The Natural and Artificial Colour Origin of Gems: The Geological Context and the Artificial Modification of Chromophores and other Colour-Causing Defects

Dr. Thomas Hainschwang

thomas.hainschwang@ggtl-lab.org

GGTL Laboratories, Balzers, Liechtenstein

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The Colour of Gemstones

Idiochromatic gems

Colored from elements that are part of their essential chemical formula, e.g. malachite $Cu_2(CO_3)(OH)_2$ coloured green from Cu^{2+} or rhodochrosite $MnCO_3$ coloured pink by Mn^{2+} and Mn^{3+}. Colour rarely modifiable by treatment.

Allochromatic gems

Colourless in their «pure» state, coloured by impurities and/or defects, e.g. ruby Al_2O_3 coloured by Cr^{3+} or blue diamond coloured by boron. The vast majority of gemstones are allochromatic. Colour frequently modifiable by treatment.

The Colour Treatments of Gemstones

Dyeing:

All gemstones

Coating:

All gemstones

Heat treatment:

Corundum, diamond, aquamarine, tanzanite, spinel, tourmaline

Heat treatment with additives (Diffusion treatment):

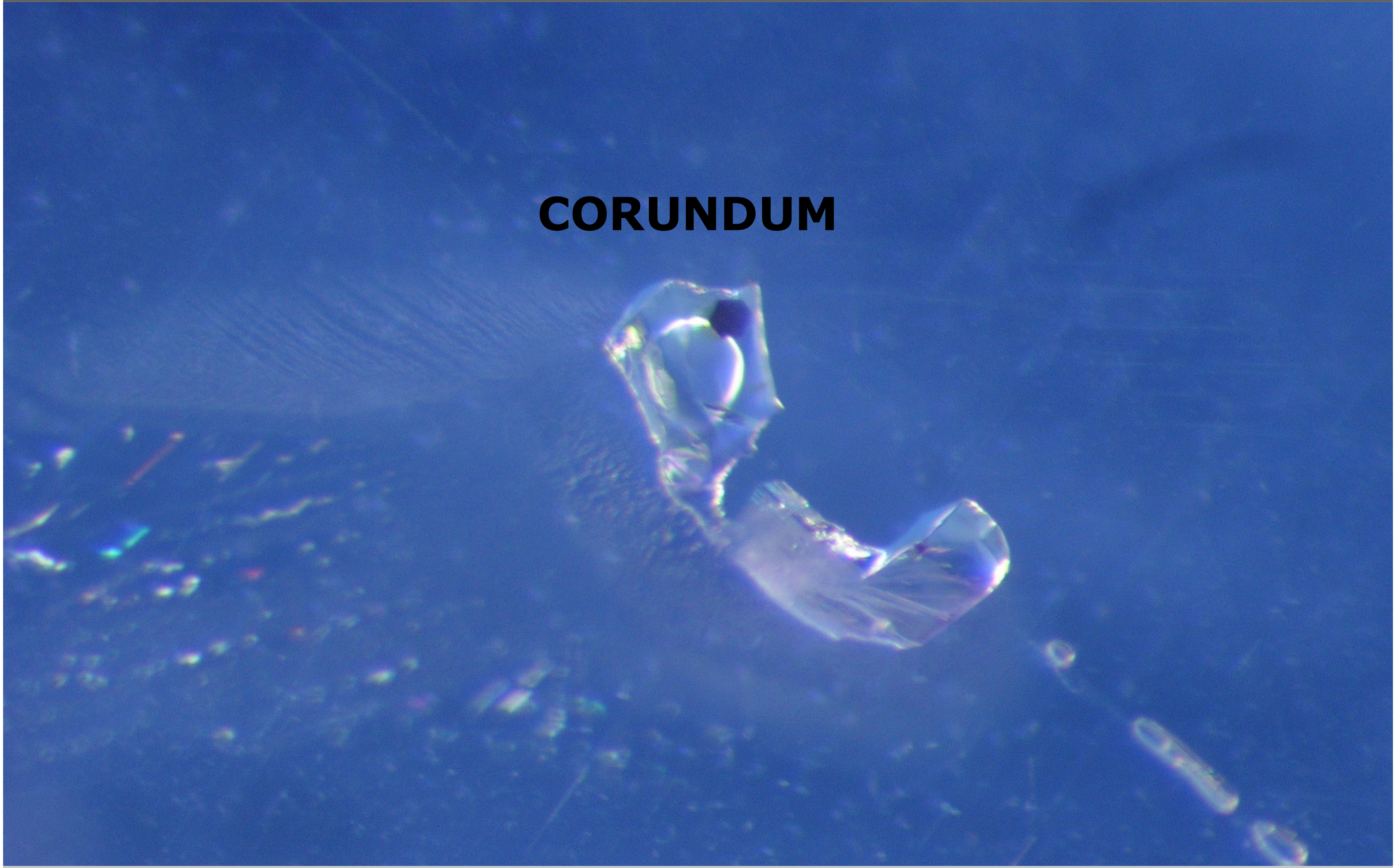
Corundum (Be, Ti, Cr), feldspar (Cu)

Irradiation (x-rays, gamma rays, electrons, neutrons etc.):

Diamond, topaz, pink tourmaline, beryl (→ Morganite, emerald), quartz

HPHT (High Pressure High Temperature) treatment:

Diamond


CORUNDUM

The Colour Causes of Corundum

Fe^{3+}: Yellow

$Fe^{2+} \rightarrow Ti^{4+}$ charge transfer: blue

$Fe^{2+} \rightarrow Ti^{4+}$ charge transfer + Fe^{3+}: Green

Cr^{3+}: pink to red

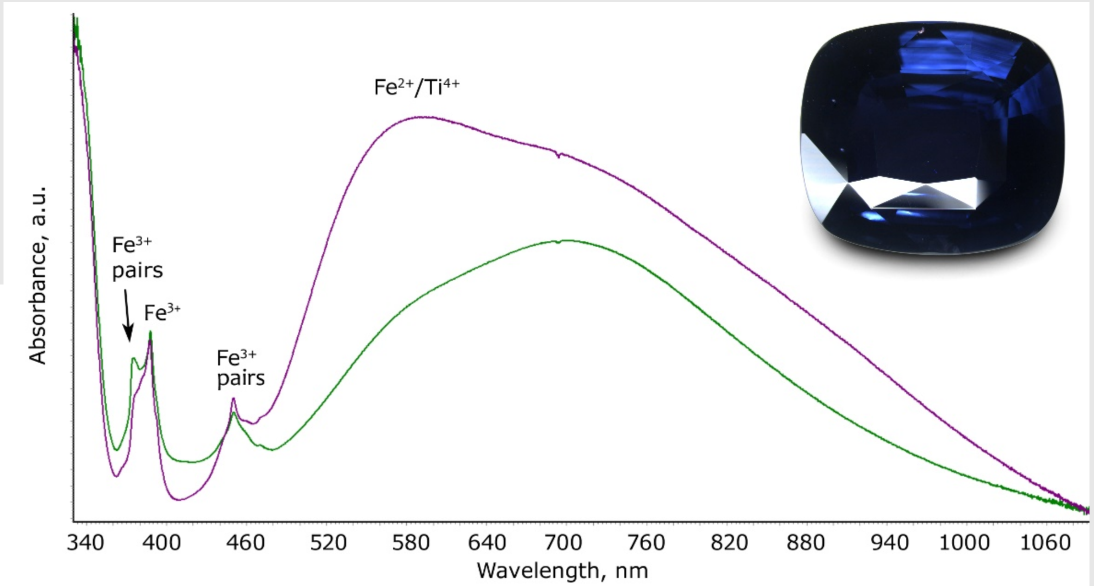
Cr^{3+} + Fe: Orange

V^{3+}: Green – red colour change

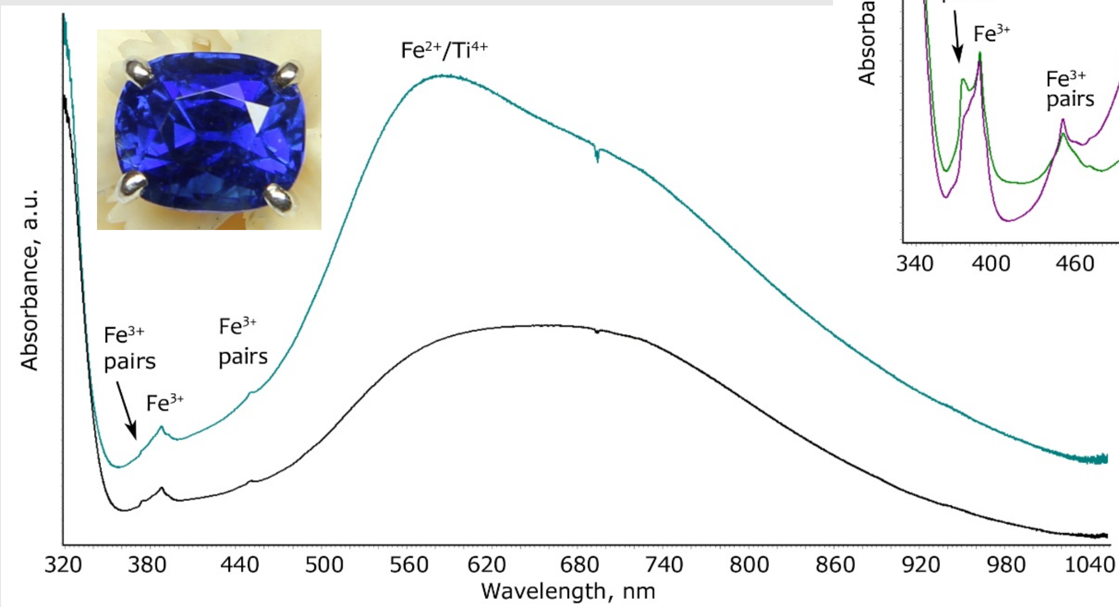
$Cr^{3+} + Fe^{2+} \rightarrow Ti^{4+}$ charge transfer: Purple, colour change

Mg^{2+}-trapped-hole colour centre: Yellow

UV-Vis-NIR Spectroscopy -- Sapphire

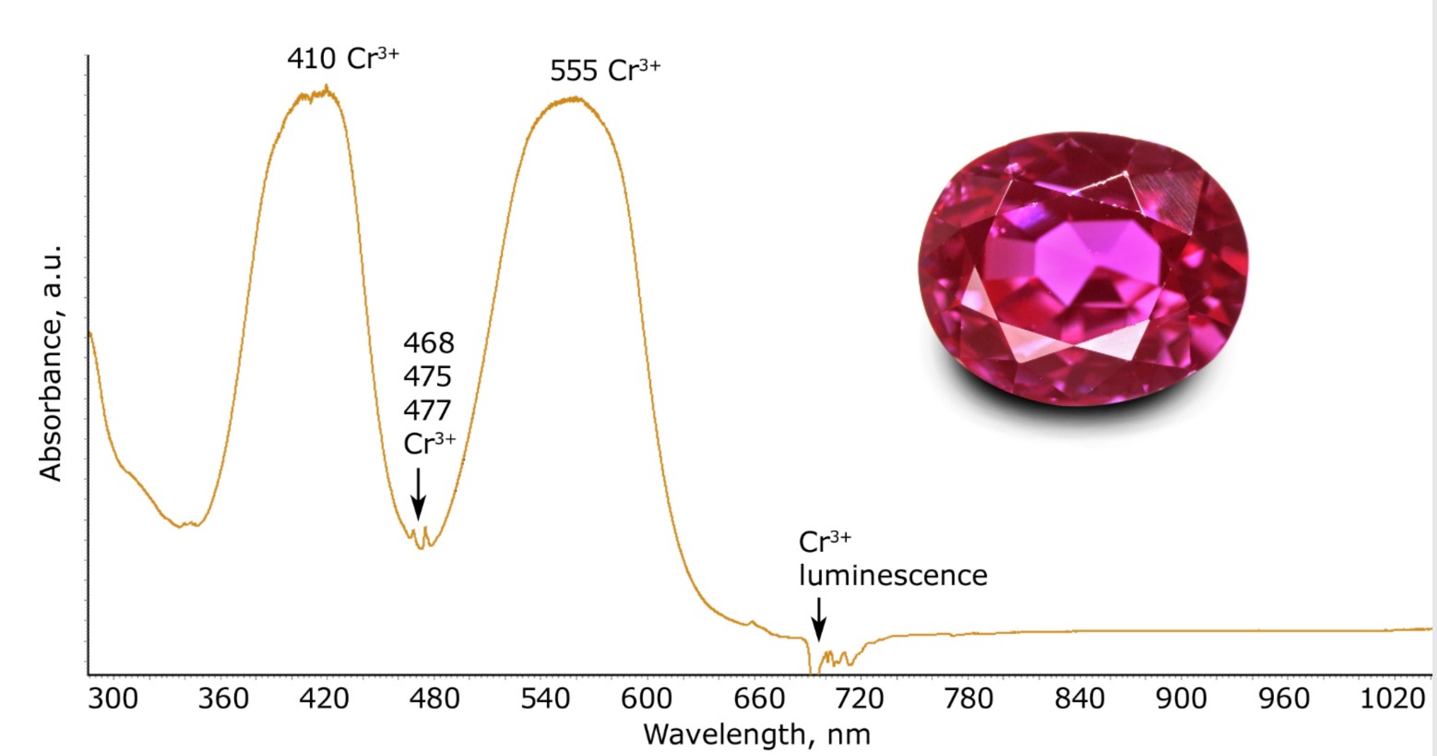


Umba/Tanzania

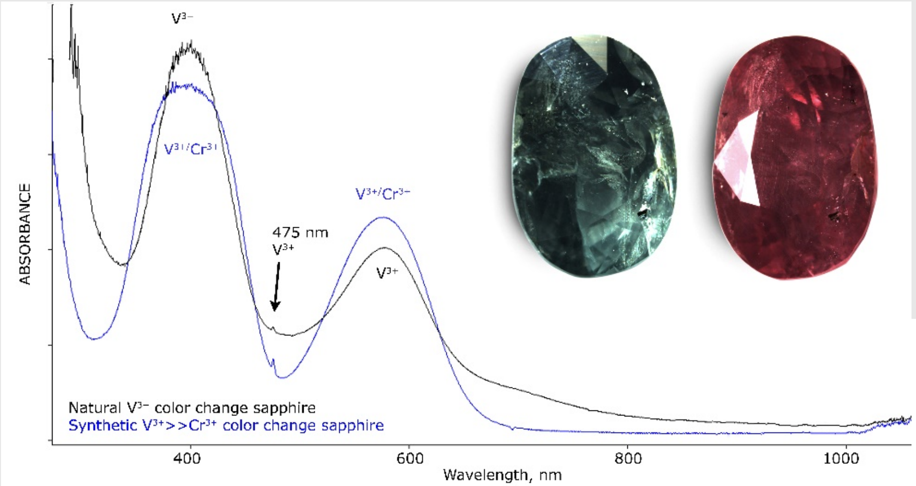


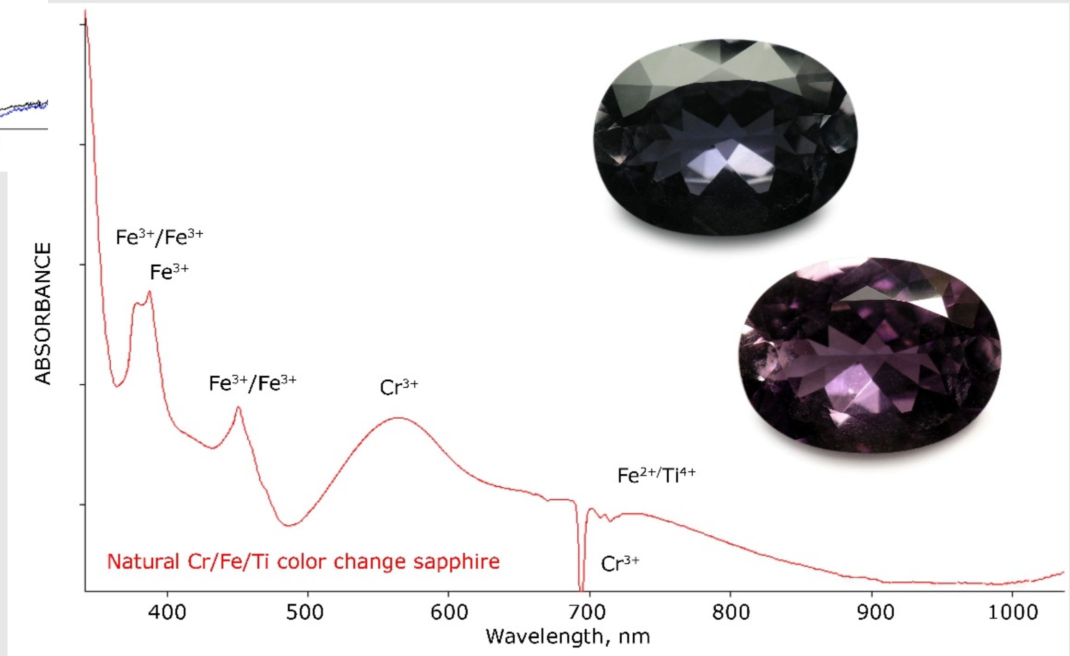
Kashmir (India)

UV-Vis-NIR Spectroscopy -- Ruby



UV-Vis-NIR Spectroscopy – Colour Change Sapphire





Colour Treatments of Corundum

Heat treatment:

Simple heat treatment at temperatures between 1100 and 1600°C, oxidising or reducing atmosphere: *Modifies the valency of Fe and/or melts rutile to supply* Ti^{4+}

Change «geuda» saphires to blue by melting of rutile: Ti^{4+}

Deepen blue color (reducing atmosphere): $Fe^{3+} \rightarrow Fe^{2+}$

Lighten blue color (oxidising): $Fe^{2+} \rightarrow Fe^{3+}$

Destroy blue colour in rubies with blue zones (oxidising): $Fe^{2+} \rightarrow Fe^{3+}$

Enhance the red colour of ruby (oxidising)

Heat treatment with additives (Diffusion treatment):

Ti or Cr diffusion → superficial blue / red colour, high temperature

Be diffusion → Traped hole colour centre from Be^{2+} → Yellow colour

In blue sapphire: colourless outer layer.


BERYL

The Colour Centres of Beryl

Beryl:

Fe^{2+} → Fe^{3+} charge transfer: blue (aquamarine)

O^{2-} → Fe^{3+} charge transfer: yellow

Fe^{2+} → Fe^{3+} charge transfer and O^{2-} → Fe^{3+} charge transfer: green to green blue («green beryl»)

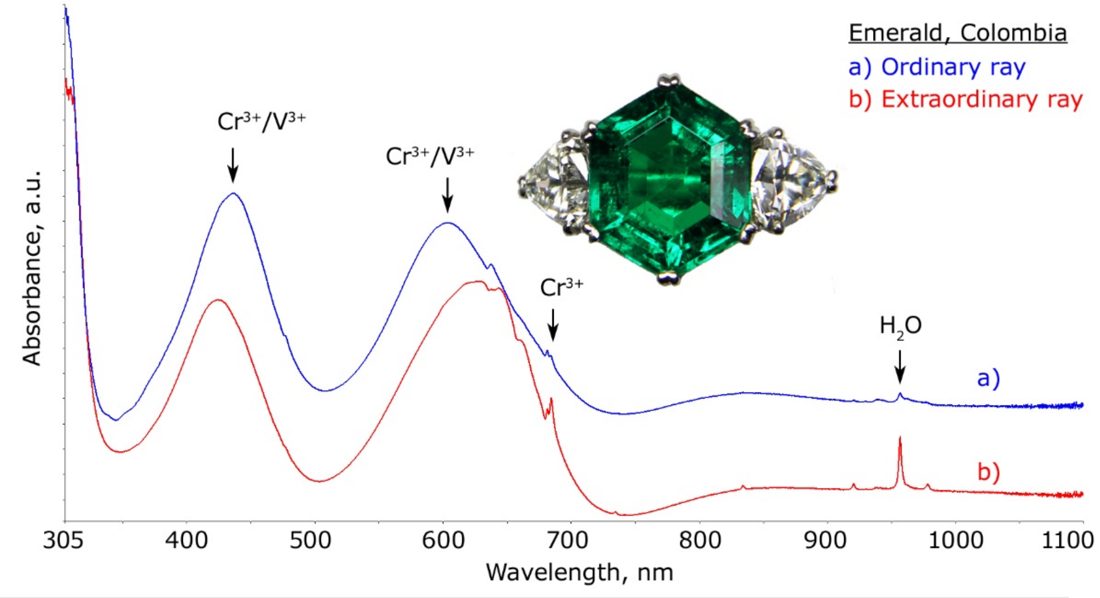
Cr^{3+}: green to bluish green

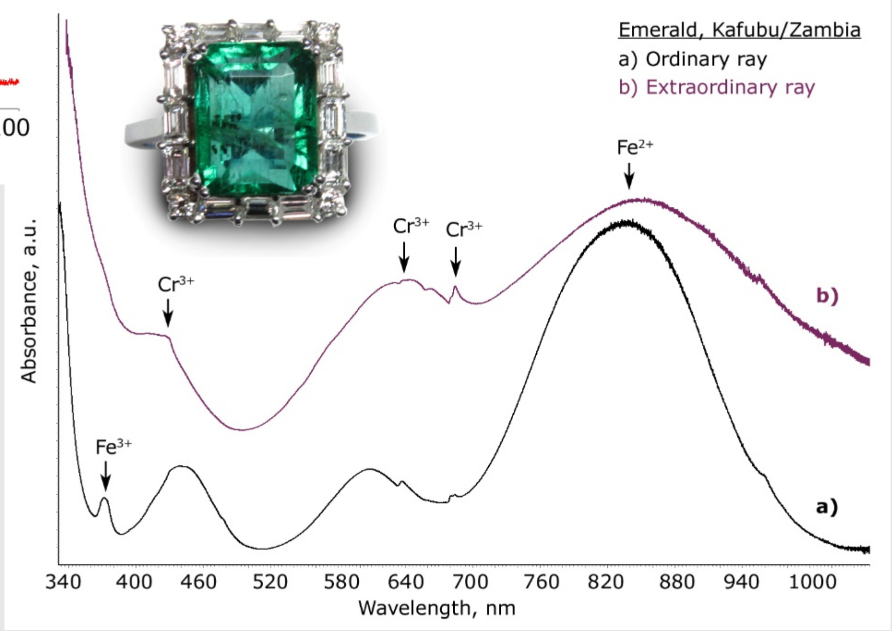
V^{3+}: Green to yellowish green

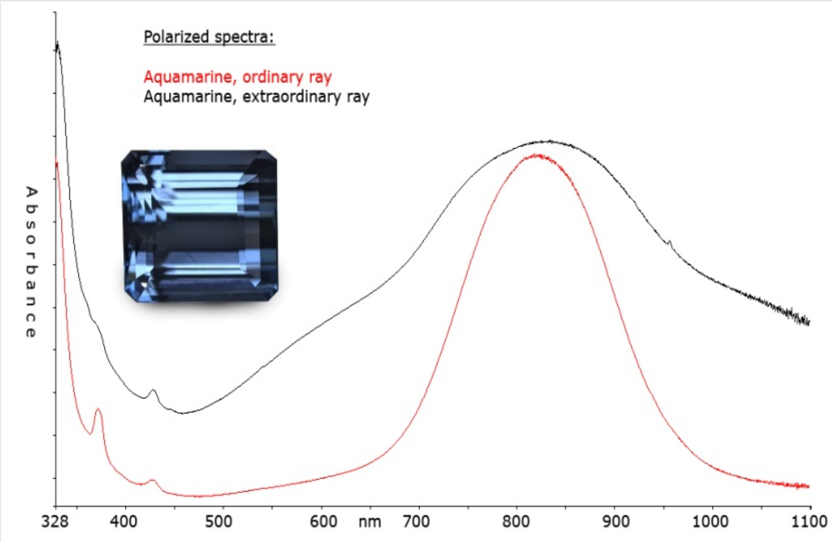
Mn^{2+}: pink to red

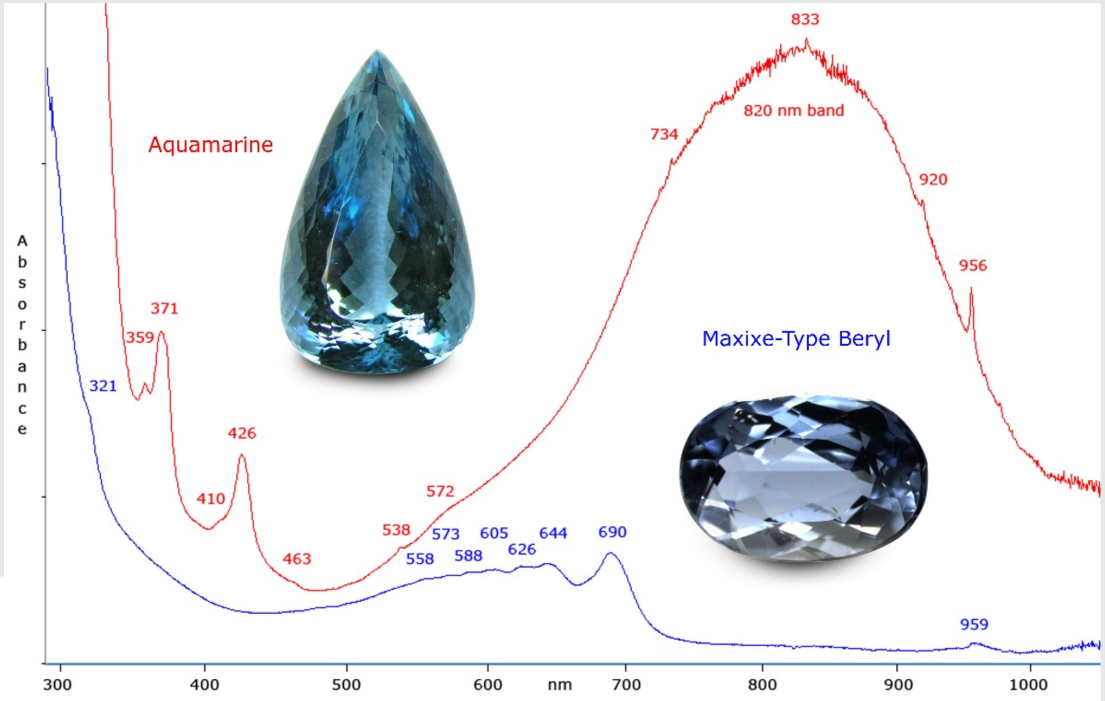
NO_3 colour centre: blue to violet, unstable («Maxixe beryl»)

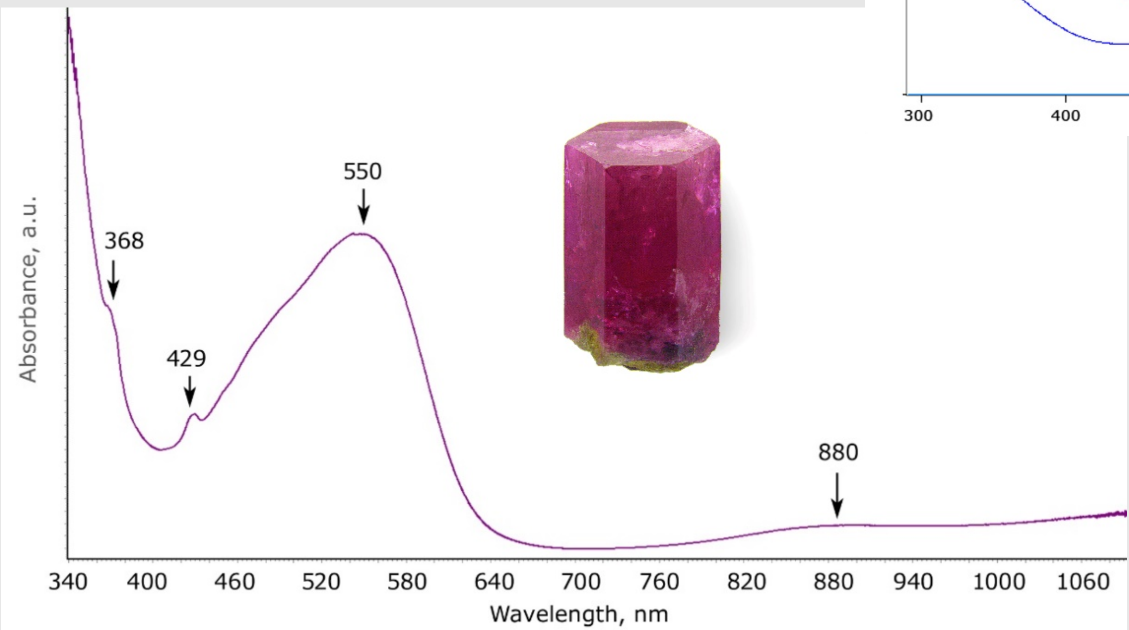
UV-Vis-NIR Spectroscopy -- Emerald






Polarized spectra:
Aquamarine, ordinary ray
Aquamarine, extraordinary ray
Absorbance
328
400
500
600
nm
700
800
900
1000
1100


Aquamarine
Maxixe-Type Beryl
Absorbance
833
820 nm band
734
920
956
371
359
321
426
410
463
572
538
573
558
605
588
626
644
690
959
300
400
500
600
nm
700
800
900
1000


Absorbance, a.u.
550
368
429
880
340
400
460
520
580
640
700
760
820
880
940
1000
1060
Wavelength, nm

Colour Treatments of Beryl

Heat treatment:

Simple heat treatment at temperatures around 450°C: *Modifies the valency of Fe.*

Green blue color is transformed to blue: Fe^{3+} → Fe^{2+} (Oxidising)

Emerald is heat sensitive, hence never heat treated.

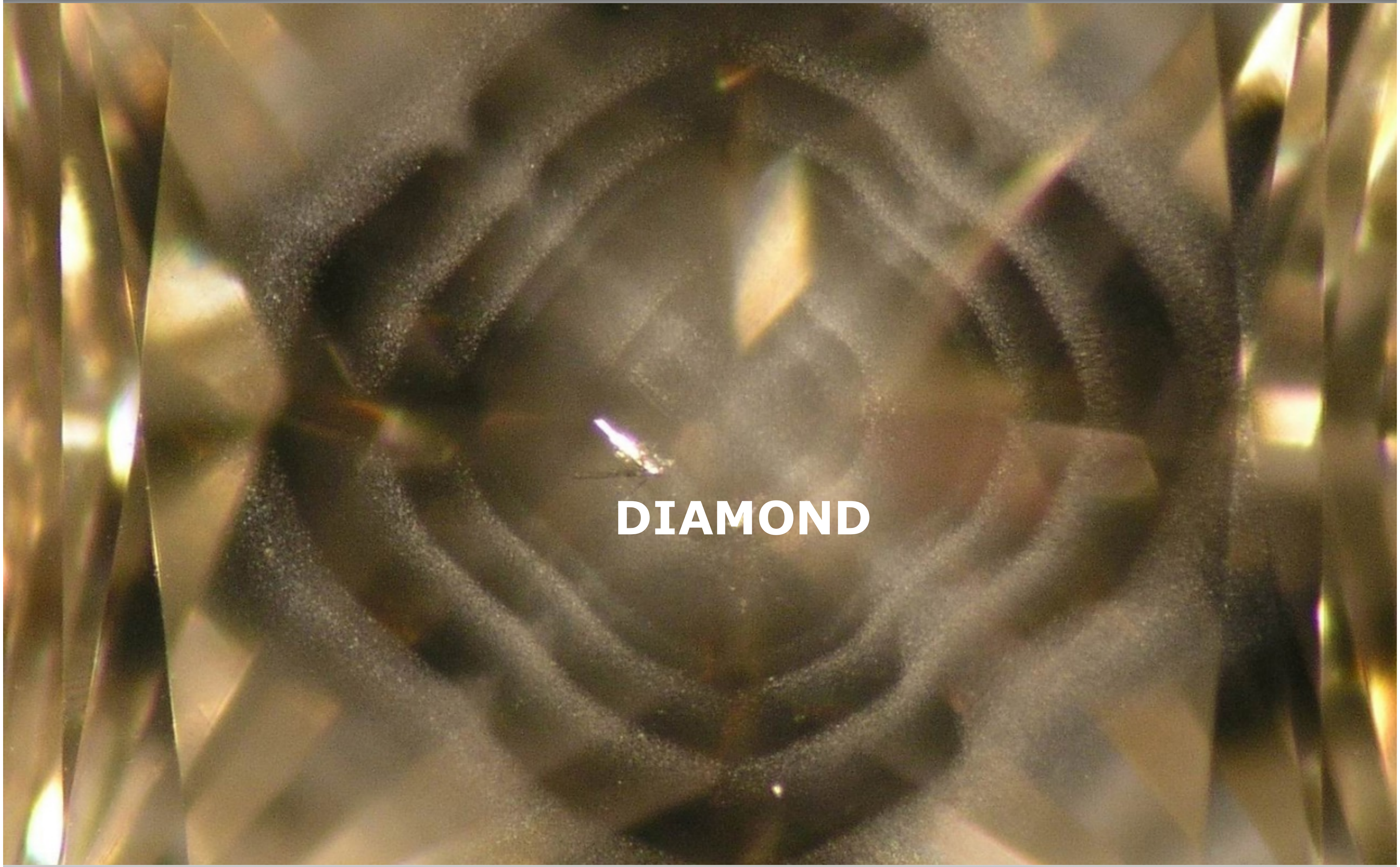
Irradiation (mainly by Gamma or electron irradiation, sometimes neutrons):

Colorless beryl → Yellow (Heliodor)

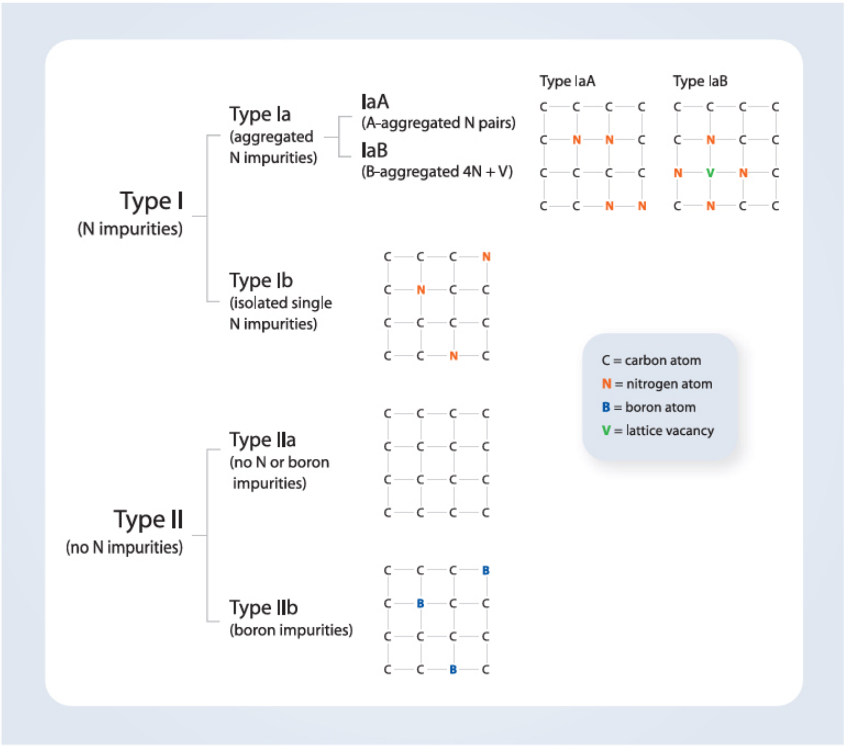
Beryl with NO_3 precurser → «sapphire» blue (unstable colour)

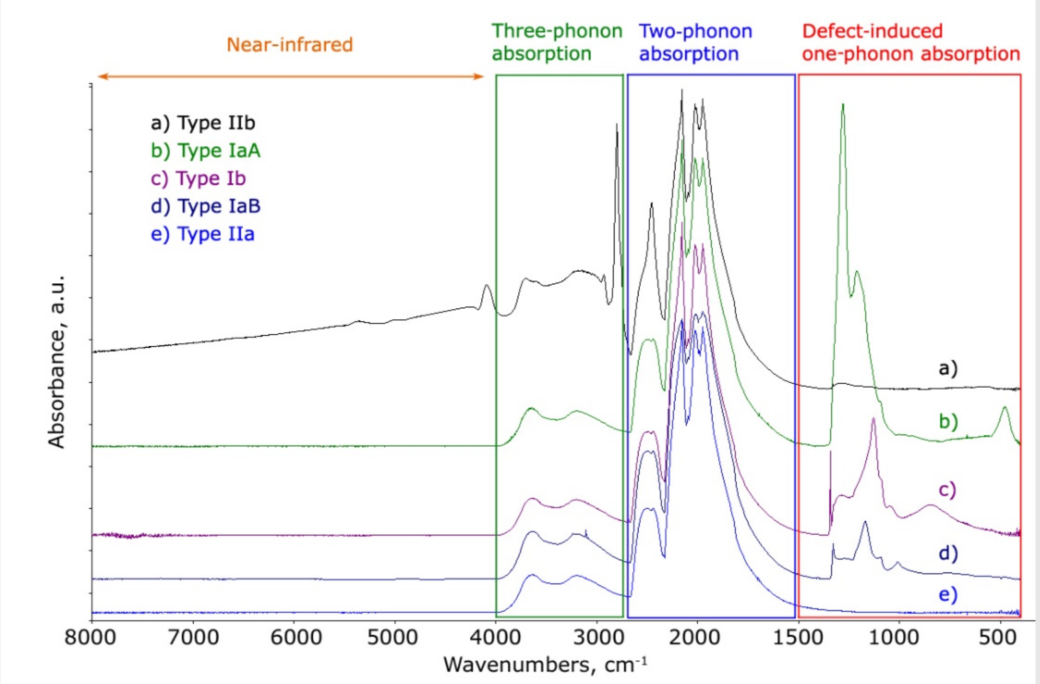
Pale pink morganite → deep orangey pink

Strongly bluish emerald → more pure green (yellow colour)


DIAMOND

What are Defects? Example N and B in Diamond: The Type System

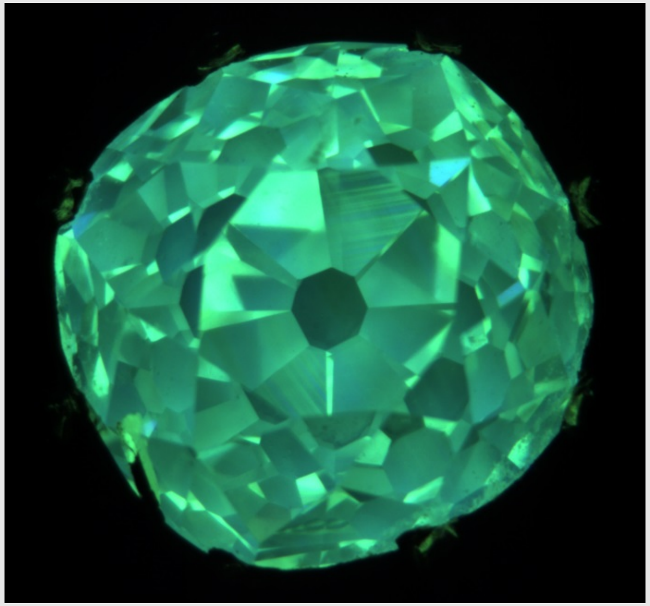


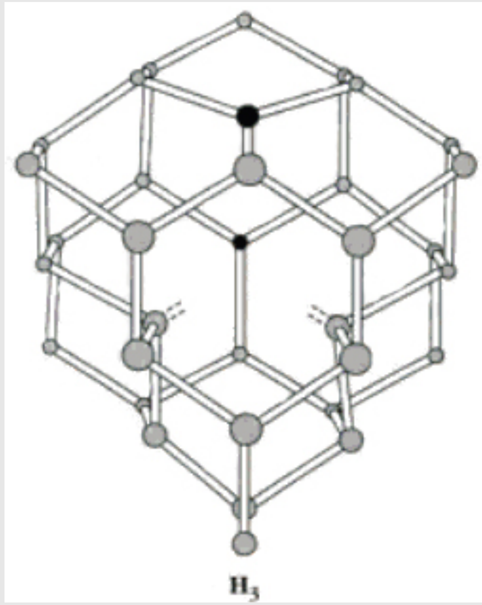


Source: Breeding and Shigley, 2009

Example of Colour-Causing Defect in Diamond: The H3 Centre

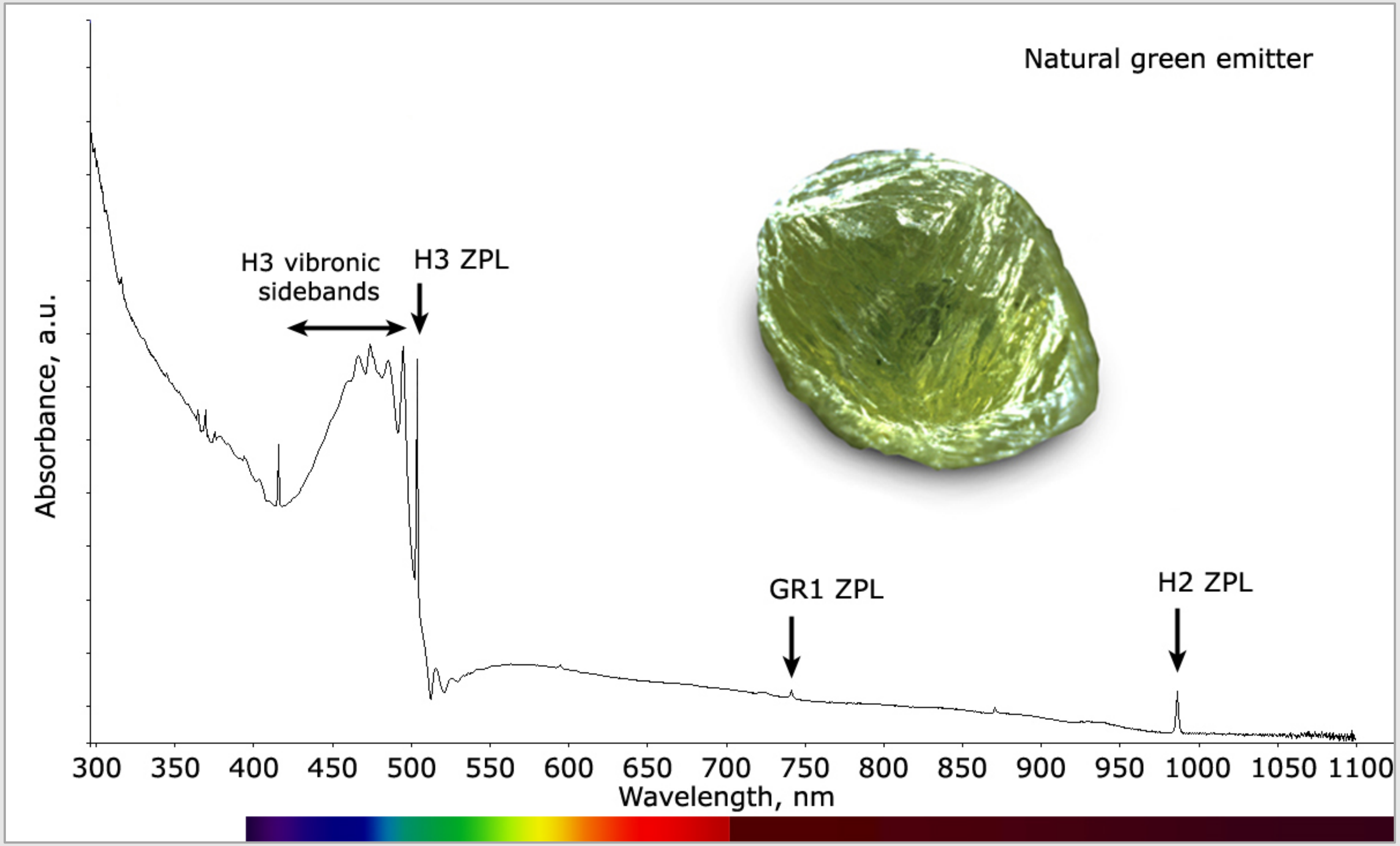
Apparent color by absorption + luminescence



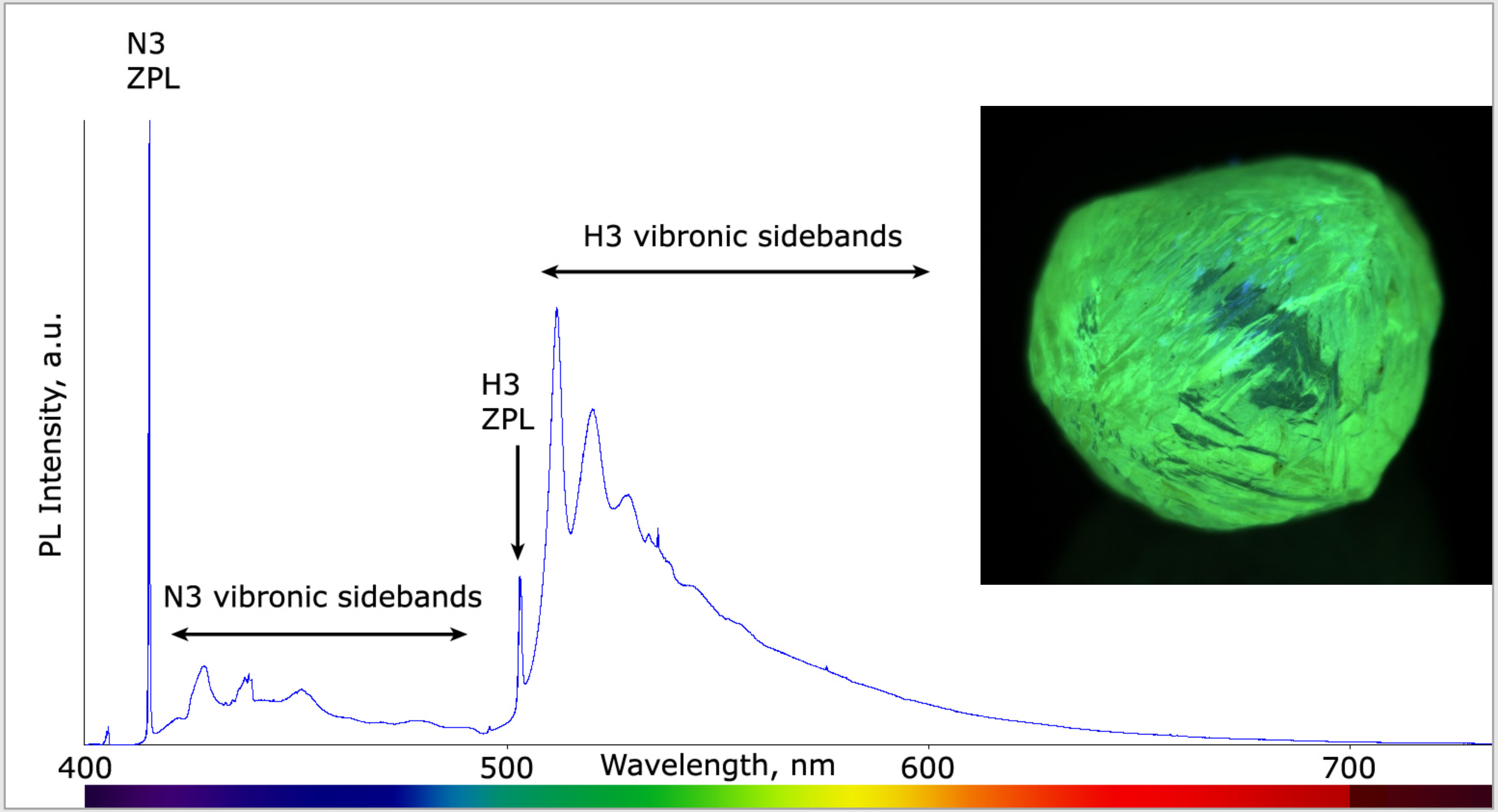


Adapted from Bursill and Glaisher, 1985

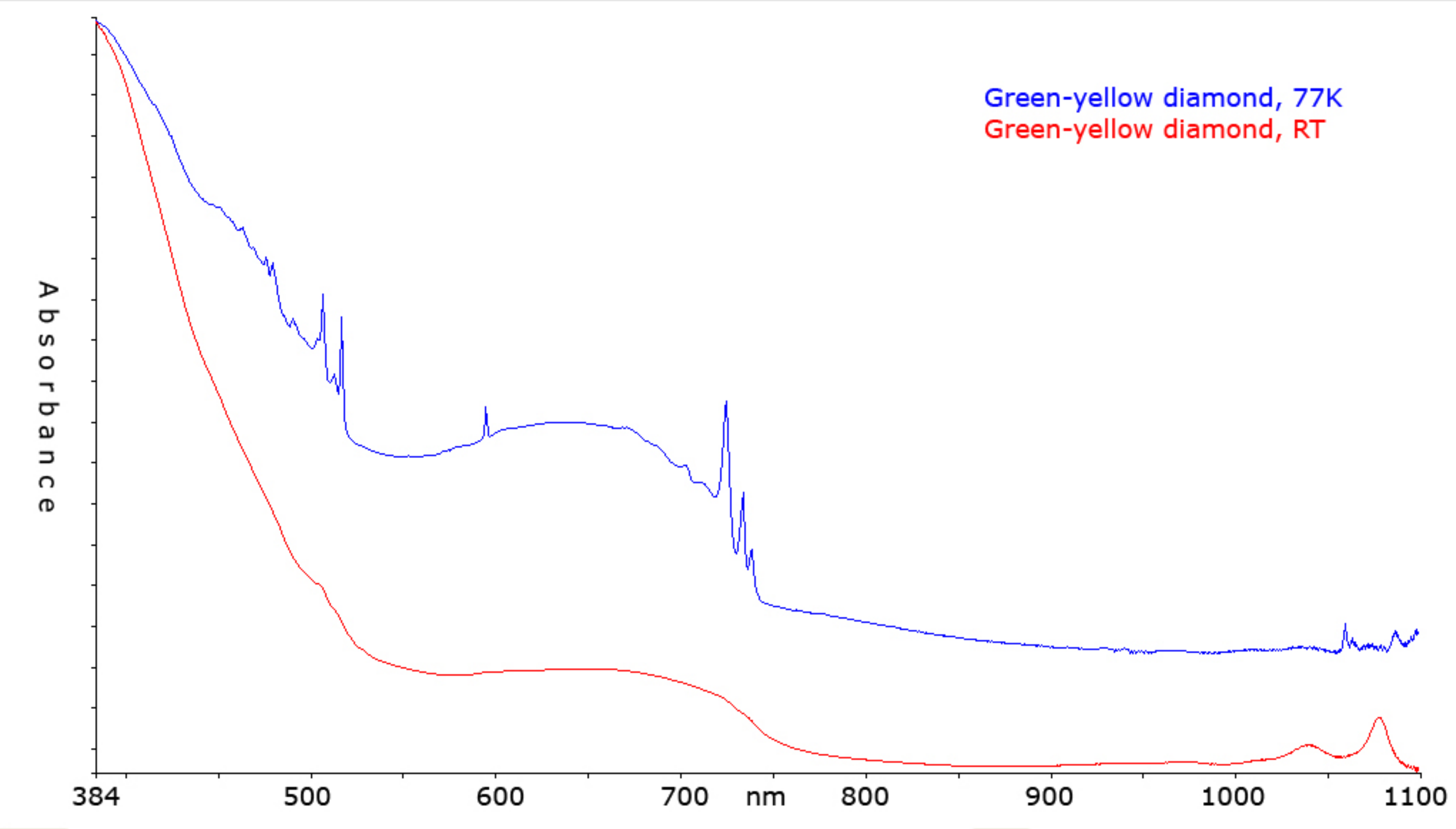
Absorption by H3 defect: yellow color



Emission by H3 Defect: Green Luminescence



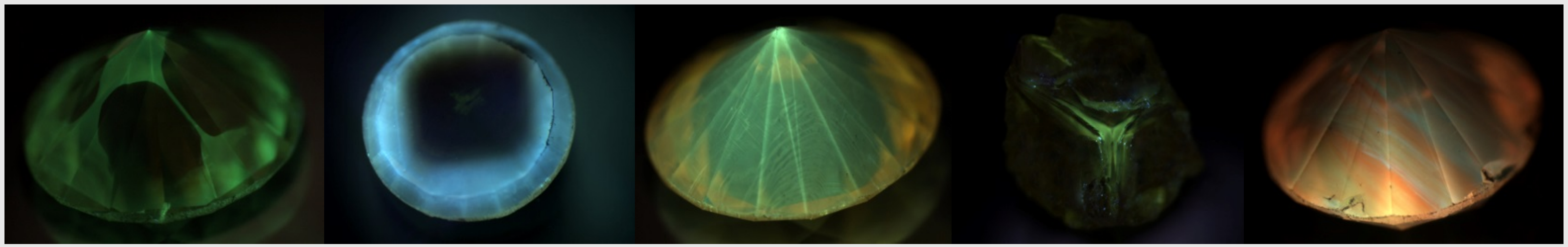
UV-Vis-NIR – Why low temperature?



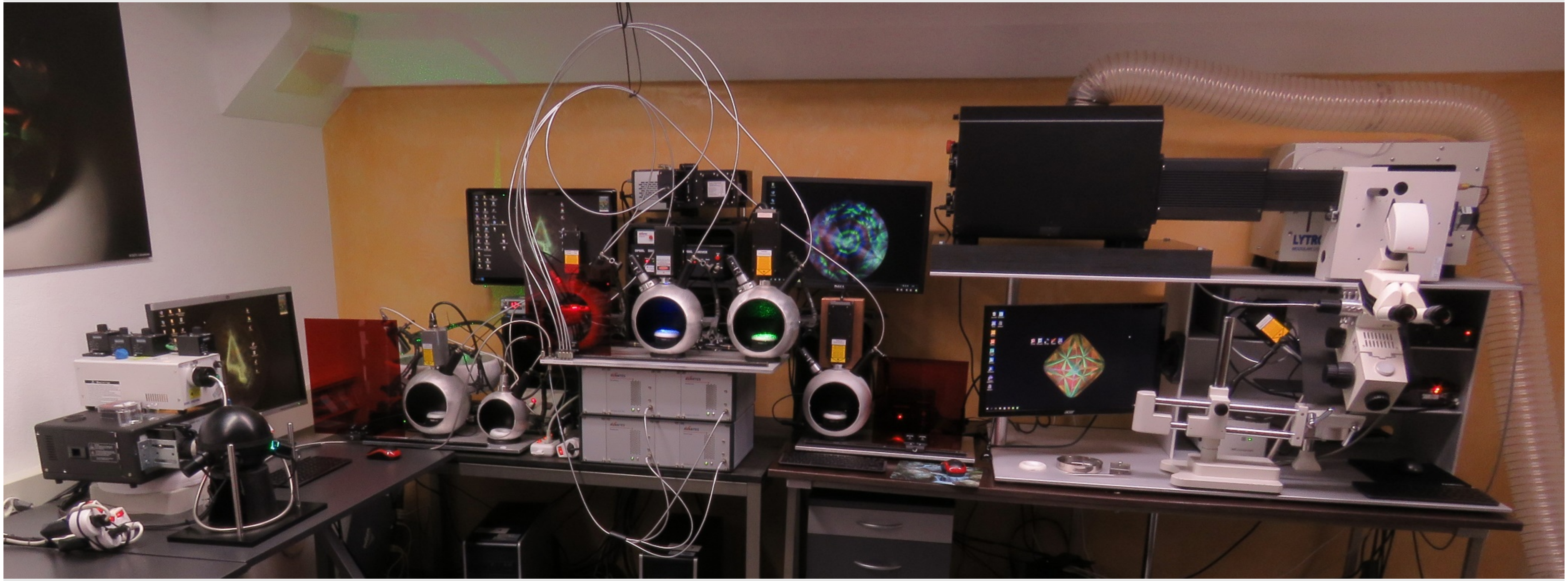
ID of Authenticity + Colour Origin of Diamond

Thanks to the many defects and its large band gap diamond shows an incredible variety in absorptions and emissions that we can measure by spectroscopy and observe by imaging (luminescence only).

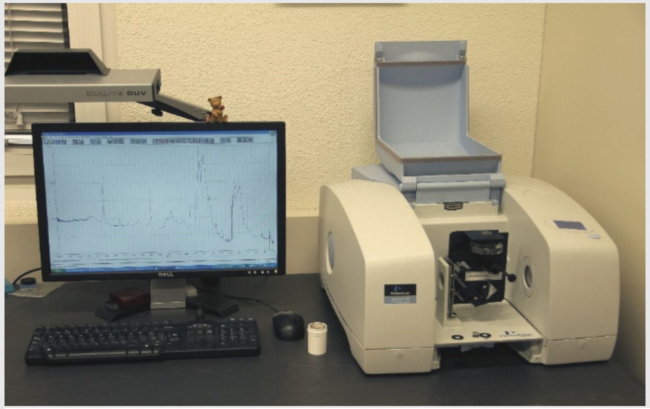
→ UV-Vis-NIR spectroscopy
→ IR spectroscopy
→ Photoluminescence spectroscopy
→ Fluorescence imaging

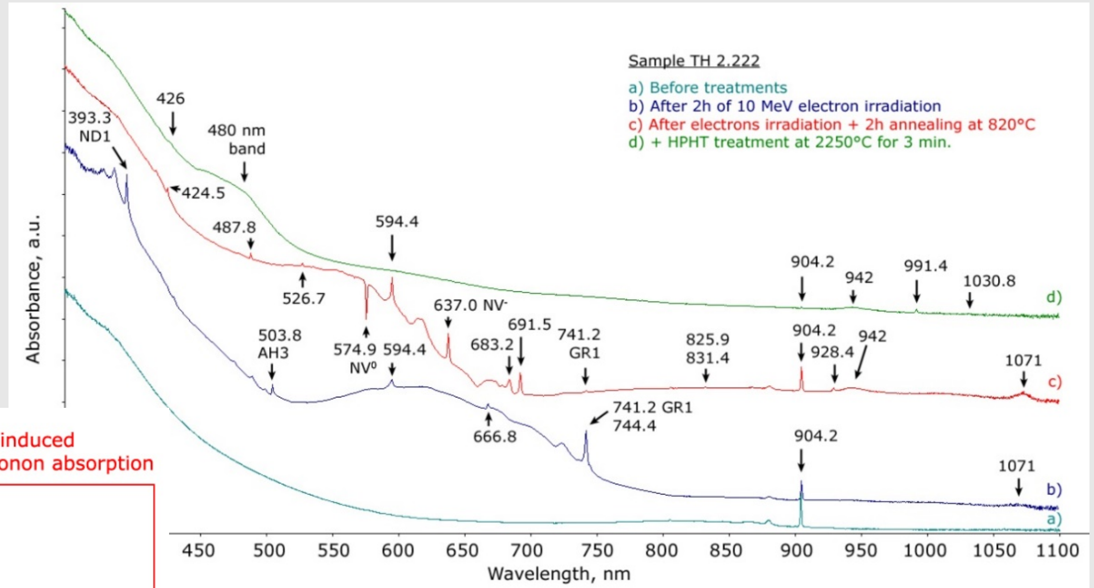


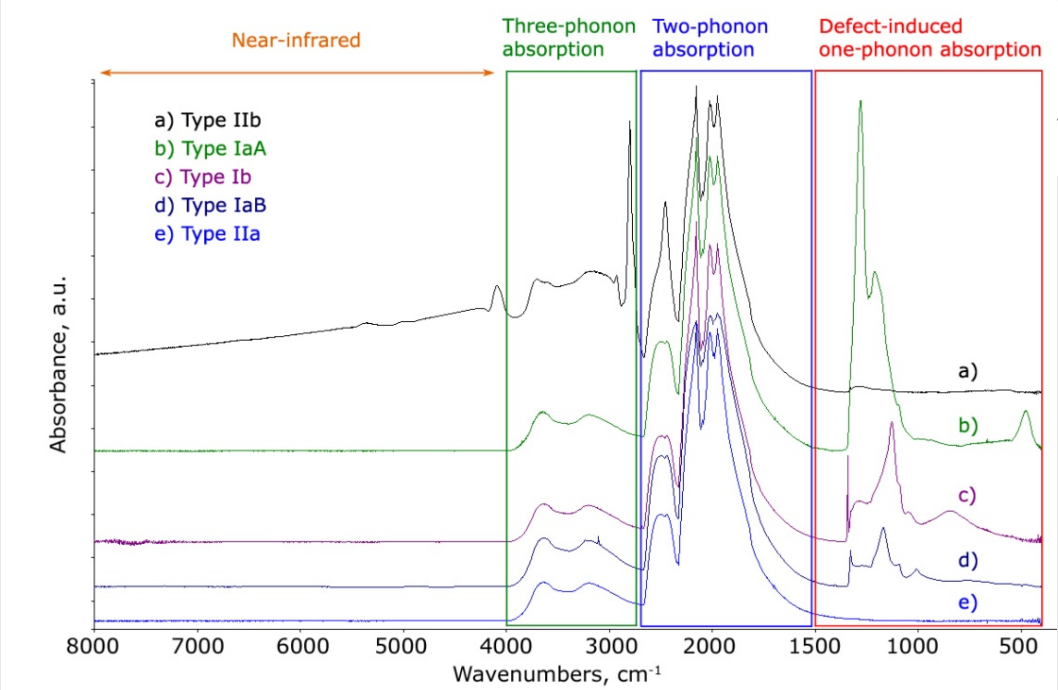
The Equipment

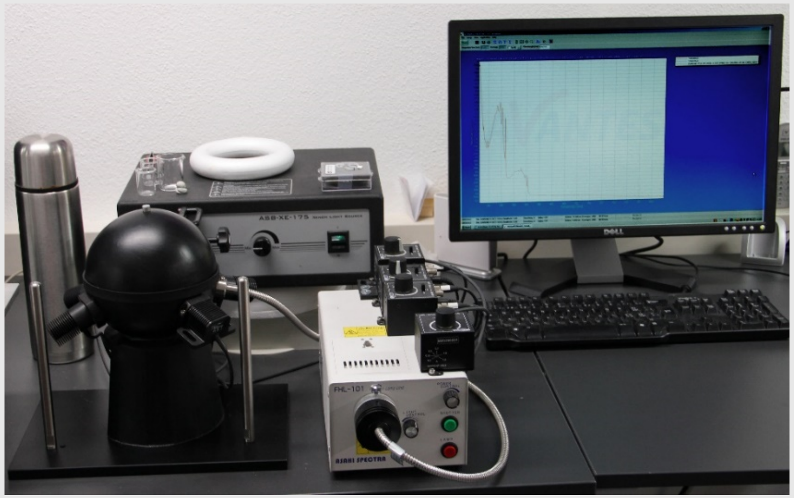


Absorption: Infrared and UV-Vis-NIR Spectroscopy

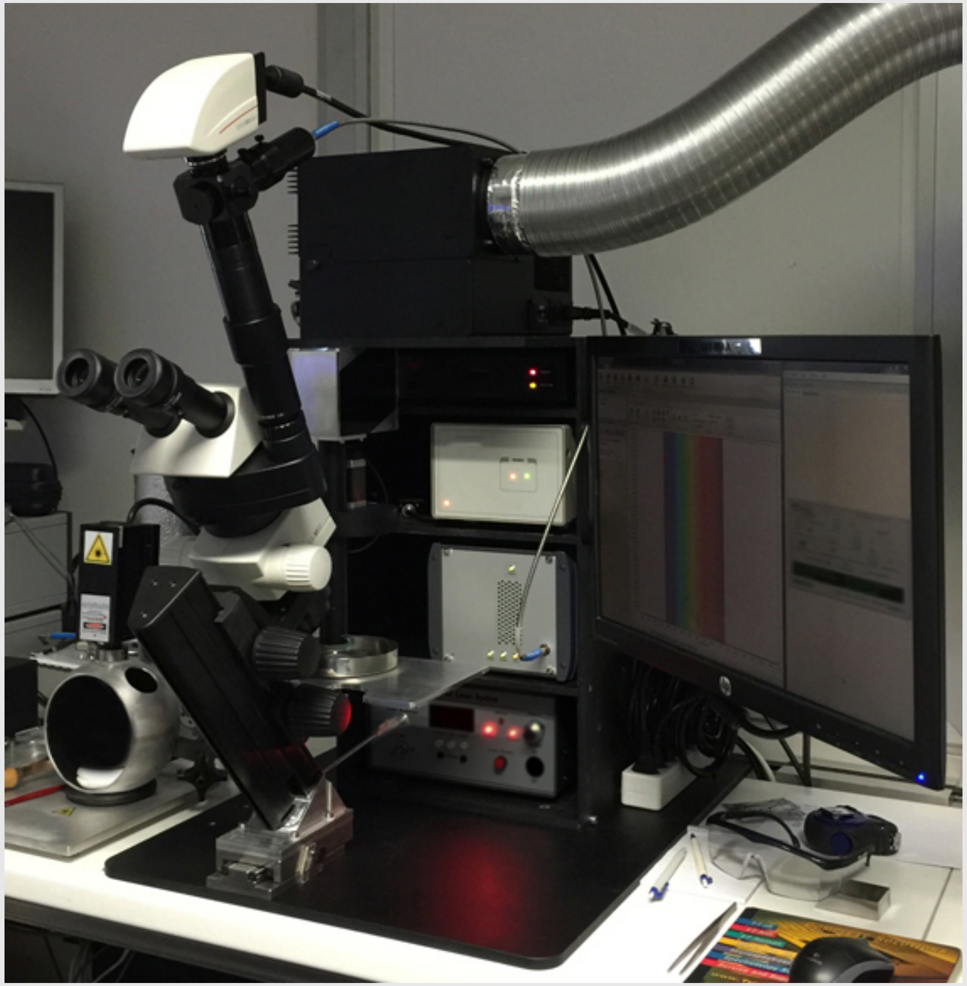


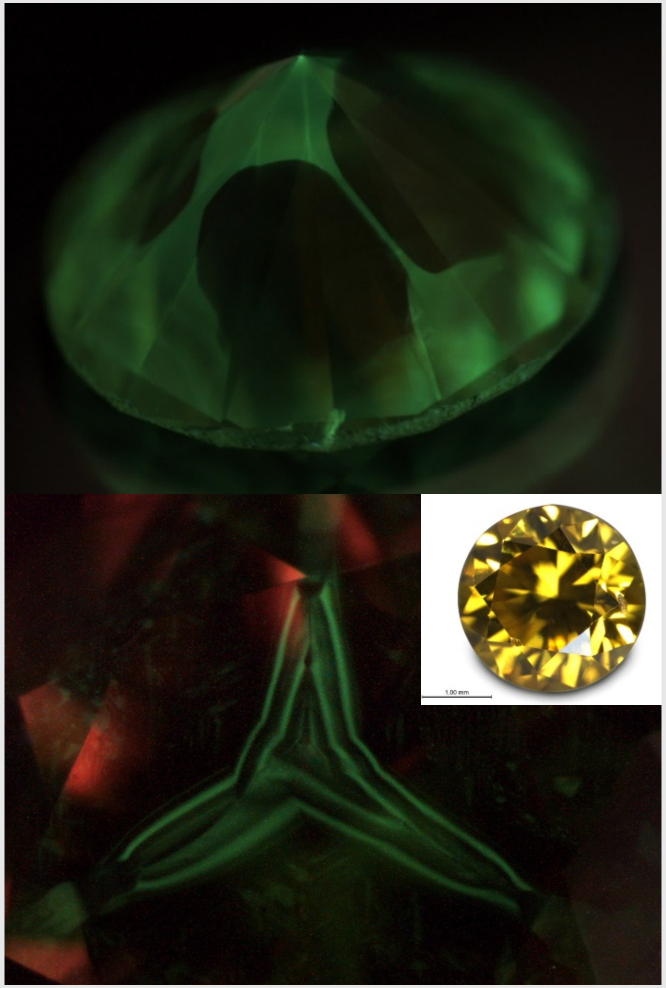




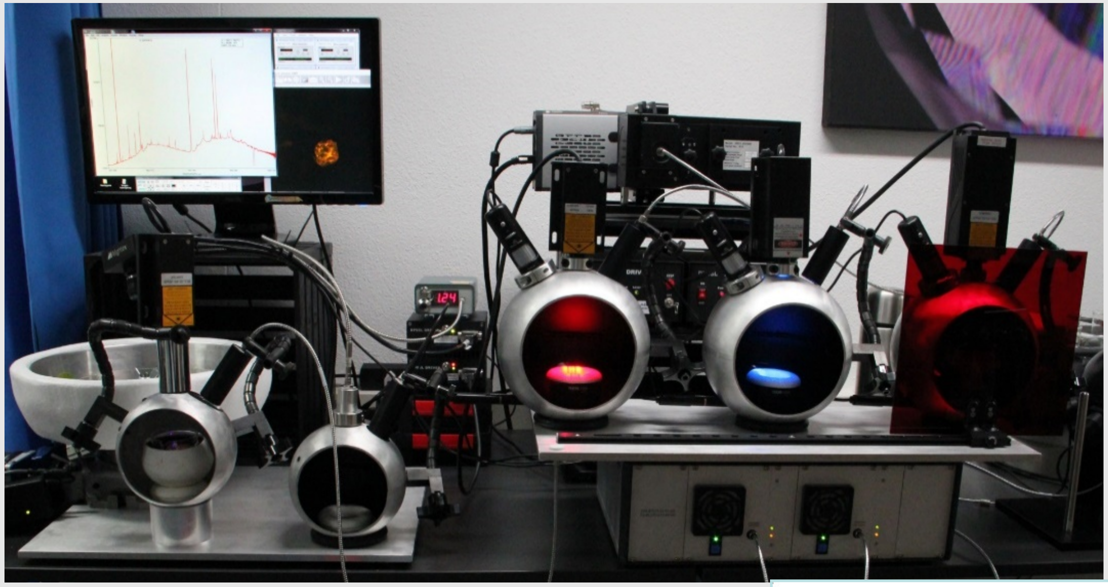


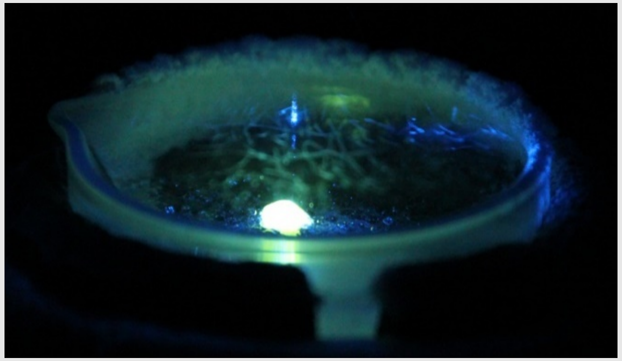
Fluorescence microscopy with PL and Raman

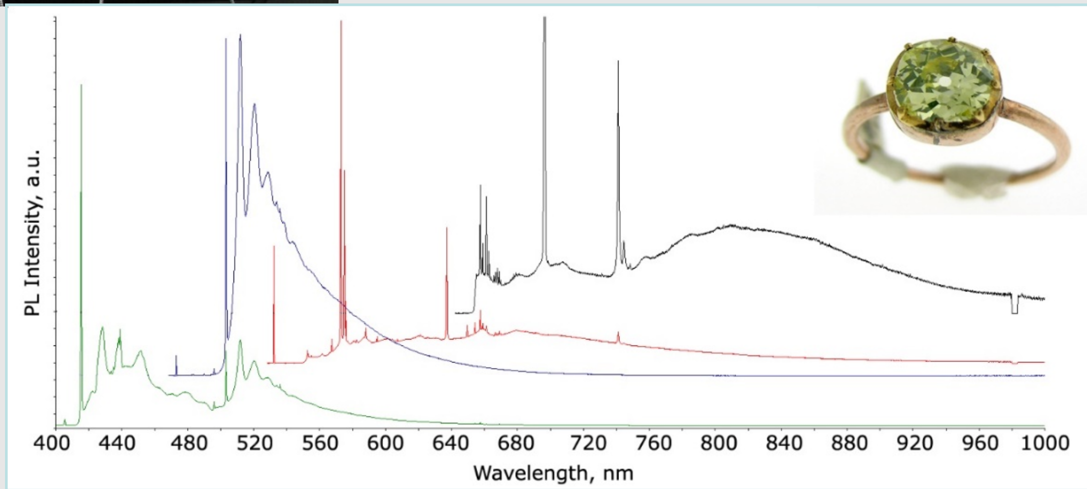




Photoluminescence spectroscopy

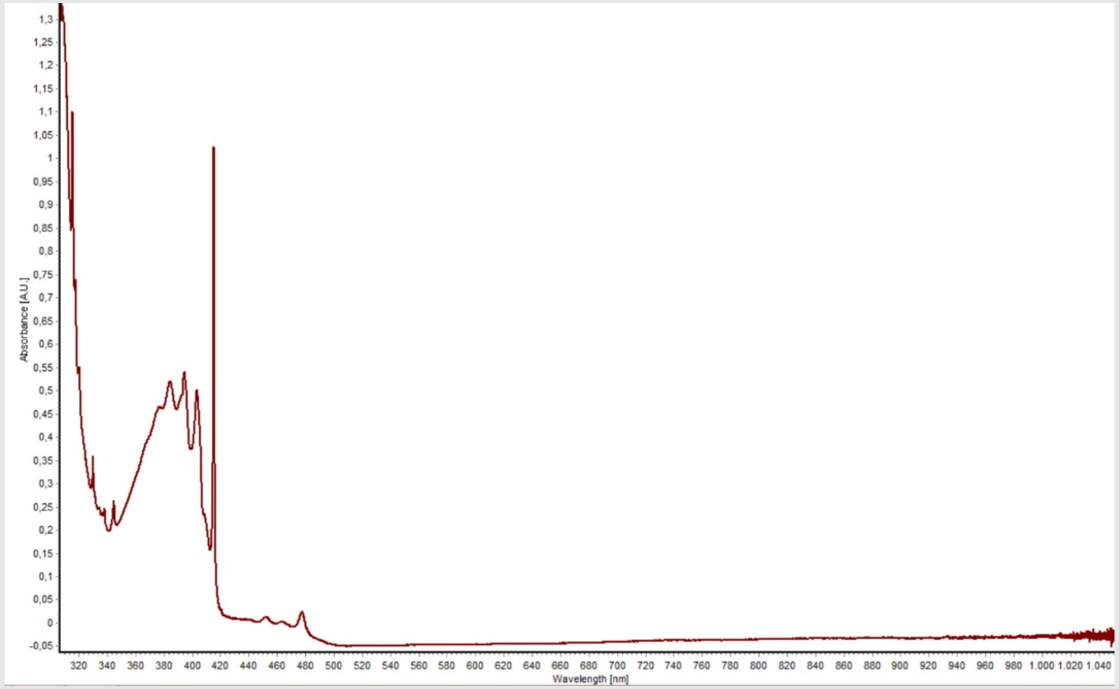




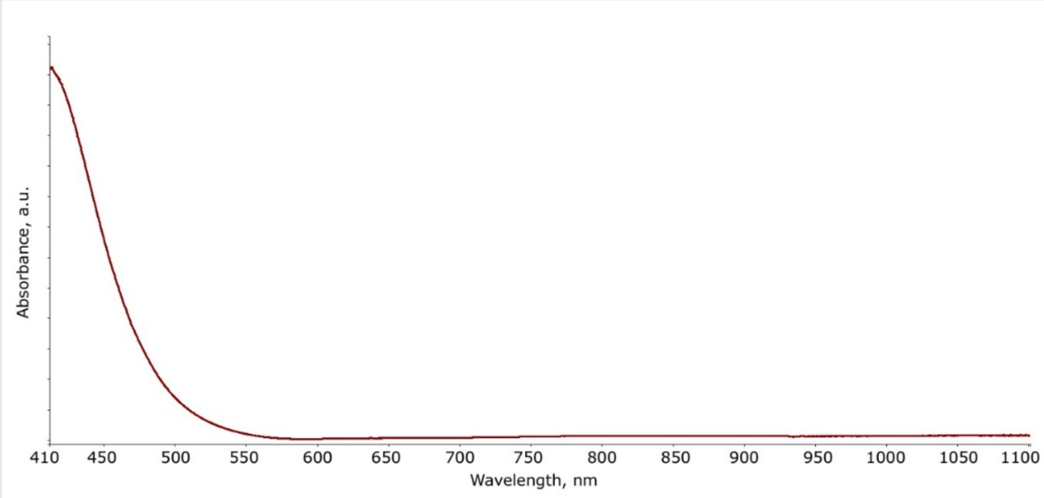


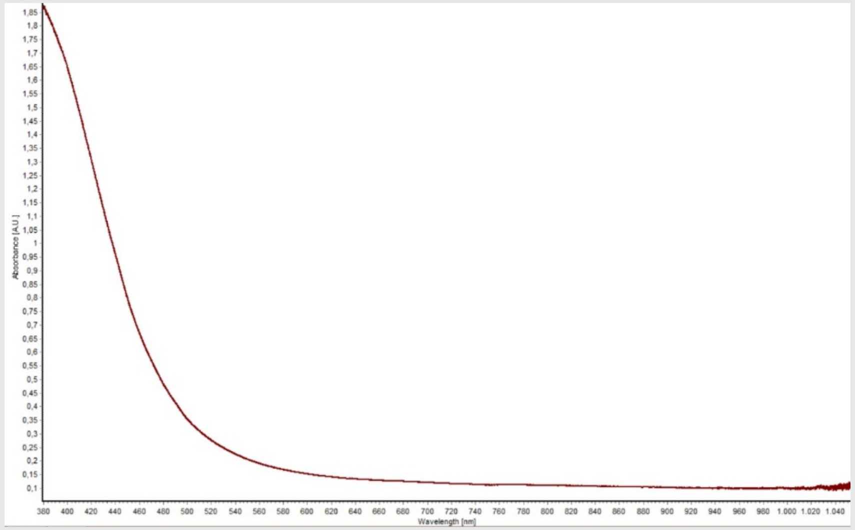
The Colours and Colour Causes of Untreated Natural Diamonds

«Cape» Yellow Diamonds

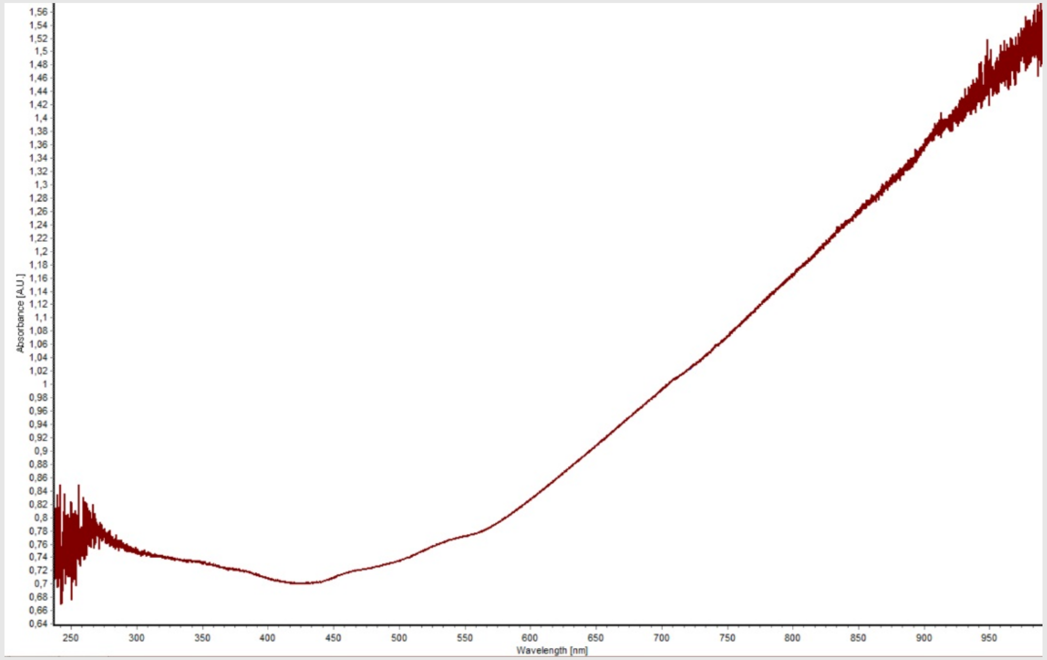


«Canary» Yellow Diamonds

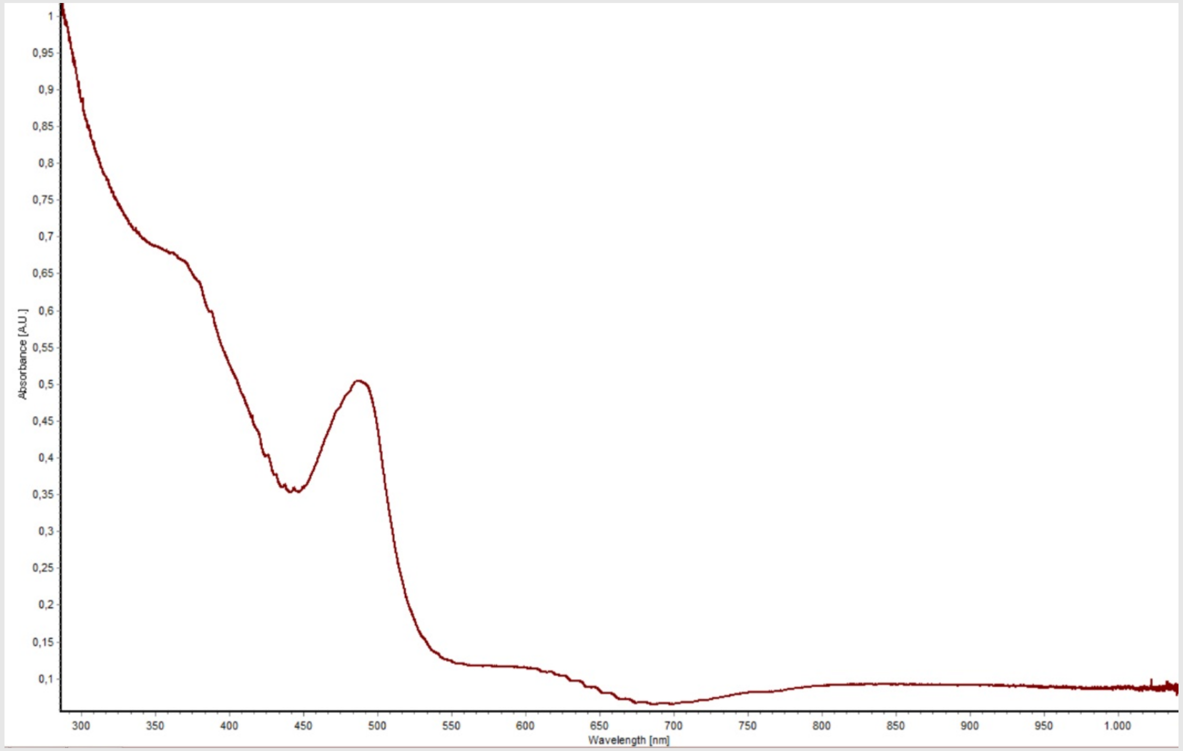




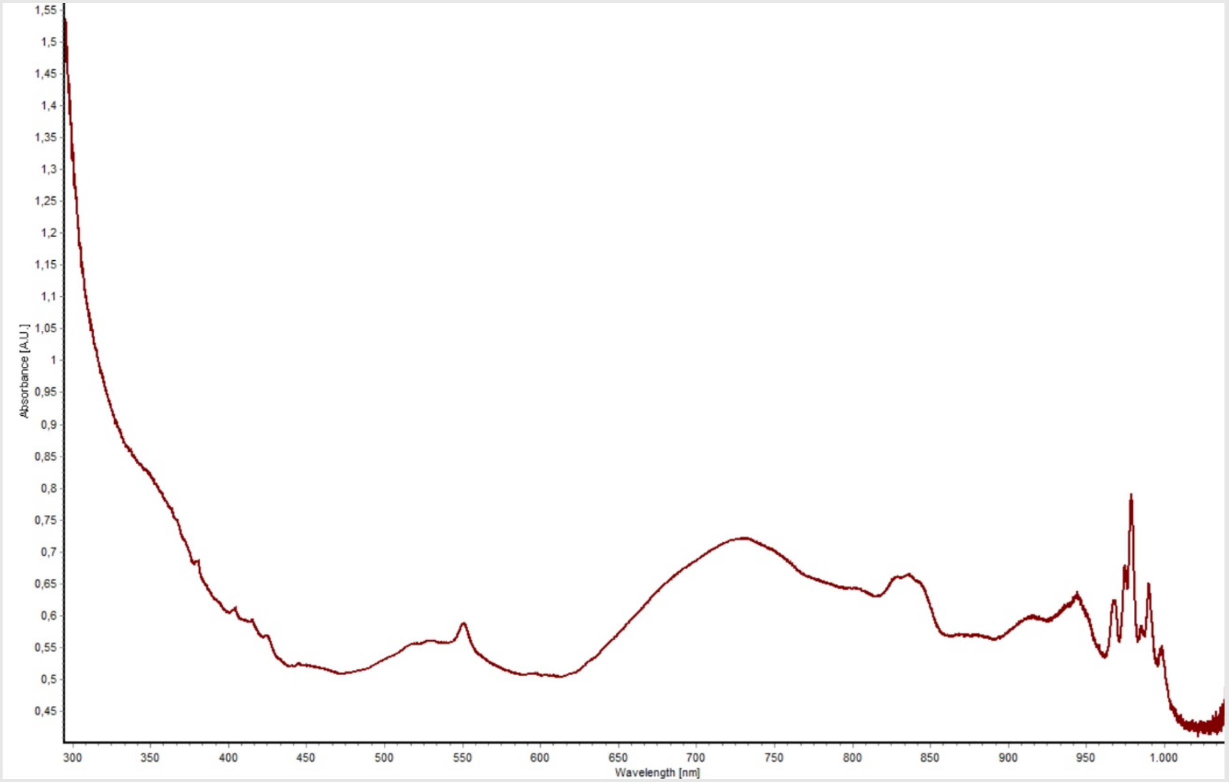
Type IIb Blue Diamonds



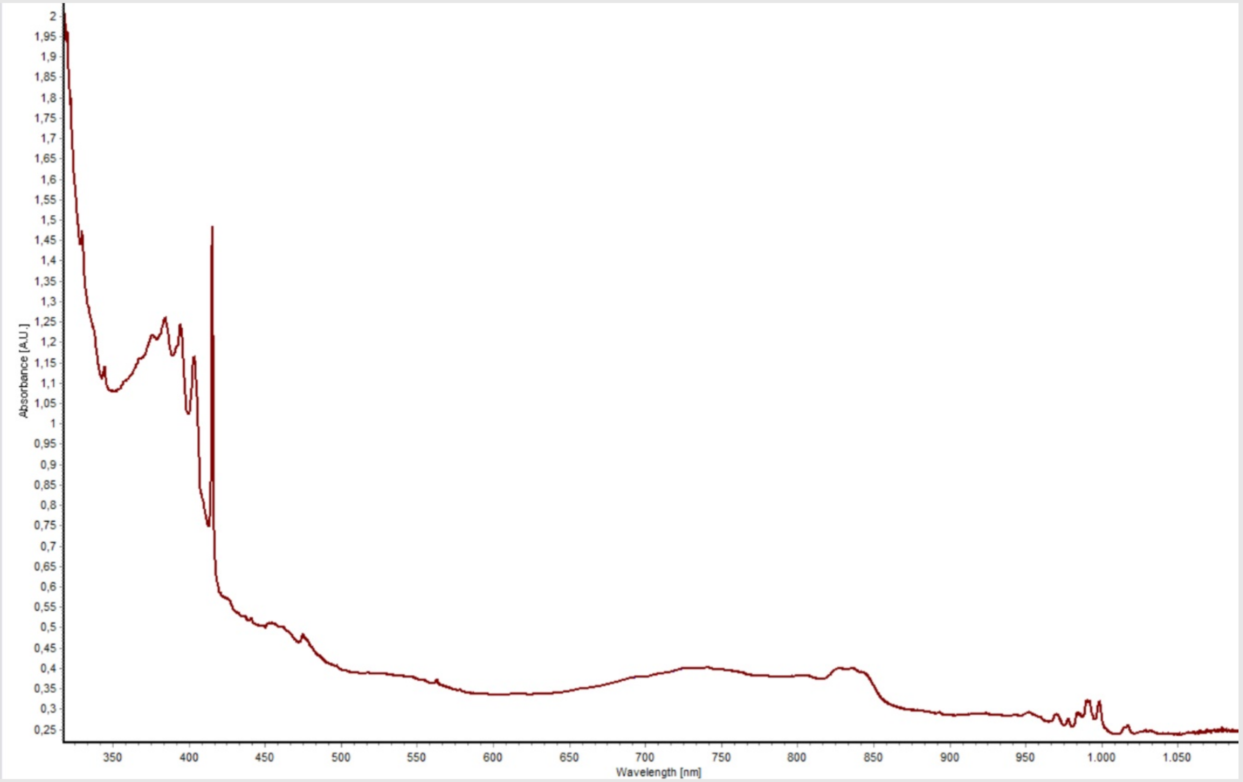
Orange to Pink Orange «480 nm» Diamonds



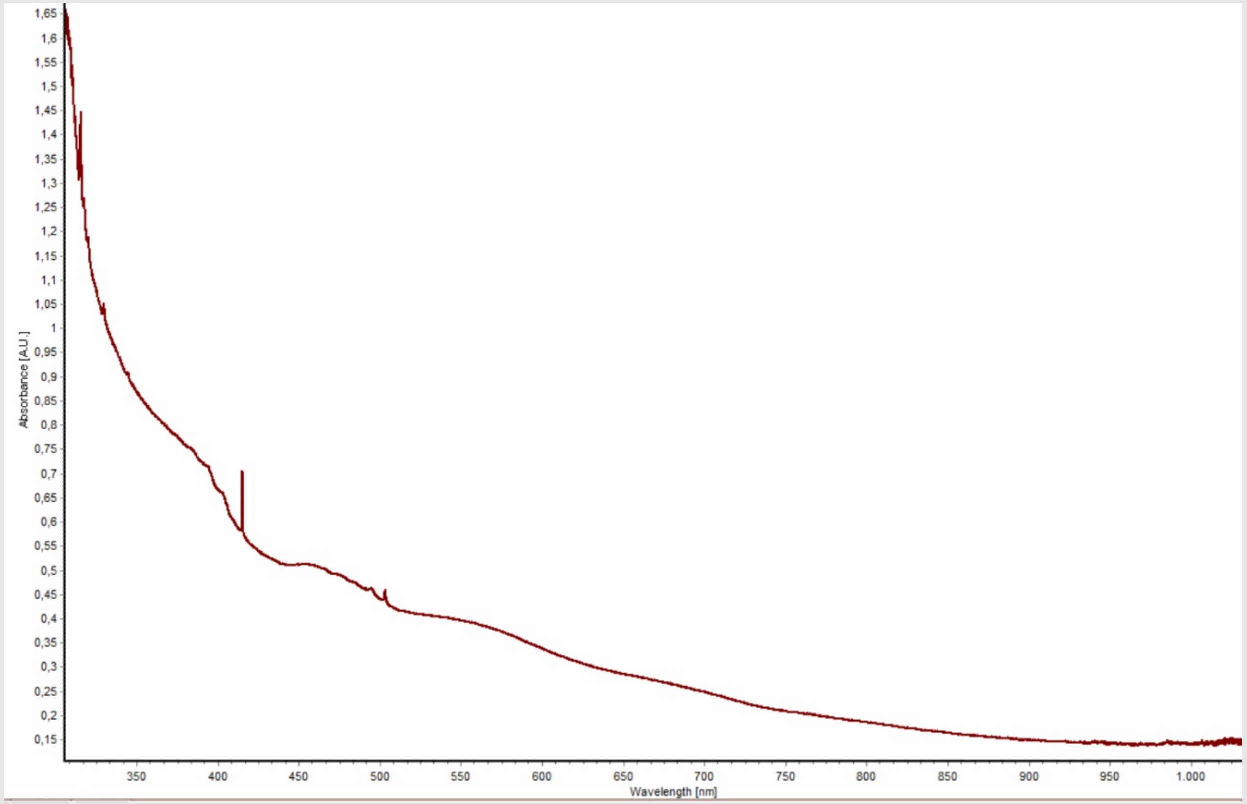
Violet Diamonds



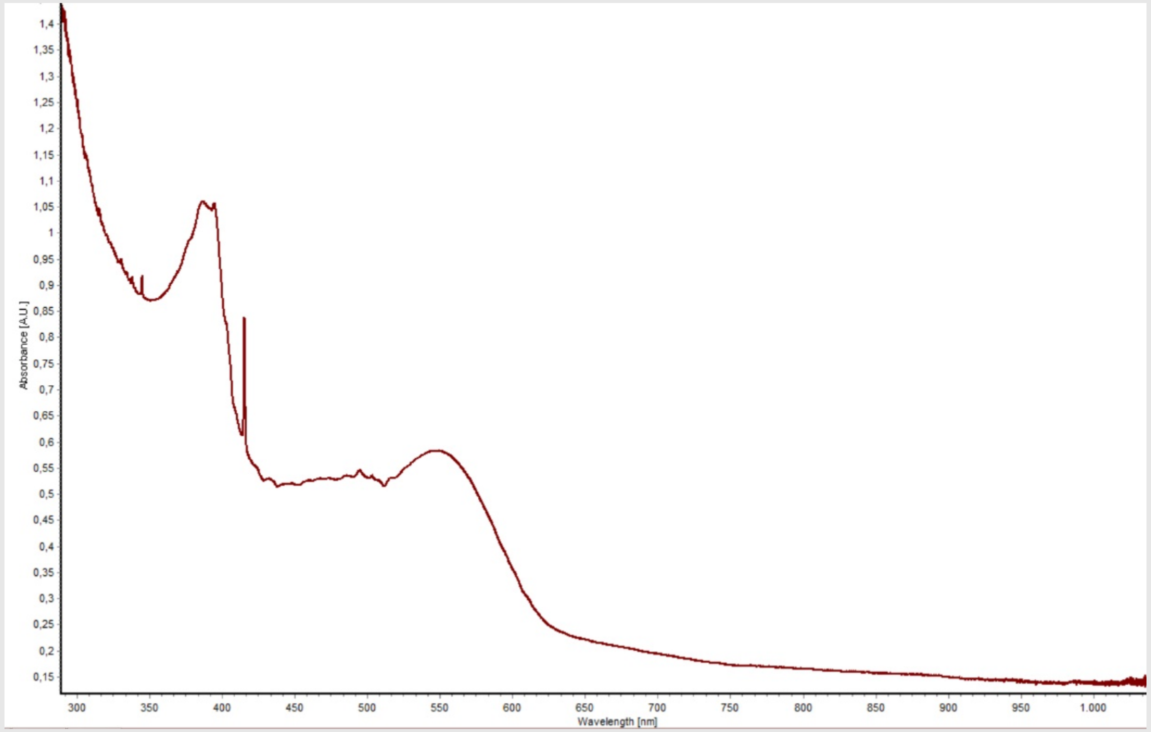
«Olive» Diamonds



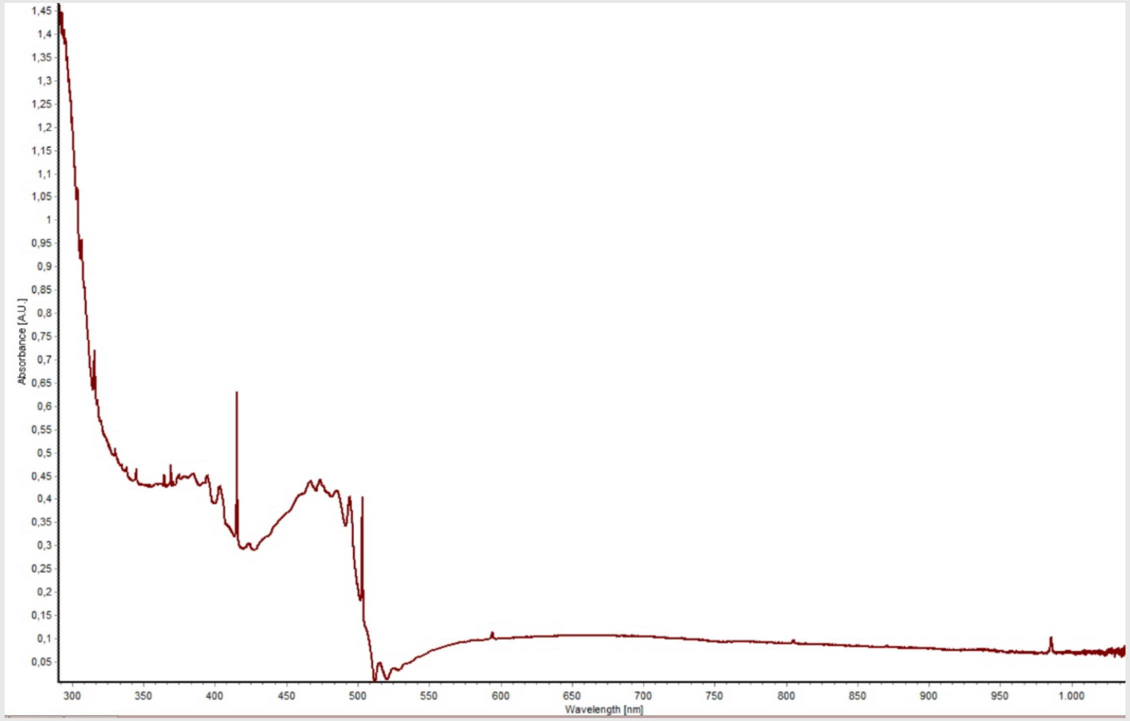
Brown Type Ia Diamonds



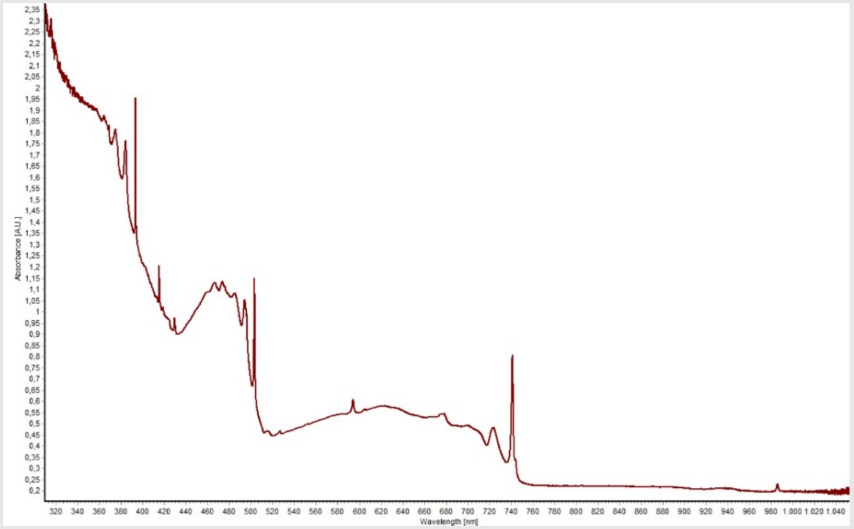
Purplish pink to red Diamonds

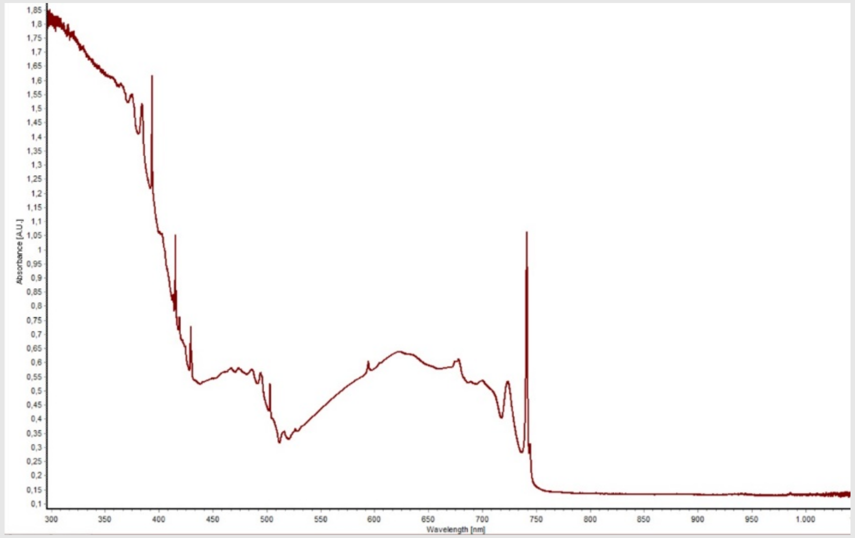


«Green Emitter» Diamonds



Green to greenish blue Diamonds





The Colours and Colour Causes of Treated Natural Diamonds

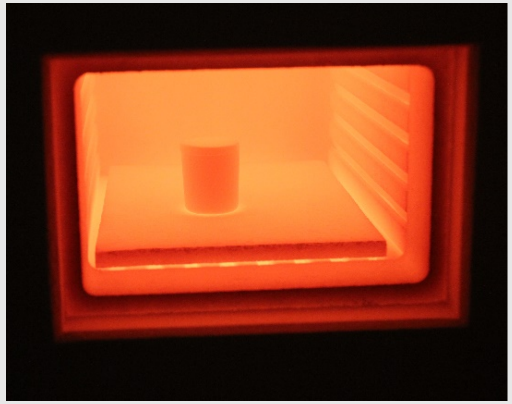
Treatments to Modify the Colour of Diamond

1) Annealing under inert atmosphere
2) Irradiation by high energy particles (electrons, neutrons, protons etc.)
3) Irradiation followed by annealing (600 to 1000°C)
4) HPHT (High Pressure High Temperature) treatment (1900 to 3000°C)
5) HPHT followed by irradiation/annealing
6) Irradiation followed by HPHT treatment
7) Coating (Not covered in this presentation)

Treatment Methods:
Electron Irradiation, HPHT Treatment and Annealing

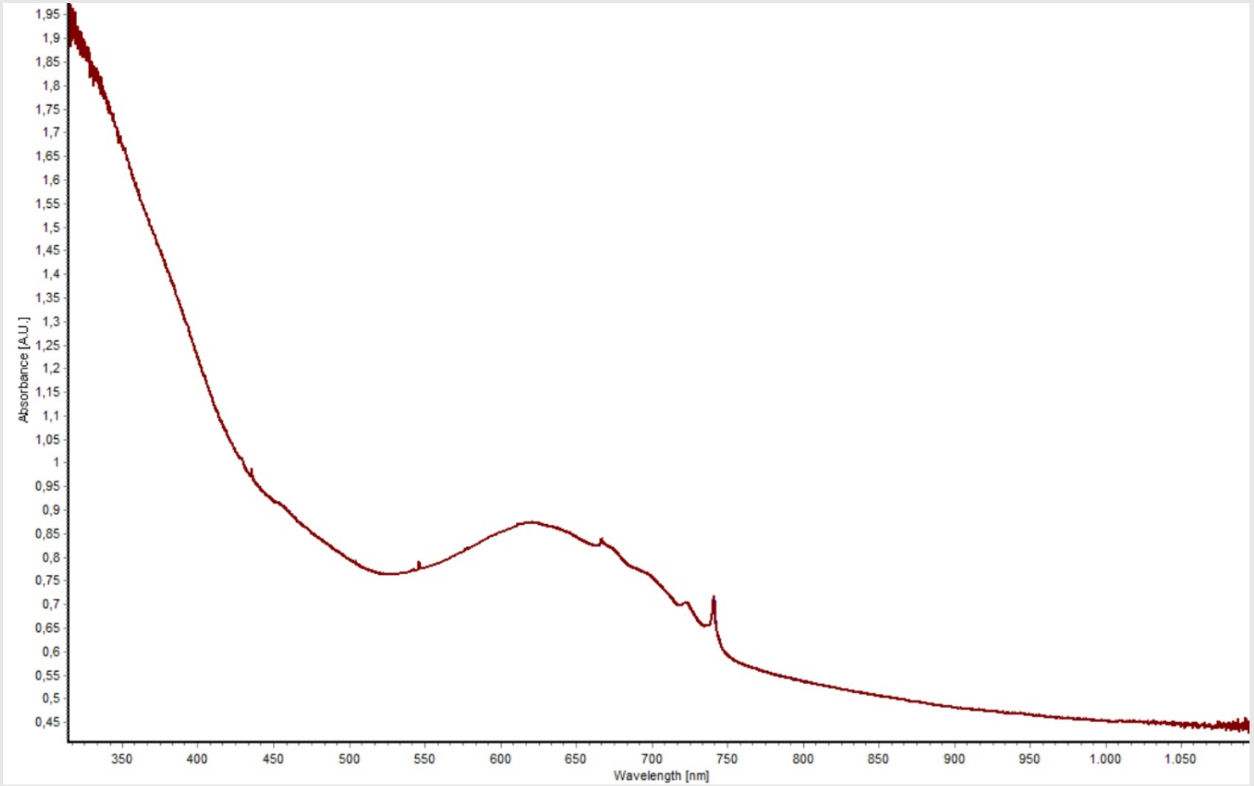
Two electron accelerators that have been used for the irradiation treatment of diamonds by GGTL

A Torroid type HPHT press used for HPHT treatment of diamonds by GGTL



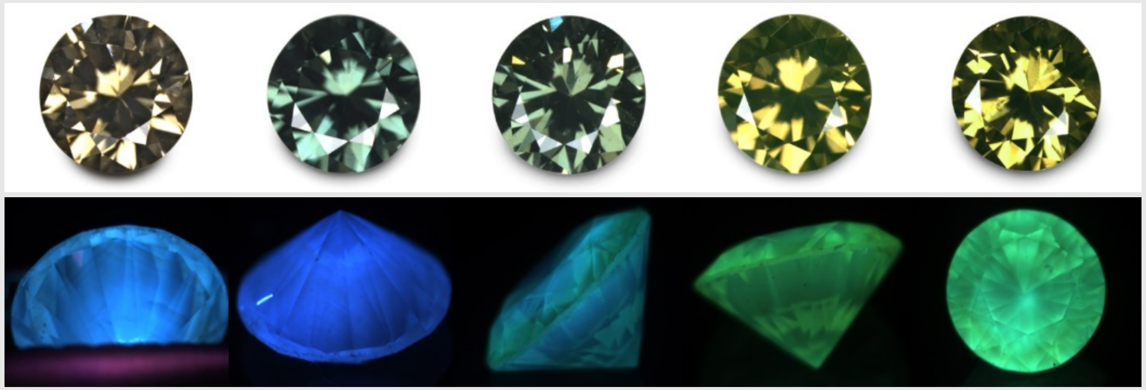
A high T° oven used by GGTL for annealing treatments up to 1310°C

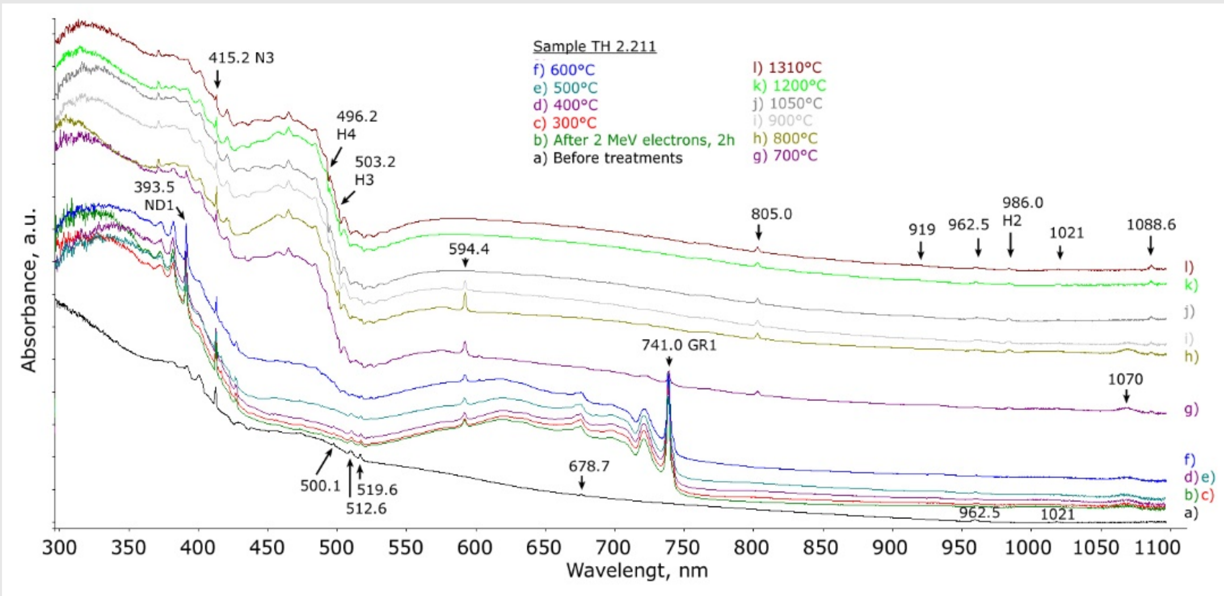
Treated Green Diamond: Irradiation



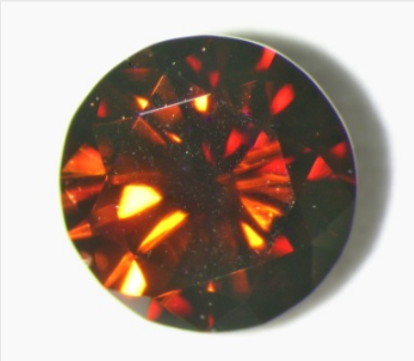
Treated Blue + Yellow Diamond: Irradiation (+ HT)

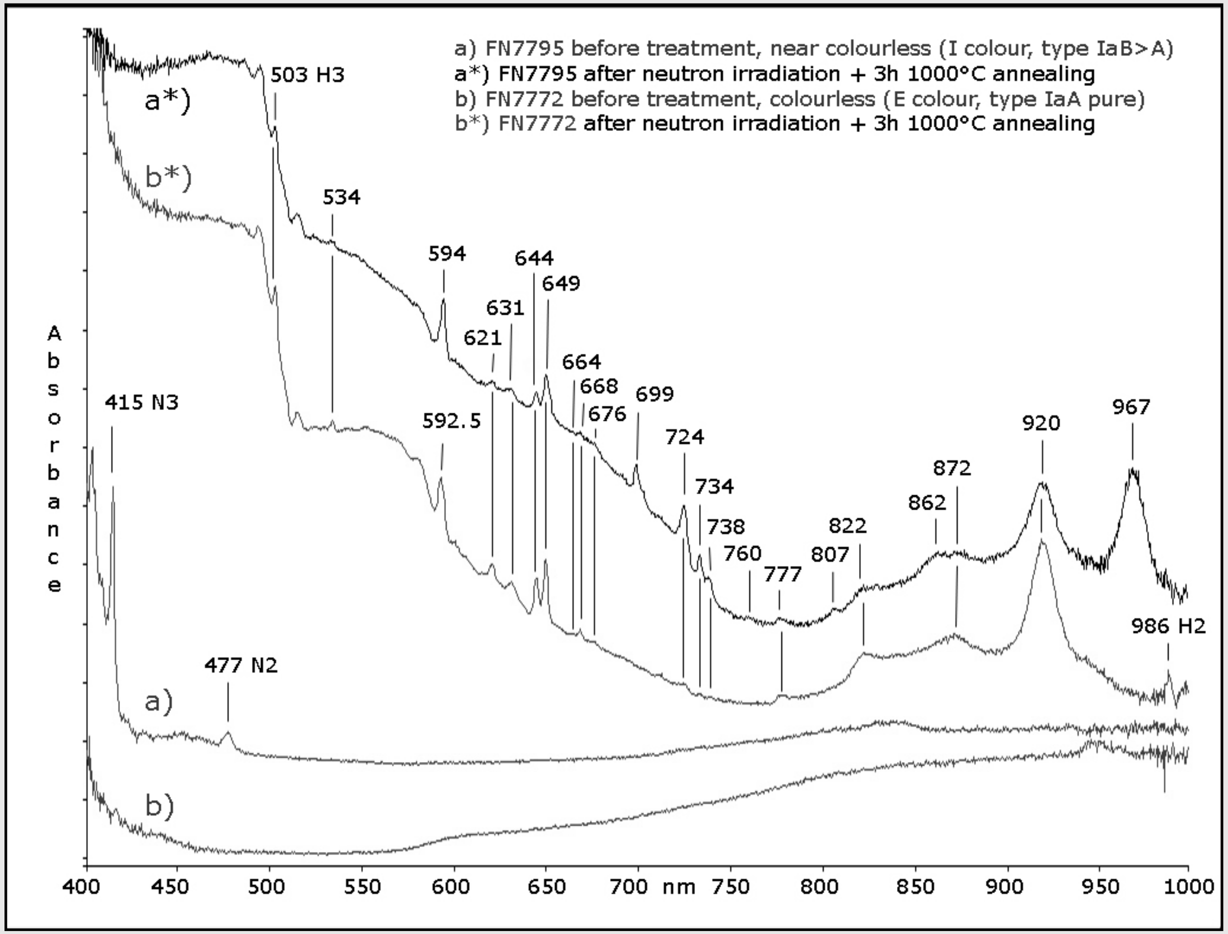
Untreated Irradiated 600°C 700°C 1310°C





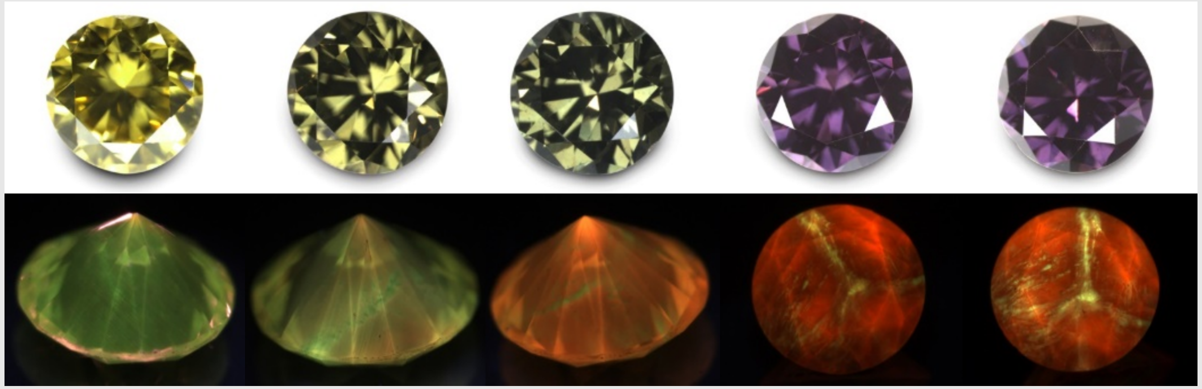
Treated Orange Diamond: Irradiation + HT

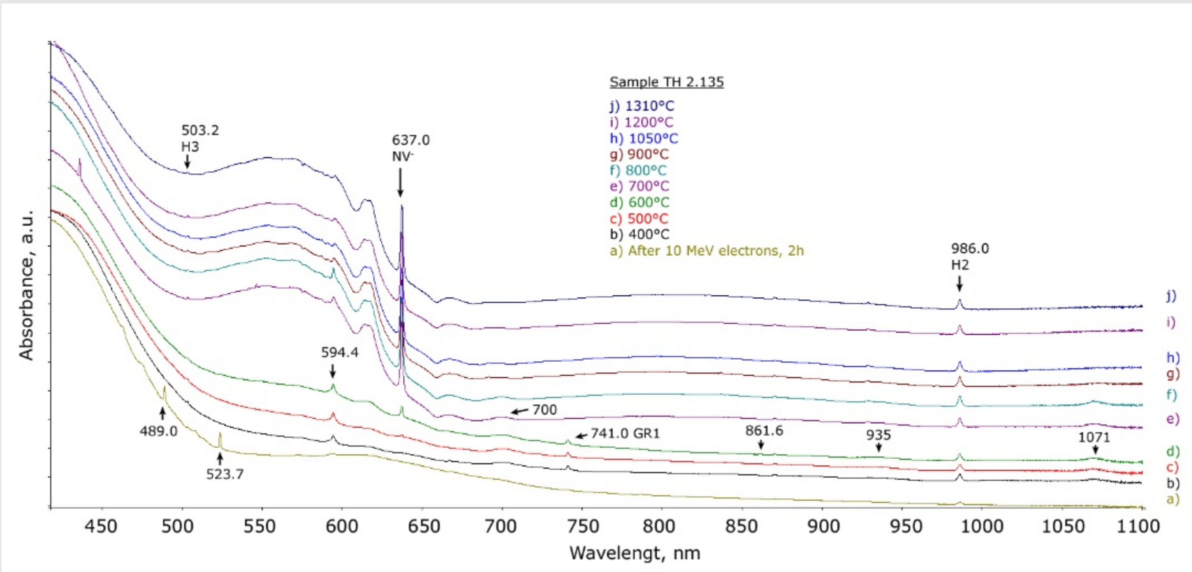




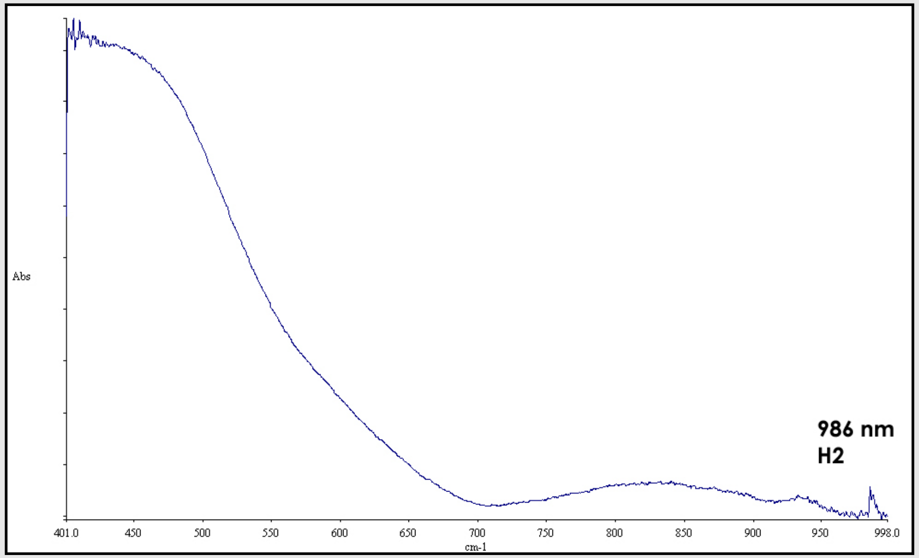
Treated Purple Ib Diamond: Irradiation + HT

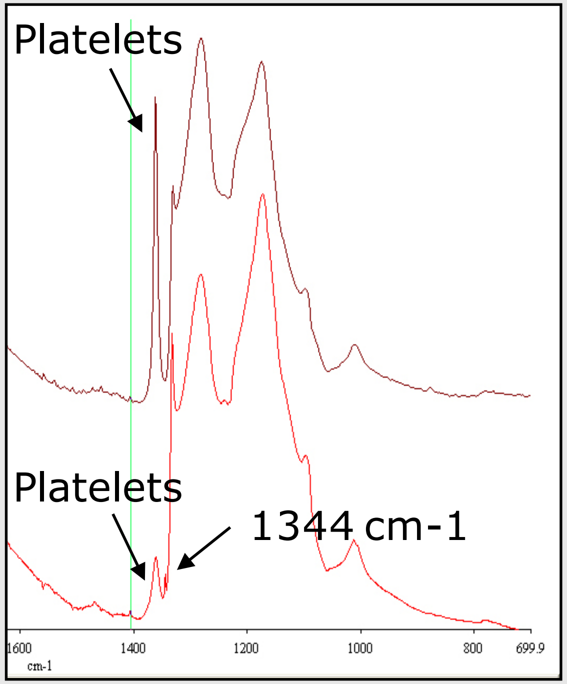
Untreated Irradiated 600°C 700°C 1310°C



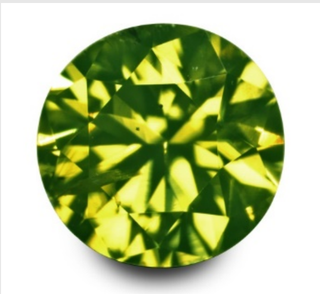


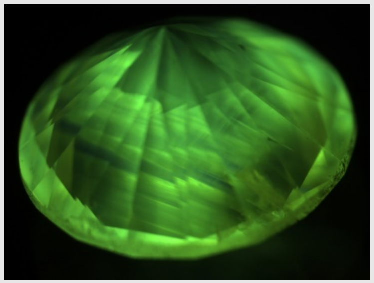
Treated Yellow Diamond: HPHT

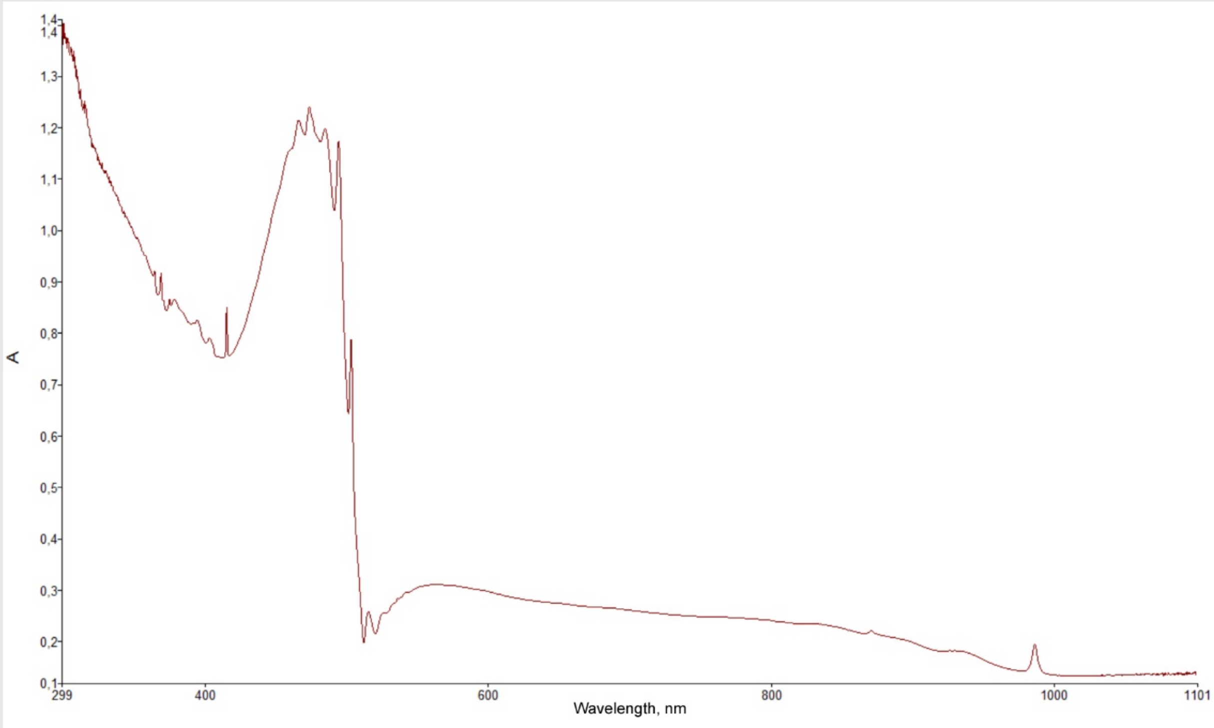




Treated «Green Emitter» Diamond: HPHT







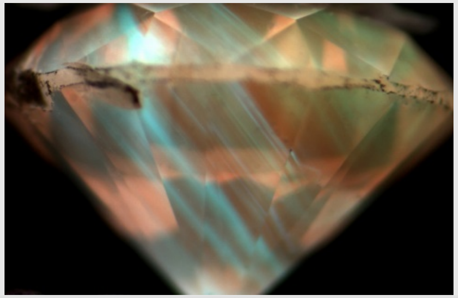
HPHT Treated Type IIb Natural Diamonds

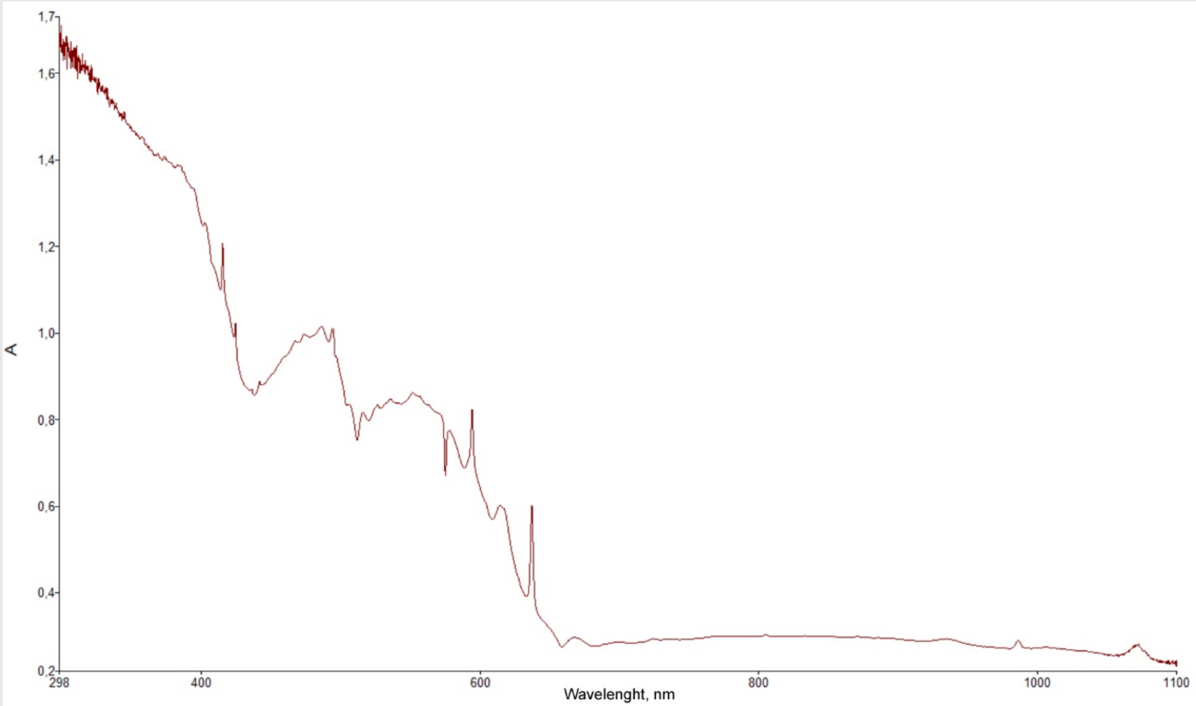
Type IIb gray olive diamond

10 Min 2500°C

Type IIb blue diamond

Treated Pink Ia Diamond: HPHT + Irradiation + HT





SUMMARY + CONCLUSIONS

- Gem materials are coloured by various mechanisms and generally through many different chromophores and/or defects.
- For many gemstones, the colour can be modified via treatment, with the goal to make them more attractive and hence valuable.
- These treatments are often processes that can also occur in nature and can hence be very difficult or even impossible to identify.
- The colour causes can often be defined based on UV-Vis-NIR spectroscopy.
- Diamond is the only material in which an astonishing quantity of absorptions and emission can be directly measured by spectroscopy, that help to identify the authenticity and origin of colour.
- In most other gems the treatments are not identifed through UV-Vis-NIR absorption spectroscopy but other methods must be used.