Photochromism and Photochromic Gems: A Review and Some New Data (Part 2)

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ABSTRACT: Part 2 of this article reports on photochromism in diamond, corundum and baryte. Diamond provides the greatest number of photochromic behaviours for a single gem species, with five varieties, only one of which is related to the well-known silicon-vacancy colour centre. The photochromic behaviour of chameleon (green/yellow) diamonds is probably related to various impurities (N, H, Ni and possibly O). Three of the other photochromic diamond varieties involve the addition of brown colour, but they are unlikely to originate from the exact same mechanism. For corundum, we propose that yellow-orange photochromism is linked to an electron moving in and out of a hole centre. For baryte, doubt remains with regard to published descriptions of the yellow-to-blue change in colour with exposure to sunlight, but involvement of sulphur is a possibility for this sulphate mineral. In general, since photochromism modifies the colours of gems, and since the effect is reversible, it is important for the gemmological community to be aware of its potential influence on colour grading.

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The aim of the second half of this two-part article is to review research on inorganic photochromic gem materials other than silicates. Here we concentrate on diamond (with no less than five different photochromic behaviours; e.g. Figure 1), corundum (mostly its yellow variety) and the collector's gem material baryte. Compared with silicates, and especially the aluminosilicates with cages in their structures (as presented in part 1 of this article: Blumentritt & Fritsch 2021), diamond and corundum are chemically simpler materials. However, the large number of defects known in diamond makes it one of the most challenging gem materials for understanding the nature of the absorption centres responsible for photochromism. This is compensated in part by the extensive research on diamond for various material properties, which provides fairly detailed knowledge of many of its defects (e.g. Zaitsev 2001). Corundum offers a different challenge, in that absorption linked to metal ions is very well documented, but that of intrinsic defects and colour centres is lagging far behind. Baryte stands apart, with only a few publications describing a colour behaviour that could correspond to a photochromic property.

MATERIALS AND METHODS

Because we were unable to procure some of the rare photochromic materials covered in the present article, we report only the information available in the published literature for such cases (sometimes including photos or spectra). For diamond, we studied a 0.39 ct marquise-cut chameleon diamond from the collection of the University of Nantes. For corundum, we obtained four rough photochromic yellow-orange sapphires from Madagascar from gem dealer Emmanuel Piat, and the one showing the strongest photochromism (0.19 g) was selected for further examination.

Figure 1: This 6.15 ct chameleon diamond exhibits photochromic behaviour. Its stable 'olive' green colour (left) turns orangey yellow after being kept in the dark (right). Courtesy of Alan Bronstein; photos by Robert Weldon.

The experimental setup by which we obtained ultraviolet-visible-near infrared (UV-Vis-NIR) absorption spectra of the two photochromic gems we procured is identical to the conditions described in the Materials and Methods section of part 1 of this article (Blumentritt & Fritsch 2021). A summary of the properties of the photochromic gems discussed in this article can be found in Table I.

DIAMOND

Articles on the photochromism of diamond have been published since the 1960s, but they are relatively uncommon. Nevertheless, interest in such gems has grown along with the increasing popularity of coloured diamonds, and they are now a well-known curiosity for gem collectors. Despite the relatively small number of

Table I: Properties of the photochromic gems diamond, corundum and baryte.

Gem material		Stable/ metastable colour	Photo-generated colour induced by	Approximate time to induce photo-generated colour	Photo-generated colour(s) reversed by	Approximate time to fade photo-generated colour	Proposed mechanism	Principal references
Diamond	Natural	Green/yellow* (chameleon)	White light	Seconds	Heat (around 100°C)	Seconds to minutes	Centre involving N, H, Ni and possibly O	Fritsch & Delaunay (2018)
					Darkness	Several days		
	Natural	Pink/ pinkish brown	Short-wave UV	Seconds to minutes	Visible light	Seconds to minutes	Colour centre	Byrne *et al.* (2012, 2014)
	Natural	Light yellow/ light brown	Long-wave UV	Seconds to minutes	Visible light	Seconds to minutes	Unknown	Butler *et al.* (2017)
	CVD synthetic	Yellow/brown	Short-wave UV	Minutes to hours	Heat (around 450°C)	Minutes to hours	Colour centre	Khan *et al.* (2010)
	CVD synthetic	Near-colourless/ greyish blue	Short-wave UV (~225 nm)	Minutes	Visible light	Seconds to minutes	$[\text{Si-V}]^{2-} \leftrightarrow [\text{Si-V}]^{-}$ $[\text{Si-V}]^{0} \leftrightarrow [\text{Si-V}]^{-}$	D'Haenens-Johansson *et al.* (2011); Breeze *et al.* (2020)
					Heat (around 550°C)	Seconds to minutes		
Corundum (sapphire)		Addition of yellow to orange component	Short-wave UV	Minutes to hours	Daylight or visible light	Minutes to hours	Hole centre	Nassau & Valente (1987)
					Heat (around 100°C)	Seconds to minutes		
Baryte		Colourless to greyish yellow/blue	Bright sunlight	Hours	Visible light or darkness	Months to years	Sulphur-related?	King (1987)

* From the point of view of an electronic energy diagram, Fritsch *et al.* (2007) indicated that the stable state shows the yellow to yellow-orange colour and the metastable state is greyish or 'olive' green.

photochromism-related publications, diamond probably remains one of the most-researched and well-documented photochromic gems. In the past, photochromic diamonds tended to be a subject of non-gemmological studies because the effect could be useful for various industrial applications such as quantum optics (Byrne *et al*. 2014; Breeze *et al*. 2020). However, work published to date is limited to observations and hypotheses, and lacks detailed interpretations for some reversible colour changes, partly because of the very large number of defects (i.e. hundreds) identified in diamond.

Information on five different varieties of photochromic behaviours in diamond is compiled below. Natural photochromic diamonds (chameleon, pink and cape) are presented first, followed by synthetic ones (brown and greyish blue). Since even subtle colour variations in diamond are closely tied to their value, photochromism should be checked for in gemmological laboratories before assigning a colour grade.

Chameleon Diamond

Today's most accepted definition of 'chameleon diamond' pertains to photochromism involving a greyish green (or 'olive' green) stable colour that turns yellow to yellow-orange when kept in the dark[1] (Figures 1 and 2). This change in colour can also occur via thermochromism with slight heating, typically below 300°C (Raal 1969; Fryer 1981, 1982; Koivula & Kammerling 1991; Fritsch *et al*. 1995, 2007; De Weerdt & Van Royen 2001; Hainschwang *et al*. 2005; Breeding *et al*. 2018), or even when cooled to liquid-nitrogen temperature (De Weerdt & Van Royen 2001).

Curiously, chameleon diamonds have long been presented to the public, owing to the famous French author Jules Verne, whose novels—such as *Journey to the Centre of the Earth*, *From the Earth to the Moon* and *Twenty Thousand Leagues Under the Sea*—often predicted events that happened long after the publication of his books (Fritsch & Delaunay 2018). In *L'Étoile du Sud* (*The Star of the South*; Verne 1884), his description of an extraordinary diamond was not purely the fantasy of his imagination or coincidence, because a chameleon diamond had already been reported by French scientific journalist Louis Figuier (1867). However, these two references mentioned only the thermochromic aspect. The first published description of a photochromic diamond was in *The Diamond Dictionary* (Copeland *et al*. 1960, p. 44):

> A 2.24-carat diamond purported to change color from bronze to green when exposed to light. C. A. Kiger of Kansas City purchased the stone about 1953 and consigned it 'to a Texas dealer who sold it to an oil man.' No further information is available.

Chameleon diamonds have been described variously as type IaA (Fritsch *et al*. 1995; Hainschwang *et al*. 2005), a mixture of types IaA and Ib (De Weerdt & Van Royen 2001) or dominantly type IaA/B (with A>>B) including traces of type Ib (Fritsch *et al*. 2007). Even though diamond types for chameleons differ slightly, they are not in blatant contradiction.

All of the references cited below provide some explanation of the photochromism mechanism in chameleon diamonds, and they generally agree that the change in colour is due to a charge transfer between an acceptor and a donor defect. The articles mostly begin with a precise description of the defects present in such diamonds. These include defects that are Ni-related (De Weerdt & Van Royen 2001; Hainschwang *et al*. 2005; Ardon 2014), H- or N-related (Fritsch *et al*. 1995, 2007; De Weerdt & Van Royen 2001; Hainschwang *et al*. 2005), and even an O-related one (480 nm band; Hainschwang *et al*. 2008).

Cuboid growth sectors have been documented in chameleon diamonds and could explain the presence of Ni, which is very common in H-rich cuboid growth sectors (even in non-photochromic diamonds; Lang *et al*. 2004). For the charge transfer, both Ni- and N-related defects are considered good donors (De Weerdt & Van Royen 2001).

Hydrogen appears to be a necessary defect for photochromism. Theoretical calculations (Goss *et al*. 2011) show that some N-H-N complexes might form; they amount roughly to an A aggregate with a hydrogen atom. These complexes induce an absorption feature in the near-infrared (again, see Figure 2), which appears to be responsible in part for the photochromic effect. This absorption, induced by a charge transfer, causes a structural modification of the N-H-N complex (Fritsch *et al*. 2007; Goss *et al*. 2011). A complex of Ni-H-N has also been proposed to explain diamond photochromism (Fritsch *et al*. 2007). In general, though, the mechanism given by most authors implies an electronic structure with a trap level and a donor level.

However, Byrne *et al*. (2018) proposed another scheme, mostly to explain phosphorescence, but also to include photochromic behaviour. They suggested

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[1] Fritsch *et al*. (2007) indicated that, from the point of view of an electronic energy diagram, the stable state of a chameleon diamond shows the yellow to yellow-orange colour, and the metastable state is greyish or 'olive' green.

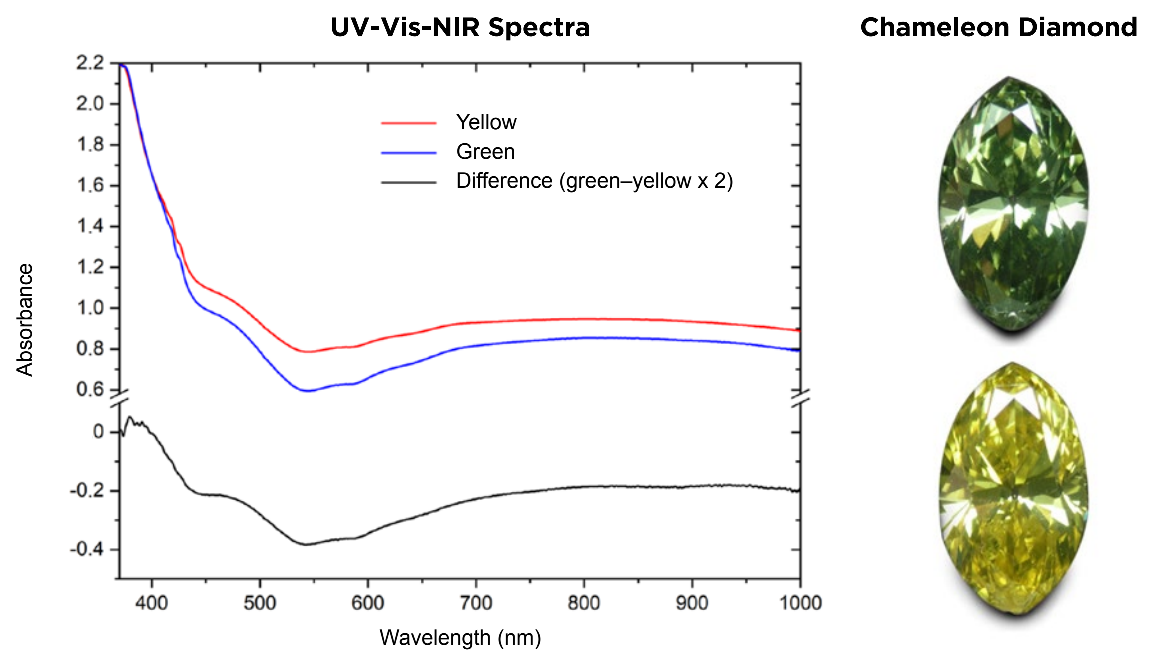

Figure 2: Spectra of the two colour states of a 0.39 ct chameleon diamond are shown here, together with the difference spectrum between the greyish green (stable) and yellow (unstable) colours. Other spectra recorded on chameleon diamonds show slightly variable but generally consistent results (cf. Hainschwang *et al.* 2005; Fritsch *et al.* 2007; Byrne *et al.* 2018). The path length of the beam was approximately 4 mm, and the difference spectrum is multiplied by a factor of 2 for clarity. Photos by Thomas Hainschwang.

that the change in colour is not directly induced by the trap level but by an electronic transition from the valence band to the donor level, which has already lost its electron. This transition occurs in the near-infrared to visible range and leads to the greenish colouration. This particular electronic model was designed exclusively to fit the luminescence of chameleon diamonds. Such diamonds generally show a long-lasting yellow persistent luminescence (phosphorescence; Fritsch *et al.* 1995; De Weerdt & Van Royen 2001; Byrne *et al.* 2018) and sometimes fluorescence that appears white (blue + yellow = white; Hainschwang *et al.* 2005; Fritsch & Delaunay 2018), but the link between photochromism and fluorescence has not yet been clearly established. Fritsch and Delaunay (2018) listed at least nine characteristics to define a chameleon diamond, demonstrating the complexity of the issue of photochromism in a gem material with many different defects.

Pink Diamond

The second variety of photochromism in diamond reported in the literature, known for several decades (Crowningshield 1960), occurs in some pink to purplish pink diamonds. These stones turn more brown (Figure 3) after short-wave UV irradiation and return to their initial pink colour after exposure to visible light (Fryer 1983a; De Weerdt & Van Royen 2001; Fisher *et al.* 2009; Byrne *et al.* 2012, 2014; Chapman 2014; Eaton-Magaña *et al.* 2018). To our knowledge, this behaviour has been observed only in diamonds with pink or purplish pink graining and that are coloured by the 550 nm band (see, e.g., Eaton-Magaña *et al.* 2018). Surprisingly, while some articles dealing with the grading of pink diamonds mention the photochromic property, none of them discuss its effect on colour grading, despite the obvious relationship (Hofer 1985; King *et al.* 2002), especially when the grading process includes photoluminescence analysis with UV excitation. This problem was specifically pointed out for photochromic brown synthetic diamonds grown by chemical vapour deposition (CVD; see below and Khan *et al.* 2010).

In general, pink and brown diamonds are coloured by plastic deformation. This process probably induces the formation of a variety of defects responsible, at least in part, for the pink colour (De Weerdt & Van Royen 2001; Fisher *et al.* 2009; Byrne *et al.* 2014; Gaillou & Rossman 2014). The absorption spectra of such photochromic pink diamonds typically show two bands centred at 390 and 550 nm (i.e. commonly reported in the literature as 3.18 and 2.25 eV, respectively; De Weerdt & Van Royen

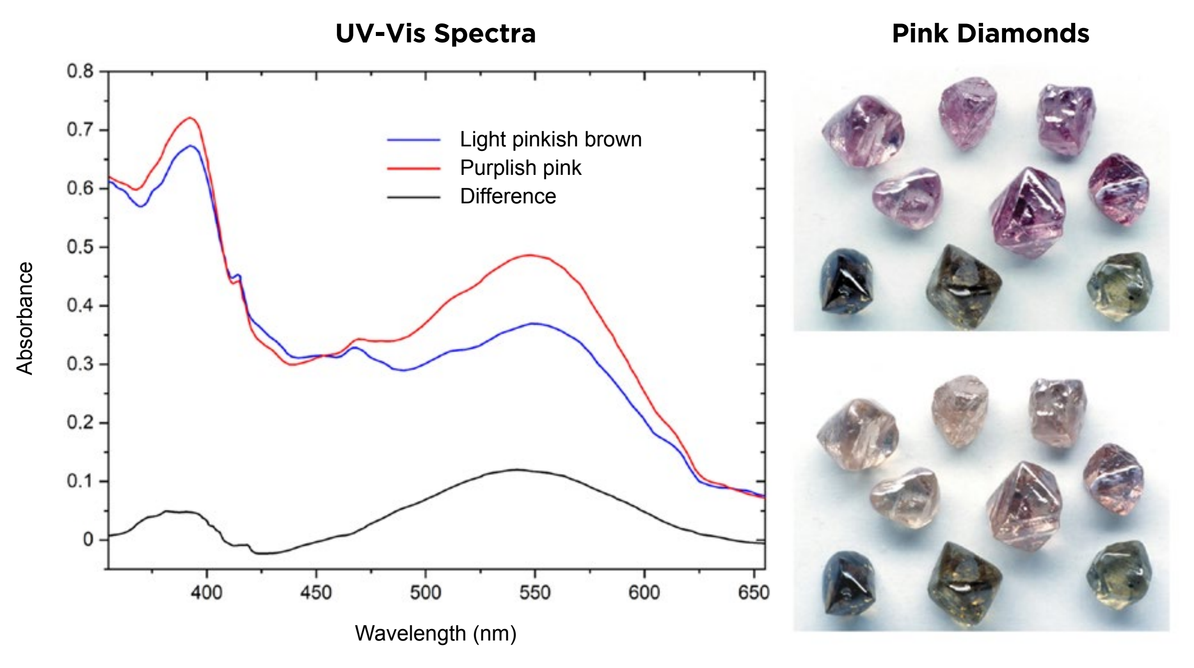

Figure 3: Spectra of a photochromic diamond from the Argyle mine, Australia (adapted from Byrne *et al.* 2012), illustrate the results before (purplish pink) and after (light pinkish brown) short-wave UV exposure, together with the associated difference spectrum. The photos show several diamond crystals (approximately 1 ct each) from Argyle displaying photochromic behaviour; the bottom three diamonds are not photochromic but are included for colour reference. Photos courtesy of John G. Chapman.

2001; Fisher *et al.* 2009; Byrne *et al.* 2014; Breeze *et al.* 2020), plus an underlying continuum rising towards the UV which induces the brown colour component (again, see Figure 3). A list of common defects found in such pink diamonds can be obtained by perusing the literature. Single substitutional nitrogen (N_s) might have an important implication for their pink colour, but it has not yet been proved (Noble 2001; Byrne *et al.* 2014). The vacancy clusters that often form with plastic deformation are indeed present in photochromic pink diamonds (Fisher *et al.* 2009; Byrne *et al.* 2014). Byrne *et al.* (2014) introduced a tentative electronic structure to explain their observations of a bleaching effect (from brown to pink colour) due to IR irradiation. The electronic structure clearly suggests that the photochromic reaction involves a colour center generating a charge transfer (Byrne *et al.* 2012, 2014).

Figure 4: The cape-yellow pear-shaped brilliants in these earrings (37.87 and 36.80 ct) were cut from the 187.63 ct Foxfire diamond, which was documented by Butler *et al.* (2017) as showing photochromism. Private collection; photo © Christie's Images/Bridgeman Images.

'Foxfire' Cape Diamond

A third variety of photochromic natural diamond was reported by Butler *et al.* (2017) for the Foxfire diamond, the second-largest (187.63 ct) gem-quality rough diamond found in Canada to date, which was subsequently faceted into two pear brilliants weighing 37.87 ct and 36.80 (Figure 4). When exposed to a typical

Figure 5: This 0.83 ct cape-yellow diamond (left) turns brown when exposed to strong long-wave UV radiation (right). It reverts to its normal cape-yellow colour by simple exposure to visible light. Composite photo courtesy of Thomas Hainschwang.

long-wave UV lamp, the light yellow crystal became light brown. It returned to its initial light yellow colour upon exposure to visible light. Interestingly, the authors further stated that such small colour changes are often observed in natural diamonds. However, there is no other mention of such a change in the published gemmological literature. The origin of this modification of colour is not clear, as no before-and-after absorption spectra were provided. However, Butler *et al*. (2017) point out that electric charges move very slowly in diamond, and photochromism could be an indirect consequence of this sluggish movement of electrons between defects, resulting in a slow change in colour. Possibly more interesting, King *et al*. (2016) mentioned that the only visible-range spectral features of this large rough diamond were the N3 and N2 absorptions associated with the N3 defect.

Thomas Hainschwang (pers. comm. 2021) has observed that this third photochromic behaviour seems common only for relatively pure cape diamonds (Figure 5)—in other words, gems with dominant N3-related absorptions and only minor contributions from other centres. Further work is necessary to explain the mechanism.

Brown CVD Synthetic Diamond

The fourth variety of photochromic diamond concerns CVD synthetic diamonds that are near-colourless (or light brown) in their stable state, but turn light brown (or deep brown) after prolonged exposure (typically more than 30 minutes) to short-wave UV radiation. They return to their initial near-colourless or light brown state after being heated to temperatures higher than 450°C (Khan *et al*. 2009; Figure 6).

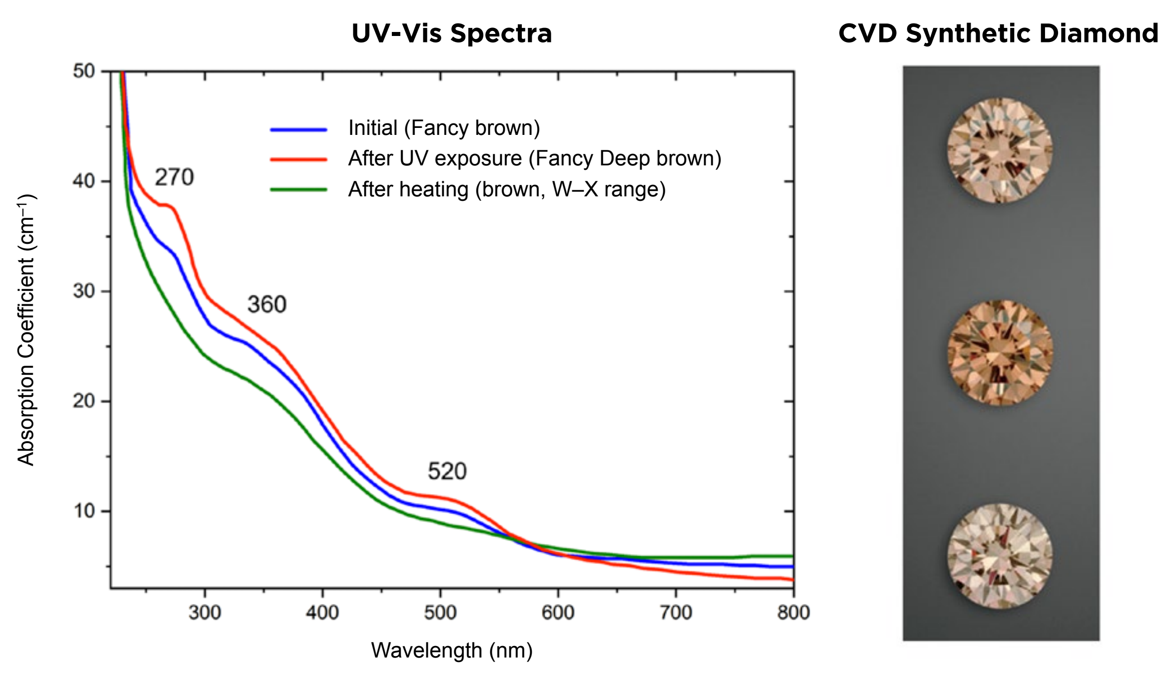

Figure 6: Photos and absorption spectra of a 0.40 ct photochromic CVD synthetic diamond (adapted from Khan *et al.* 2010) show the sample in its initial state, after exposure to ~225 nm UV radiation and after heating (seen in the images from top to bottom). The spectra have not been offset in order to directly compare the evolution of the absorption. Composite photo courtesy of R. Khan.

This behaviour satisfies the definition of photochromism—similar to the ‘classic model’ electronic structure described in part 1 of this article (see figure 2 in Blumentritt & Fritsch 2021). According to Khan *et al.* (2009), single nitrogen with a neutral charge (N_s^0) and nitrogen-vacancy-hydrogen (NVH) defects are involved, and the colouration is related to three absorption bands centred at 270, 360 and 520 nm (again, see Figure 6) that are responsible for the overall brownish appearance in the photogenerated state. The authors also suggested that a charge transfer is the source of the photochromism and proposed the following reaction mechanism: $N_s^0 + NVH^0 \leftrightarrow N_s^+ + NVH^-$. However, since the diminution of N_s^0 occurs faster than the growth of NVH^-, they proposed the existence of a secondary process with an unknown electron acceptor. A year later, the same authors confirmed their results (Khan *et al.* 2010) and also alerted gemmologists that the colour of a photochromic CVD synthetic diamond can be temporarily enhanced, thus influencing its colour grade. This observation concerns all varieties of photochromic diamonds.

Greyish Blue CVD Synthetic Diamond

A fifth variety of photochromic diamond concerns near-colourless CVD samples that change to greyish blue (Figure 7) from the UV radiation of a DiamondView (approximately 225 nm), and return to their initial near-colourless state after exposure to visible light or heating to around 550°C (Chauhan 2015; Breeze *et al.* 2020; Del Re 2020). This photochromic variety involves a completely different change in colour from the type exhibited by the brown CVD synthetic diamonds described above. The colour-causing defect is the silicon vacancy, $[Si\text{-}V]^-$, which absorbs in the green-to-red (and near-infrared) range and thus transmits blue. Breeze *et al.* (2020) proposed that a doubly charged silicon-vacancy complex, $[Si\text{-}V]^{2-}$, is responsible for this photochromic behaviour by forming $[Si\text{-}V]^-$ under short-wave UV excitation (approximately 225 nm). Absorption due to $[Si\text{-}V]^{2-}$ occurs entirely in the UV range, thus inducing no colour prior to UV excitation. Alternatively, $[Si\text{-}V]^-$ can be produced by charge transfer from $[Si\text{-}V]^0$ (D’Haenens-Johansson *et al.* 2011), since the latter also absorbs in the near-infrared and thus does not induce any colour prior to UV excitation. Clearly, this type of photochromism is related to silicon-vacancy defects.

Origin of Brown Colouration in Photochromic Diamonds

The photochromic change in colour involves a brown component for the pink, cape and CVD brown synthetic diamonds described above, and also for chameleon

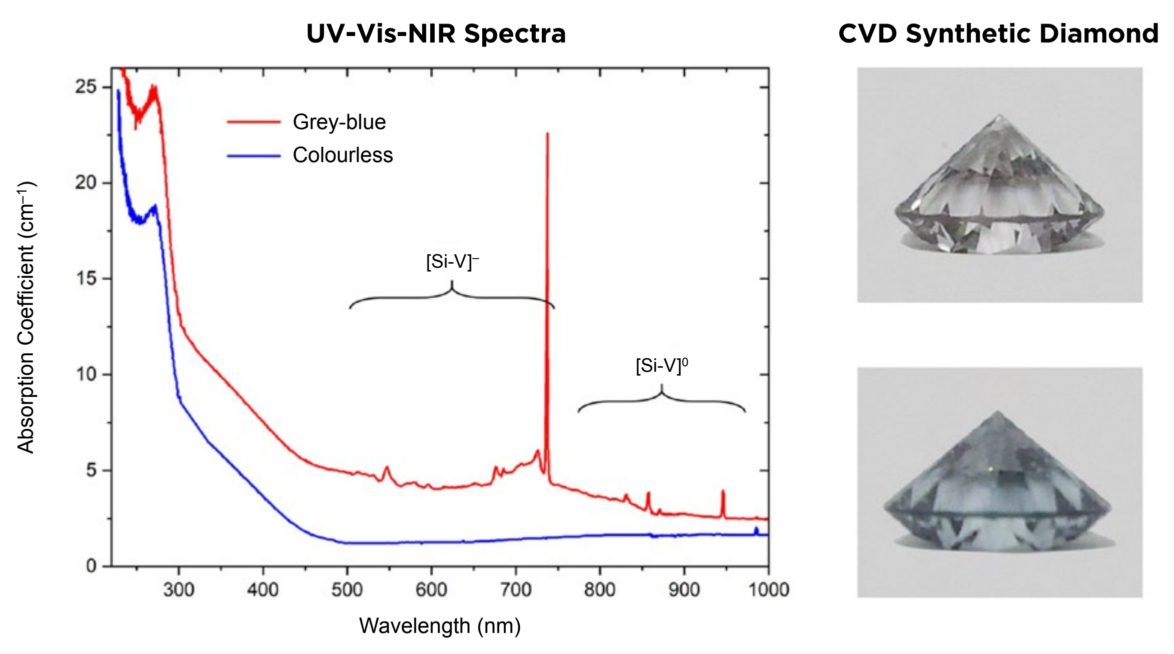

Figure 7: These photos (from Chauhan 2015) show a near-colourless 1.42 ct CVD synthetic diamond (top) and the same sample after exposure to short-wave UV radiation (bottom). The UV-Vis-NIR spectra, adapted from Breeze *et al.* (2020) and collected at 80 K, reveal the production of metastable $[Si\text{-}V]^-$ (500–750 nm) and $[Si\text{-}V]^0$ (780–980 nm) centres following UV exposure (225 nm in the DiamondView). Heating to 550°C causes it to return to its stable $[Si\text{-}V]^{2-}$ (near-colourless) state.

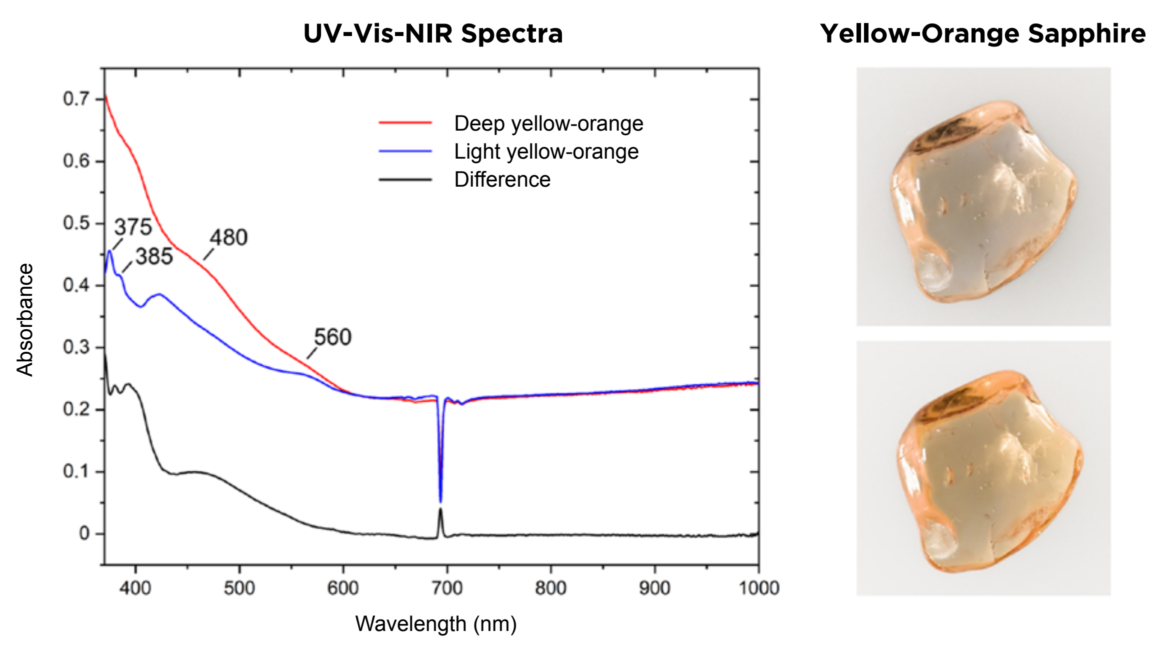

Figure 8: A 0.19 g photochromic yellow-orange sapphire (top) becomes visibly darker (bottom) following short-wave UV exposure. The corresponding spectra are consistent with those presented by Krzemnicki (2018) and Krzemnicki *et al.* (2018), who observed more intense absorption bands related to Cr^{3+} (only a weak 560 nm absorption band is visible in our spectra). (The sharp fluorescence-related emission feature due to Cr^{3+} at about 694 nm is unrelated to photochromism.) The difference spectrum shows that UV exposure increases the absorption continuum from 600 nm towards the UV region, as well as intensifies a feature at 480 nm. On the other hand, Fe^{3+}-related absorptions at 375 and 385 nm nearly disappear after UV exposure. The path length of the beam was approximately 3 mm. Photos by Philippe Deniard.

diamonds to some degree. Is it simply a matter of brown appearing and disappearing, or is it more complex? Brown is caused by an absorption continuum rising from the near-infrared towards the UV region, no matter what the material is. The continuum found in diamonds with a brown component might be related to a variety of defects: clusters of carbon vacancies, a type Ib component, H-related defects and so on (Hainschwang 2020a, b). Thus, there is no reason to believe that all photochromic changes in diamond involving a brown colour are simply due to a single defect causing the associated absorption continuum, which appears and disappears reversibly.

CORUNDUM (SAPPHIRE)

One of the oldest published descriptions of photochromic corundum is by Pough and Rogers (1947). They showed that X-ray irradiation creates a reversible change in every colour of natural sapphire. Schiffmann (1981) verified this on an orangey yellow 45 ct Sri Lankan sapphire, for which he provided before-and-after visible-range absorption spectra. He indicated that X-ray irradiation increased the absorption, thus giving a darker orangey yellow colour. This raises the question of whether a reversible colour reaction to X-ray excitation can be considered photochromism (see definition in part 1 of this article; Blumentritt & Fritsch 2021). It was later reported that the same increase of intensity of colour could be observed in some yellow sapphires using a simple short-wave UV lamp (Nassau & Valente 1987). So, it appears that a change in colouration in sapphire can be induced by X-rays as well as by UV irradiation (typically below 300 nm).

Nassau and Valente (1987) proposed a classification of yellow sapphires into seven types, one of which included those with an unstable colour. Thus, the observation of photochromism in a yellow sapphire turning more yellow-orange apparently could be a means to recognise samples that have been ‘irradiated’, naturally or artificially (Nassau & Valente 1987). Gem dealers have reported to us that some rare parcels of yellow sapphire darken or turn more orange after exposure to sunlight (i.e. outdoors) compared with being illuminated by mixed shop lighting (i.e. indoors; Emmanuel Piat, pers. comm. 2006–2021). This is not a colour-change effect due to observations in different lighting, because the change of colour associated with photochromism is consistent under both lighting conditions. The photogenerated component in sapphire could be a yellow to deep orange colouration (Figure 8)

Figure 9: A 0.86 ct blue sapphire (left) appears muddy green (right) after irradiation with a powerful, broad-band UV radiation source. When exposed to visible light, the colouration reverses in a few minutes to the original blue colour. Composite photo courtesy of Thomas Hainschwang.

that disappears slowly under daylight or more quickly when samples are heated (Pough & Rogers 1947; Schiffmann 1981; Fryer 1983b; Nassau & Valente 1987; Wang *et al.* 2021).

This process does not seem to be linked to the initial stable colour of a sapphire, since this effect (i.e. the addition of a yellow to orange colour component) has also been seen in blue and pink sapphires (Pough & Rogers 1947; Nassau & Valente 1987; Krzemnicki 2018; Krzemnicki *et al.* 2018): blue sapphire turns muddy green (Figure 9), and pink sapphire turns pinkish orange, after short-wave UV exposure (Figure 10). The latter stones have been described as *padparadscha-like* sapphires (Nassau & Valente 1987; Krzemnicki 2018; Krzemnicki *et al.* 2018), although the orange component of the colour is unstable.

Another example of photochromism in sapphire was published by Gaievskyi *et al.* (2014), who described a light bluish violet sapphire—containing Fe, Cr and Mg, with traces of Ti and Ga—which turned light brown upon exposure to the UV radiation of a DiamondView. The initial, stable colour returned after exposure to natural daylight for 12 hours. This is essentially consistent with the behaviour described by Pough and Rogers (1947), who concluded that since every natural sample reacts to X-ray irradiation, the phenomenon must be due to an intrinsic colour centre, structural deformation or impurity present in all sapphires. The effect is less apparent with some pure synthetic samples (again, see Pough & Rogers 1947). However, although all sapphires react to X-rays, they do not all respond to standard long- or short-wave UV radiation (Figure 11). Thus, extrapolating Pough and Roger's conclusion to UV radiation is not valid, because photochromic yellow sapphires are relatively rare (at least at the present time).

Other options have been explored to explain the photochromism observed from UV radiation in sapphire, such as the presence of an unknown colour centre, Fe impurities, both of these, or even Ni (Nassau & Valente 1987). In all these proposed explanations of photochromism, no precise mechanism is given, but the observations tend to fit fairly well with the 'classic' model of photochromism presented in figure 2 of part 1 of this article (Blumentritt & Fritsch 2021).

The difference spectrum we obtained from a photochromic yellow-orange sapphire demonstrates that the major difference between the two colour states is an increase of the continuum rising from about 600 nm towards the UV region (consistent with Schiffmann 1981), as well as the formation of a band around 480 nm (Figure 8). In our photochromic sapphire, the Fe^{3+}-related bands at about 375 and 385 nm disappeared after exposure to UV radiation. This is consistent, although not identical, with results reported by SSEF (Krzemnicki 2018; Krzemnicki *et al.* 2018).

Research on beryllium diffusion has addressed the 480 nm band in corundum, which is attributed to a hole centre compensated by a divalent cation (in this case Be^{2+}; Fritsch *et al.* 2003). This centre is not stable when produced by UV radiation and, logically, is also unstable when produced by X-ray exposure (assuming UV and X-ray radiation produce the same type of defect).

Figure 10: A 6.08 ct photochromic sapphire is shown in its stable pink state (left) and in its photogenerated orangey pink state after short-wave UV exposure (centre). It returns to its initial pink state after illumination by a daylight-equivalent halogen lamp (right). Composite photo courtesy of Michael S. Krzemnicki, © SSEF.

Figure 11: Three initially near-colourless sapphires (2.46–2.60 ct) gain (**a**) an orangey yellow colour after exposure to X-rays, (**b**) which fades dramatically after illumination for a few minutes by intense visible light from a 100 W halogen fibre-optic lamp. (**c**) All colour completely disappears after slightly heating the samples above the flame of a cigarette lighter. These three sapphires did not change colour following exposure to UV radiation. Photos by F. Blumentritt.

The difference spectrum seen for this photochromism resembles that for Be-diffused corundum. Thus, we surmise that the photochromic reaction is related to a hole centre, in agreement with the speculation by Pough and Rogers (1947) that photochromism might be related to an intrinsic defect. In the case of the sample in Figure 8, it can probably be attributed to an intrinsic defect in the corundum structure itself, most likely a hole centre or an oxygen vacancy (a missing oxygen ion in the structure). The latter is known to be a colour centre, and is even the dominant type of defect during the crystal growth of corundum, in nature as well as in the laboratory, where this remains true even if a dopant is added (Ramírez *et al*. 2007; Itou *et al*. 2009; Harutyunyan *et al*. 2015).[2] Oxygen vacancies create a negative charge deficit (–2) in the crystal. Commonly this is compensated by a +2 (divalent) ion, Mg being the most common in nature (Emmett & Douthit 1993). It is useful to note that Mg^{2+} alone, substituting for Al^{3+}, induces a hole centre (charge +1) in corundum that produces a yellow to orange colour, as observed in yellow sapphires from Montana, USA (Emmett & Douthit 1993). Thus there might be a link with the photochromism seen in natural, Mg^{2+}-containing yellow sapphires. More complex defects, such as those containing several Mg atoms and several oxygen vacancies, are also possible (Akselrod *et al*. 2003).

We propose a global explanation for the photochromism of natural yellow corundum as being linked to hole centres that are not linked to any impurity (i.e. intrinsic defects). These colour centres are not often mentioned in gemmology, but physicists have proven them quite common. Clearly, further detailed work is needed to fully understand the factors influencing colour stability in corundum.

BARYTE

Baryte ($BaSO_4$) is faceted on occasion (see, e.g., https://gemologyproject.com/wiki/index.php?title=Barite) and is considered a gem for collectors. Only a few publications report ‘colour change’ descriptions which could correspond to photochromism in this mineral. Unfortunately, we were not able to procure any baryte samples approaching these descriptions from either museums or mineral dealers we contacted, so we were unable to confirm whether these observations could fit the definition of photochromism. We hope to examine such material in the future.

According to the literature, the first documented reversible colour change induced by light in baryte was reported by Carlon and Winchell (1975). The colourless to greyish yellow material from Illinois, USA, turned deep blue upon exposure to bright sunlight for a few hours (Carlon & Winchell 1975; King 1987). A similar description has been made for baryte from Hartsel, Colorado, USA (Belsher & Baldwin 1980). The blue colour faded slowly when the baryte was kept in the dark or otherwise protected from direct sunlight.

Given the current state of knowledge, and that baryte is a sulphate, it is not unreasonable to consider that blue photochromism in this mineral could be related to one or more sulphur-based polyanions, such as SO_3^- (Gilinskaya & Mashkovtsev 1995) or S_3^- (Fleet & Liu 2010), both known to induce blue colour in some gems. This speculation needs further study, including detailed spectroscopic research and interpretation on photochromic samples with a good change in colour following exposure to bright sunlight or UV radiation.

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[2] It should be pointed out that although photochromic synthetic corundum has been described (Mg-doped α-Al_2O_3; Tardío *et al*. 2003), it is unlikely to be encountered by gemmologists so it will not be discussed further here.

CONCLUSION

Photochromism in many gem materials remains poorly explained and, often, little documented, with the notable exception of hackmanite (reviewed by Blumentritt & Fritsch 2021) and diamond (see above). At the present time, there is no general theory to explain photochromism in gems. It is too often limited to guesswork, but a comprehensive study would require significant funding and effort (a single colour centre may require several PhDs to be fully understood). Perhaps the production of durable photochromic materials for industrial applications will provide the incentive for further research on these rare, infinitely cyclable and often beautiful gem materials.

We wish to stress the importance of testing for photochromism before colour grading, in particular for diamond and corundum. This phenomenon can lead to complications if not fully disclosed on laboratory reports and in various other circumstances (e.g. on a sales receipt or a loan document for an exhibit). As part of this disclosure, the concerned parties should be made aware of the reversibility of the phenomenon and the means by which it can be achieved (type of illumination/radiation, heating, and so on). We also feel that photochromism should be consistently included in the curriculum of gemmology courses, in the same manner as other phenomena such as asterism or colour change. This would increase awareness of this remarkable behaviour and hopefully help to avoid problems that could occur when it is not disclosed.

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