Invited public lecture:

When gemstones glow: emission phenomena of diamond, ruby, sapphire & Co

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Who is not familiar with white glowing teeth and t-shirts under the ultraviolet lamp typically installed in discotheques and clubs: the observed glow – better called "emission" – is universally known as "luminescence". Luminescence is a phenomenon that occurs when the electrons of a material rise from their ground state into an excited state by various mechanisms such as absorption of electromagnetic radiation, and then return back to their ground state. The energy that is being lost when the electrons return to their ground state can either be lost via radiative processes (luminescence [photons]) or via non-radiative processes (molecular vibrations [phonons]). Such electronic transition processes occur from the UV (ultraviolet) to the near infrared, hence there is visible and invisible luminescence. When the emission is caused by absorbed electromagnetic radiation and when it occurs together with the excitation then we talk about "fluorescence" or "photoluminescence"; when the emission occurs after the excitation has been turned off then we talk about "phosphorescence" (an afterglow).

Luminescence can be excited in a variety of ways, but UV light is the most widespread source to excite visible emissions. The UV range extends from about 40 to 400 nm, it hence comprises wavelengths longer than X-rays but shorter than visible light. In practical life only the wavelengths from about 185 to 400 nm are useful, because the shortest UV wavelengths are ionizing and strongly absorbed by nitrogen and di-oxygen. While simple 365 nm (LW, long wave) and 254 nm (SW, short wave) lamps are used to visually observe luminescence, more sophisticated and powerful microscopic methods are employed to excite luminescence with various wavelengths of high intensity UV to visible light. With such microscopic methods great details of luminescence colour and distribution can be analysed and samples can be characterized much better than by just using a regular UV lamp.

Another popular way to excite luminescence is via accelerated – hence highly energetic – electrons, so-called cathodoluminescence. This is commonly done using a scanning electron microscope (SEM), and images obtained in a SEM are usually monochrome – covering typically 200 to 800 nm – or more rarely in colour with specialized colour CL units.

The emission that is caused by the different excitations can be analysed by a spectrograph, so one can identify the cause of the observed luminescence. In order to do this the luminescence is generally excited by a laser and the technique is known as PL (photoluminescence) spectroscopy. Mostly the range of 200 to about 1200 nm is analysed by the use of spectrographs that are typically equipped with cooled CCD (charge-coupled device), EMCCD (electron multiplying CCD) or sCMOS (scientific complementary metal-oxide-semiconductor) detectors. Combining the visual observation of luminescence phenomena with the spectroscopic analysis of the emission can help to gain a great deal of information on defects in materials.

In the case of gem materials the techniques of luminescence imaging and spectroscopy are of great importance to characterize these materials. This presentation covers luminescence techniques applied for testing of gem materials, with special emphasis on luminescence microscopy.

The testing of gem materials is a very complex issue. There is an enormous diversity of materials used in the gem market today. The appearance of many of these materials is commonly enhanced or modified by various types of treatments, and certain gem materials are extensively synthesized, hence produced in a laboratory. The main challenges in gem testing laboratories are the identification of such treatments and synthetics, and these challenges have to be met via non-destructive analysis methods. The principally used methods include microscopy, absorption spectroscopy from the UV to the mid-infrared domain (190 to approx. 25’000 nm), Raman spectroscopy, non-destructive EDXRF chemical analysis and finally emission analysis via luminescence imaging and photoluminescence spectroscopy.

While many gem materials exhibit luminescence, diamonds are the perfect demonstration material for the usefulness of the emission analysis, since the electronic structure of diamond (large band gap of 5.49 eV) is particularly favourable for radiative electronic transitions. As a consequence diamond exhibits an impressive quantity of defects that cause luminescence bands from 230 to about 1200 nm wavelength (Zaitsev 2001). The emission colours of diamond defects and their distribution patterns can in many cases give indications or even lead to conclusions if a diamond is natural or synthetic (Fig. 1). While in

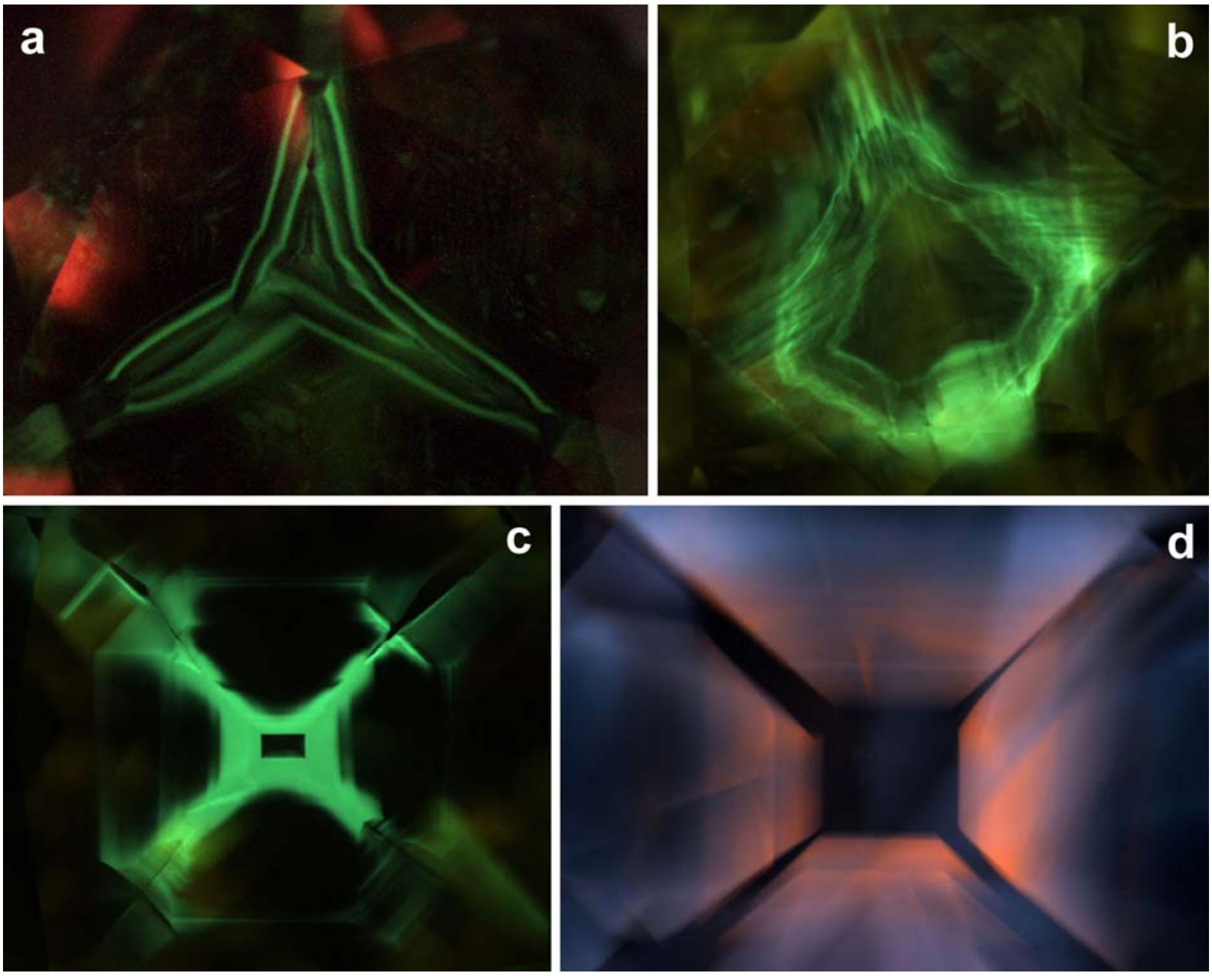

Fig. 1. *Regular fluorescence patterns observed from diamonds of various origins. (**a**) Natural IaA>>Ib diamond of mixed cuboid-octahedral growth, broad band SW excitation. (**b**) Natural Type IaA>>Ib diamond of mixed cuboid-octahedral growth, broad band LW excitation. (**c**) Yellow HPHT-grown diamonds of mixed cubo-octahedral growth, broad band SW excitation. (**d**) Synthetic (HPHT) blue Type IIb diamond, broad band LW excitation.*

synthetic diamonds the cube face is a very common feature that will show up in luminescence, it is unknown in natural diamonds.

The luminescence colour and distribution can be a good indicator for the origin of colour of a coloured diamond; in order to be capable to perform such distinction one needs enormous experience to be able to know which PL colours belong to which defect, and if this is possible in a naturally coloured diamond or not. Equal or similar luminescence colours can be caused by a variety of defects. PL spectra are recorded to confirm the nature of the defect and to know certain details such as the widths (FWHM) of emission bands. Luminescence imaging and spectroscopy are two of the most important techniques in diamond analysis. For coloured stones (i.e. all gemstones other than diamond) and biogenic gems luminescence imaging and spectroscopy have many applications, but so far they are of minor importance compared to diamond.

The most important causes that give rise to luminescence in coloured stones are (amongst others) chromium, manganese, various rare earth elements, and uranium. Chromium is always present in corundum (sapphire and ruby); it causes red PL in very low traces of a few ppm already. While in unheated natural metamorphic sapphires and rubies the PL is red under both longwave and shortwave UV, it changes to chalky white under shortwave UV in certain cases after heat treatment. This type of chalky white luminescence under SWUV is also characteristic for some synthetic sapphires and rubies. Furthermore the curved growth lines of some synthetic corundum can be visualized by SW UV microscopy.

The FWHM of the chromium emissions of spinel is used to identify the heat treatment of such material. After heat treatment the emissions strongly broaden and then resembles to the PL of Verneuil synthetic spinel. This phenomenon is thought to be caused by cationic disorder created by the treatment (Tijero and Ibarra 1993).

In biogenic gems such as coral, and pearls organic pigments give rise to luminescence; these include simple polyenes for certain coral and some type of porphyrin for certain pearls (Karampelas et al. 2011). The presence of these PL features permits the distinction of coral and pearls of natural and treated colour, and allows the attribution of certain pearls to their pearl-producing mollusc. The distinction of pearls of Pteria sp. from pearls of Pinctada sp. is

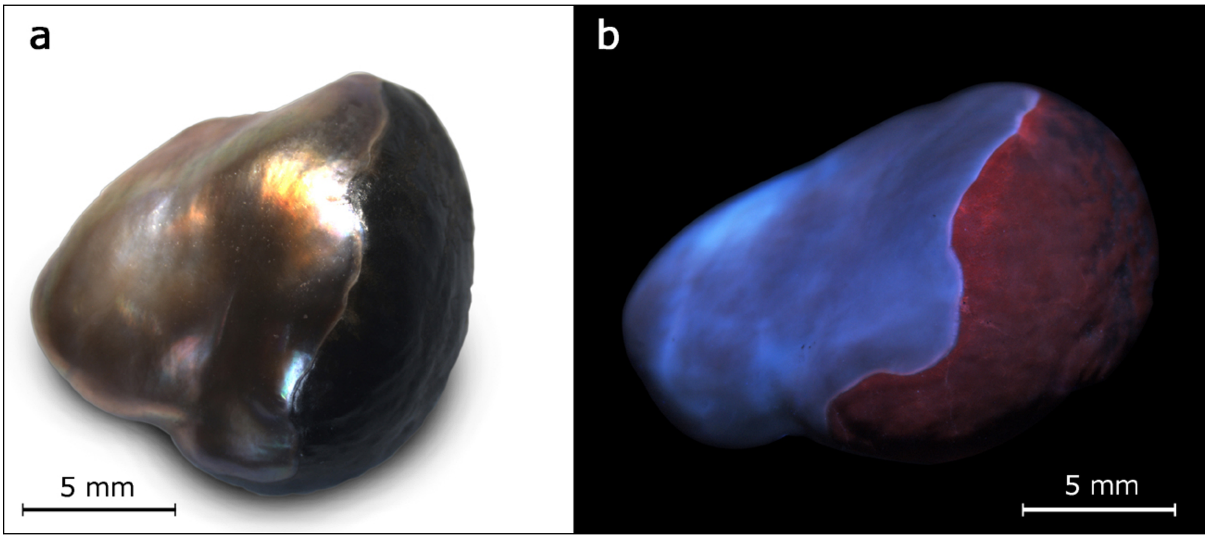

Fig. 2. *Bicoloured "bronze"/black pearl of Pteria penguin. (**a**) White light image. (**b**) Luminescence image. The red emission is related to a type of porphyrin. While the black non-nacreous calcitic part of the pearl emits deep red luminescence, the "bronze" nacreous part shows red luminescence overlaid by more distinct blue-white luminescence.*

one of the most important practical applications. Red PL under UV excitation is characteristic for pearls from Pteria sp. (Fig. 2) (amongst others) while pearls from Pinctada sp. are either inert or luminesce blue white to green white.

References

Karampelas S, Fritsch E, Hainschwang T, Gauthier JP (2011) Spectral differentiation of natural color saltwater cultured pearls from Pinctada margaritifera and Pteria sterna. Gems Gemol 47:117

Tijero JMG, Ibarra A (1993) Use of luminescence of Mn^{2+} and Cr^{3+} in probing the disordering process in $MgAl_2O_4$ spinels. J Phys Chem Solids 54:203–207

Zaitsev AM (2001) Optical properties of diamond: a data handbook. Springer, Berlin