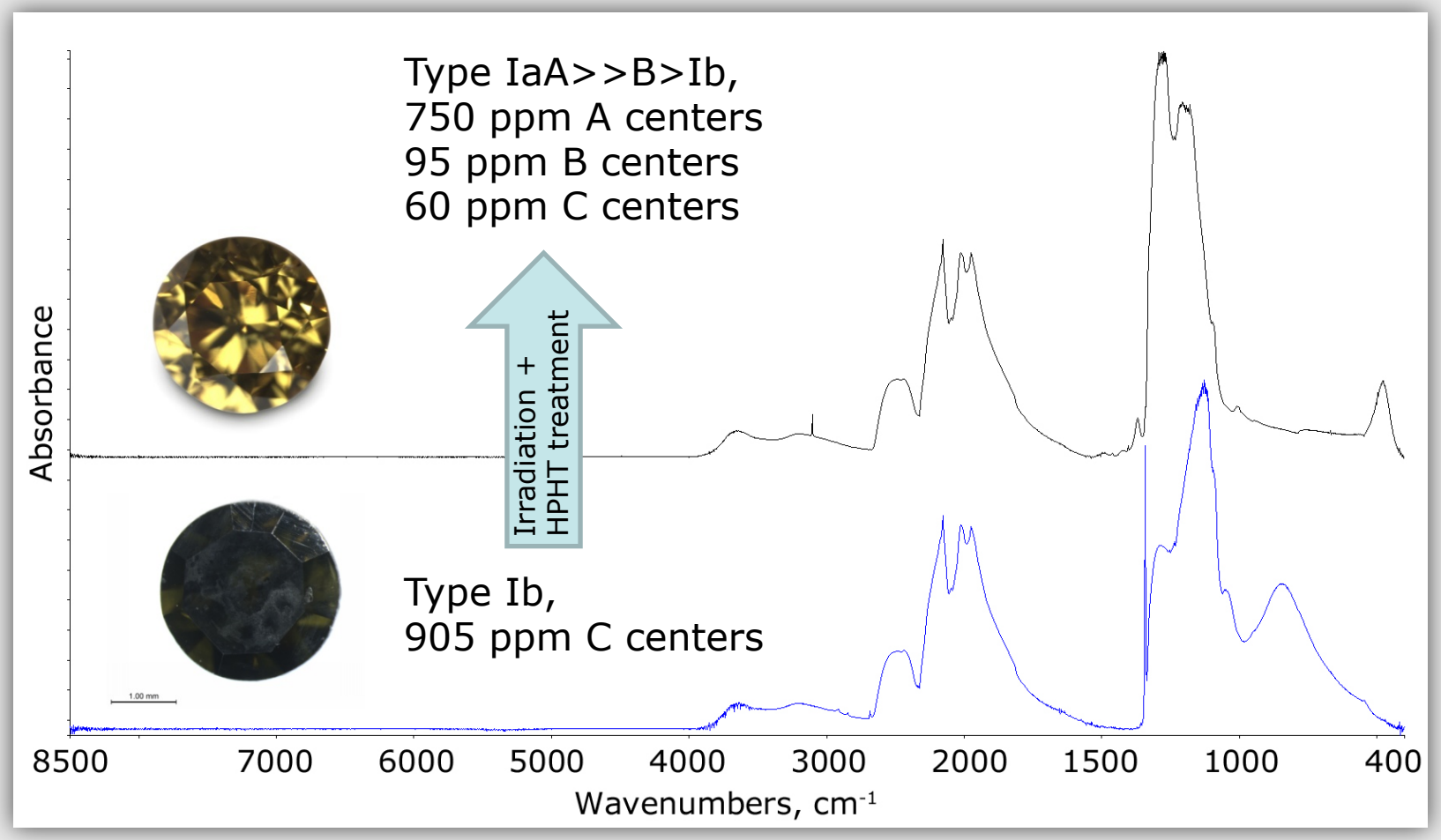




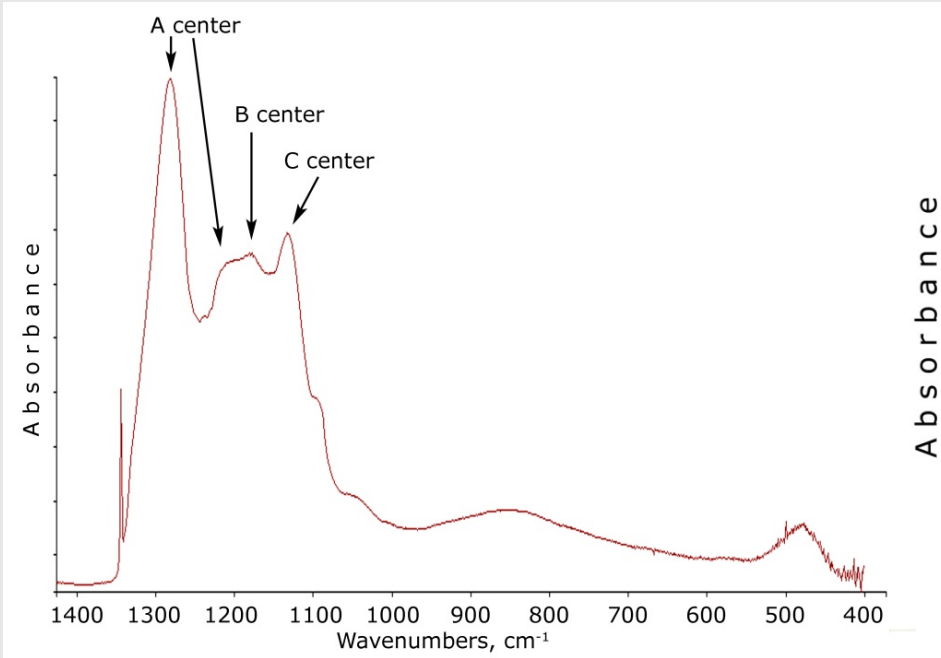
Irradiation +
HPHT treatment

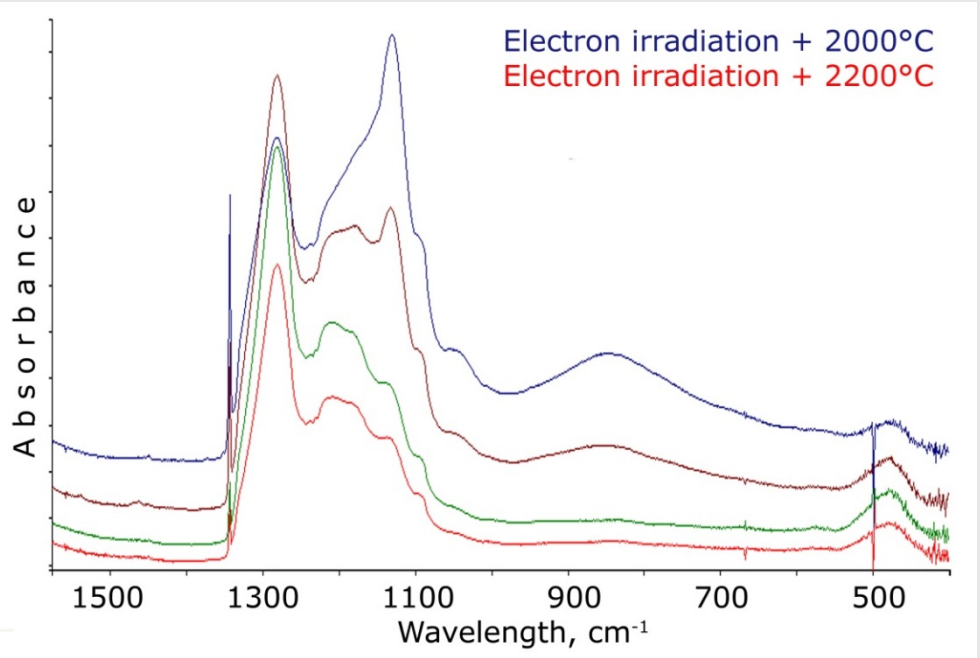


MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds



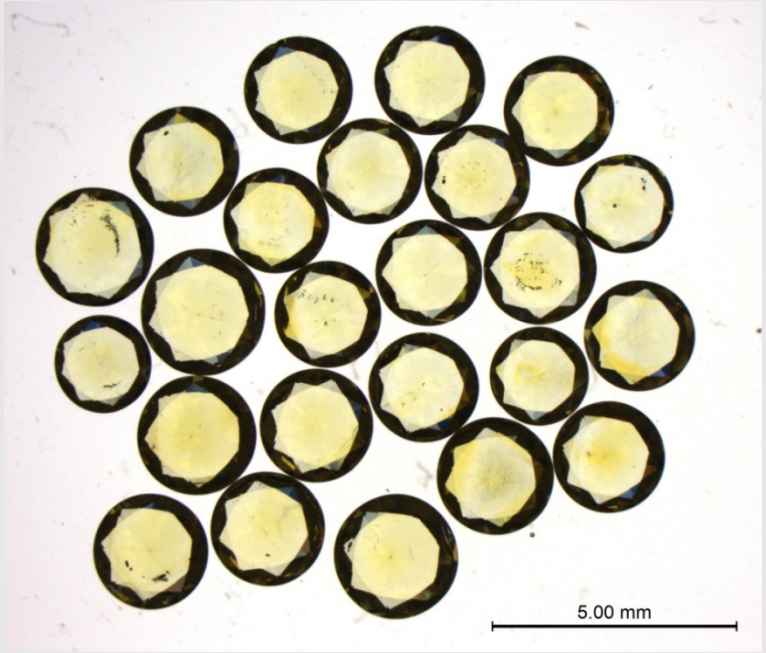
MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds

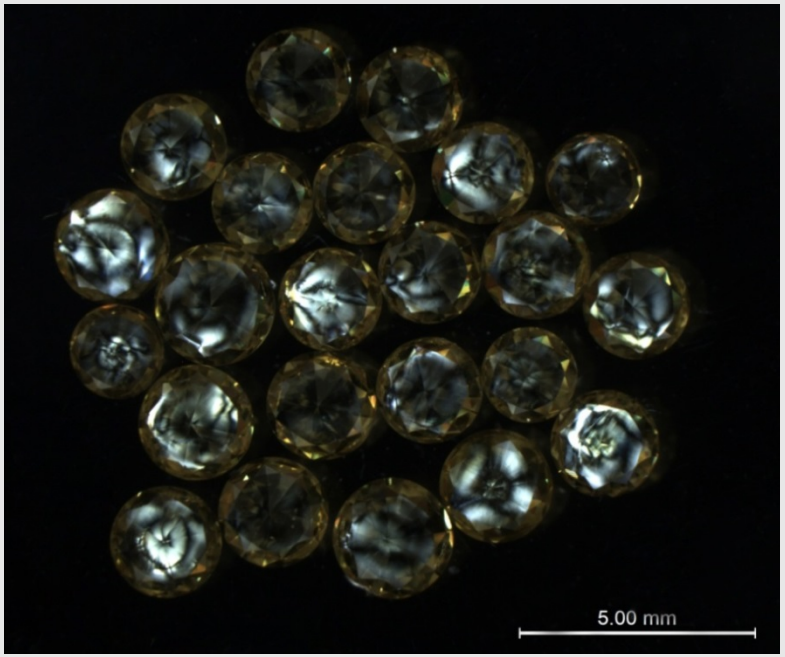




MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds

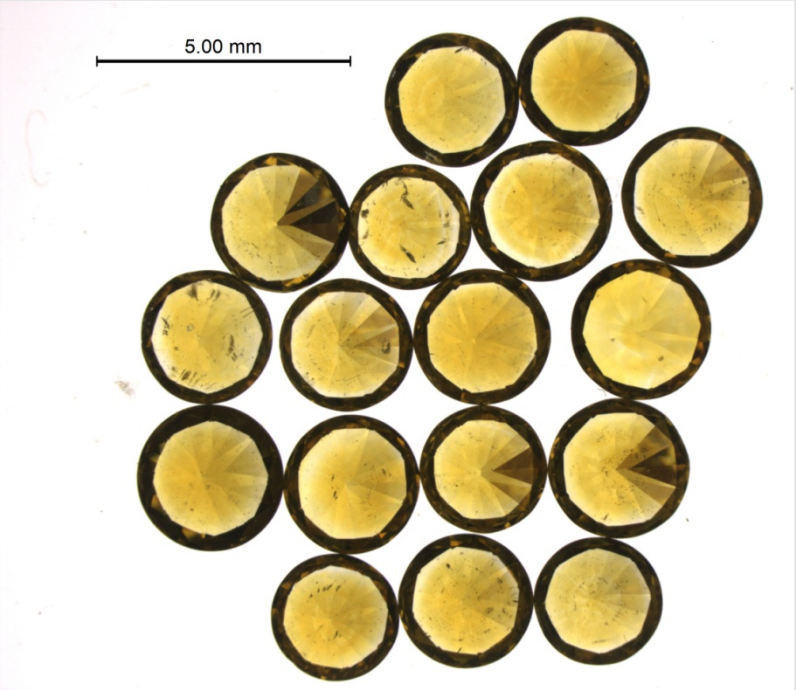
- Color zoning is frequent but not evident, and sectors are often not clearly distinguishable.
- Strain under polarizing filters is often PRESENT, sector-dependant and along (111).

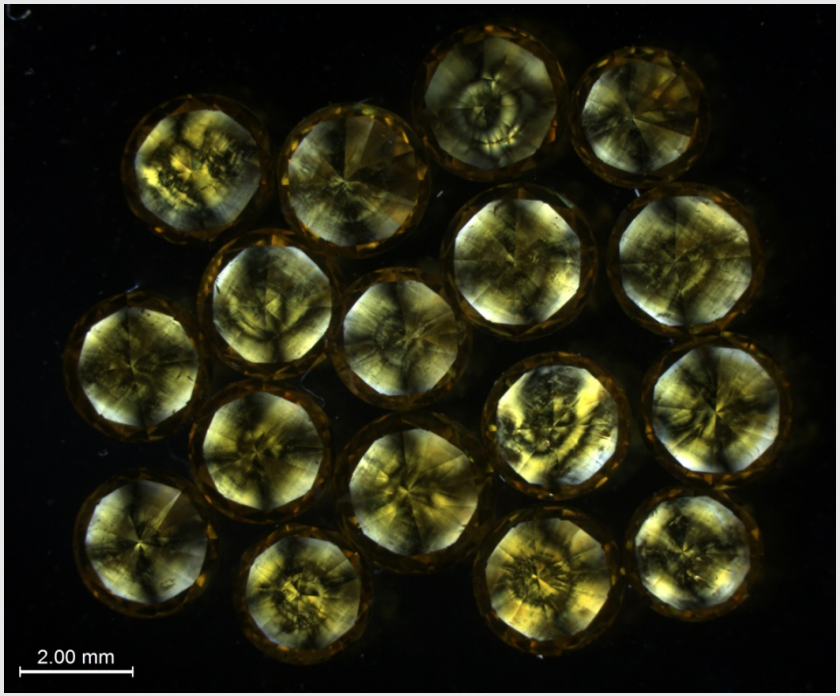




„Natural Counterpart"

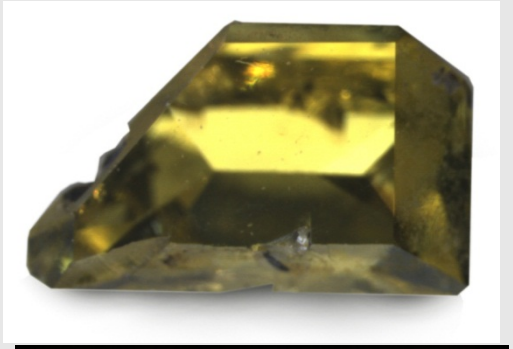
- Re-entrant cube natural diamonds…VERY similar to „HIH".
- Strain caused by alternating cuboid-octahedral growth

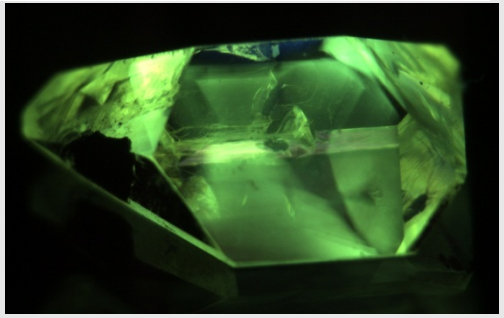


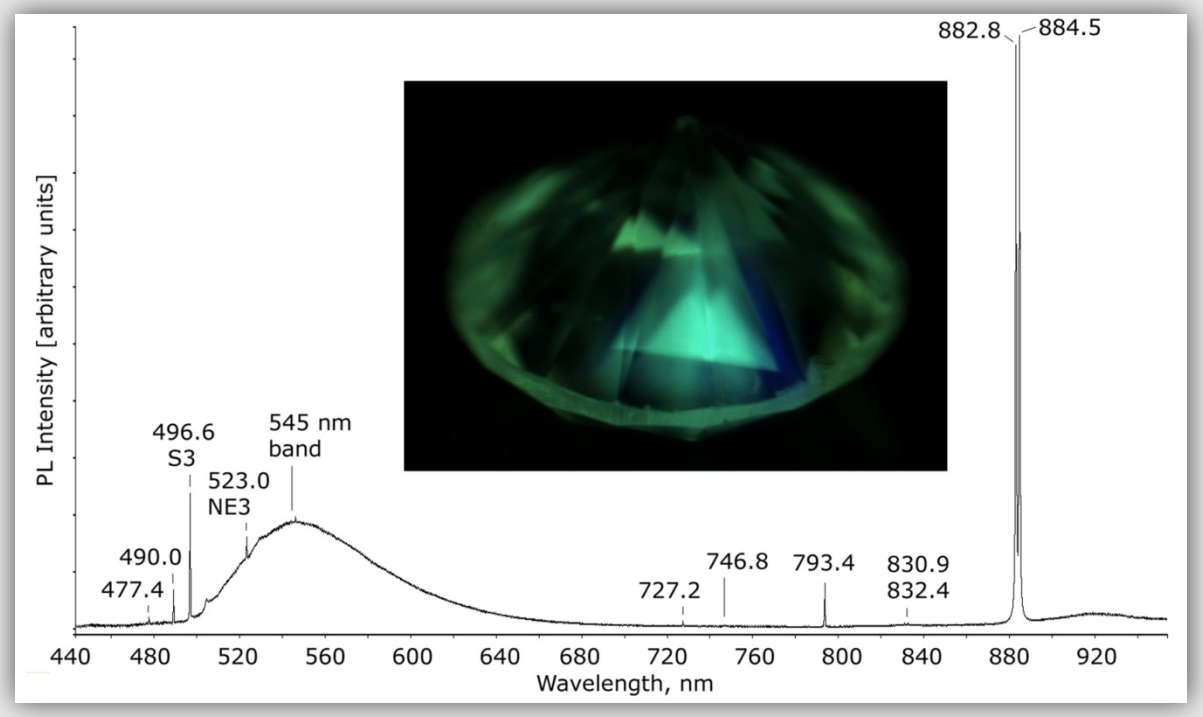


MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds (Fe-Ni)

- In Fe-Ni grown diamonds stronger green PL is formed (S3), and sometimes also some blue fluorescence from N3

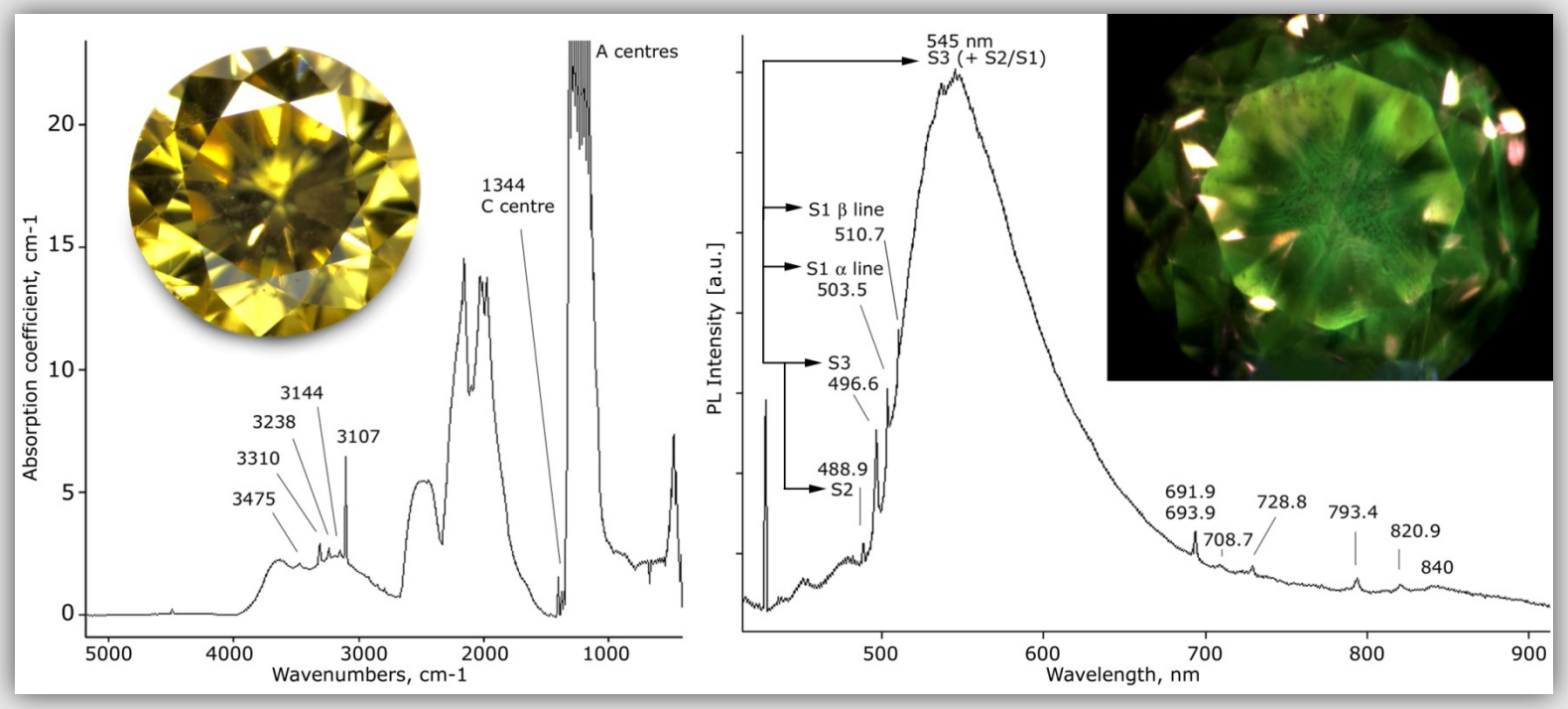






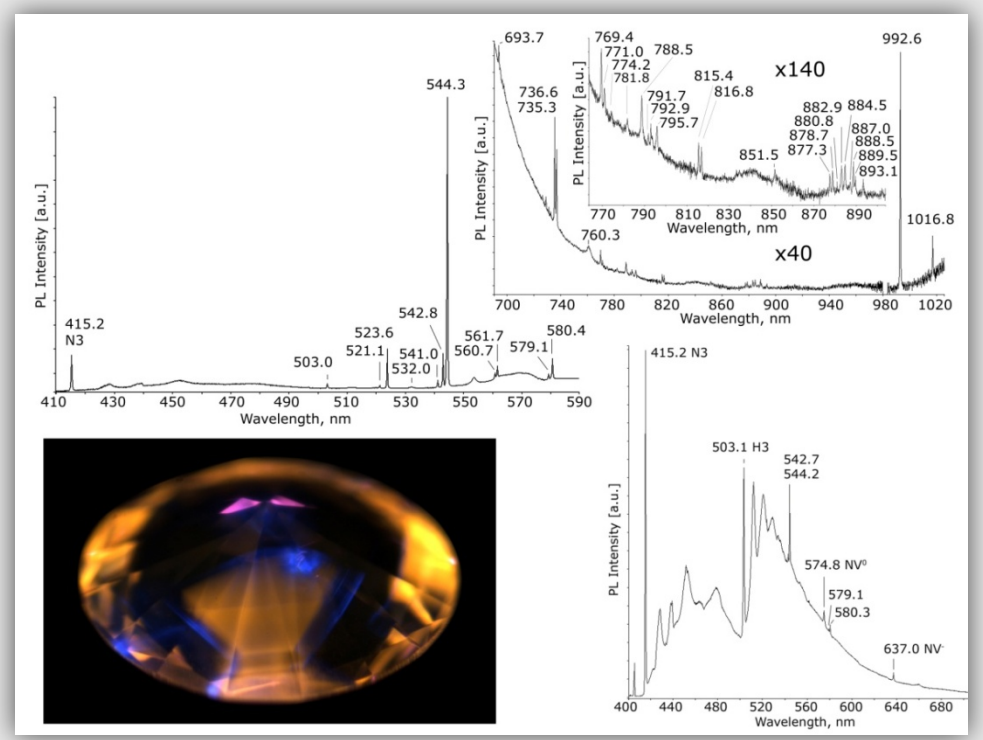
„Natural Counterpart“

- Re-entrant cube natural diamonds (mixed IaA>>Ib diamonds) exhibit the same type green PL as treated synthetics (S1, S2, S3 PL)



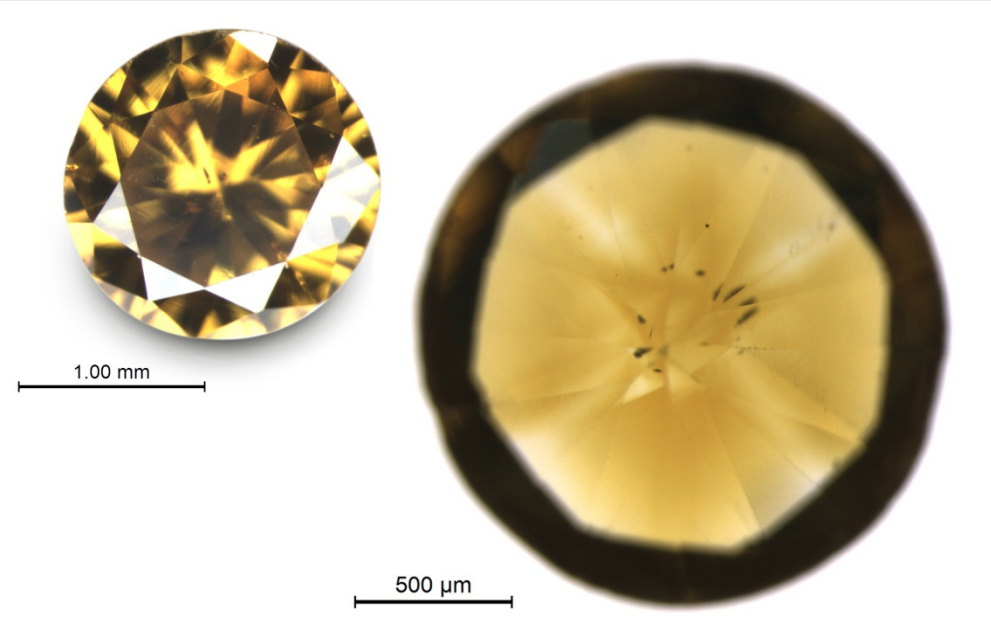
MELEE HPHT Grown Irradiated/HT treated (HIH) Synthetic Diamonds (Fe-Co)

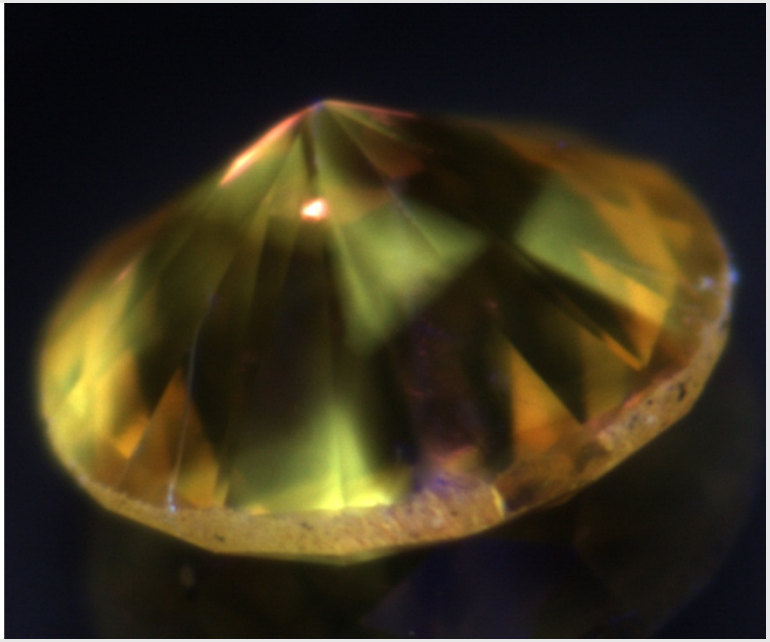
- Fe-Co grown HPHT synthetics exhibit intense yellow orange PL from cobalt related defects and often blue PL from N3, plus sectors with green H3 PL



„Natural Counterpart“

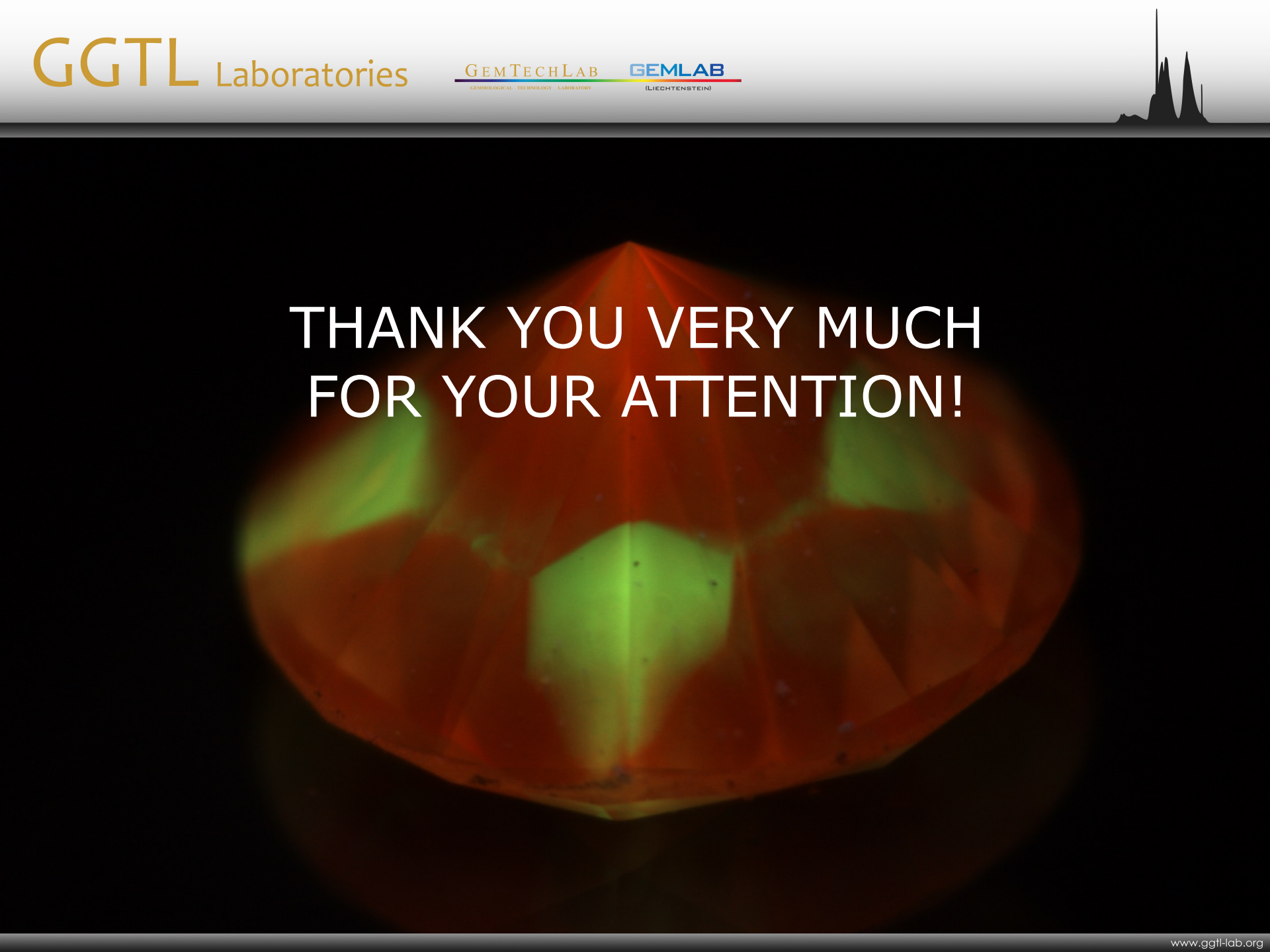
- Re-entrant cube natural diamonds (mixed IaA>>Ib diamonds) can exhibit very similar PL (to the eye) as treated Fe-Co synthetics, but spectroscopically very different (S1, S2, S3)





SUMMARY + CONCLUSIONS + OUTLOOK

- HPHT grown synthetic melee diamonds are widespread in the market and found in practically all parcels of vivid yellow diamonds.
- In contrast to «large» synthetics the melee synthetic diamonds are generally undeclared and mixed within parcels of natural diamonds.
- Mainly Fe-Ni and Fe-Co diamonds are found, either as-grown or HIH.
- HIH diamonds are employed because of $$$
- Testing procedure to detect synthetics in natural melee is highly complex.
- So far NO colorless CVD synthetic diamonds have been found in natural melee.
- It remains to be seen when CVD grown colorless melee diamonds will appear mixed in parcels of natural diamonds.



THANK YOU VERY MUCH FOR YOUR ATTENTION!