CHAPTER 5

IRRADIATION COLOUR ENHANCEMENTS

Diamonds occur in nature in various colours like grey to steel grey , white, red , blue, green yellow, orange, pink to purple, brown, and black. Coloured diamonds contain interstitial impurities or structural defects that cause the colouration, whilst pure diamonds are transparent and colourless.: The colour of a diamond caused by chemical impurities and/or structural defects in the crystal lattice.

Production of colour by irradiation and its destruction by heat or light is the touch stone of a colour center, this in itself is not sufficient proof. One example of such a change not involving a colour center occurs in aquamarine and golden beryl. As found these natural materials have a colour ranging from blue-green via green to yellow and are almost invariably immediately given a heat-treatment .The heating removes the yellow colour component and is performed in the hope of producing a pure blue aquamarine. Often the result is a colourless beryl. Irradiation will return the material to the green or yellow state. The change here involves a change in the valence of the iron impurity causing the yellow colour : the iron impurity, causing the blue colour, is not affected by either the heating or the irradiation. These colour are stable to light.

In addition to the intentional heating of green and yellow beryls, accidental heating may at times destroy the colour of some natural gemstones with stable colour centers. If the heating was not excessive, then irradiation is usually able to return the gemstone to its original colour. Such a step may be viewed merely as restoration rather than and irradiation originated colouring. Restoration may be possible with accidentally heated blue or brown topaz, amethyst or smoky quartz, and red tourmaline, as well as with golden beryl.

A change in colour produced by irradiation is most often the result of formation of a colour center. This is usually a misplaced electron which can be an excess electron (an electron colour center) which is trapped at a defect, or a deficit of an electron (a hole colour center) located at a defect (with the missing electron trapped at another defect). The pre-existing defects without the hole or the extra electron are called precursors. When light exposure or heating permits the displaced electron to return to its original

place, the colour center is destroyed and the precursors are reformed in a process called fading or beaching.

The depth of the trap is a measure of how much energy is needed to produce bleaching . The energy for beaching of a colour center can be supplied by light, by heat, or by a combination of both. When a colour center has been bleached, it is usually possible to recreate it by another irradiation. This can not be done if over heating occurred during the bleaching step. Thus, amethyst which has been gently heated to obtain a citrine colour can be returned to its original colour by irradiation, and the process can be repeated any number of times. If too high a temperature is used, however, the substitutional iron precursor changes to ferric oxide with the production of a deeper brown colour, which can not be altered by irradiation.

Details of colour in general and some colour centers in particular have been given by the author in several places and will not be repeated here. The most important factors for a given colour center are the stability to light exposure, i.e., the resistance to fading, and the characteristics which indicate that irradiation has been used. Based on the resistance to fading, three groups of irradiation produced colour effects can be distinguished. The fourth grouping a discussed some irradiation-produced changes which do not involve colour centers. In this group are included those irradiation-produced colour effects which are not stable at room temperature, even in the dark. Ordinary fluorescence can be viewed as an unstable colour center, the effect being so fleeting that the red fluorescence of emerald, as one example, stops within a few thousands of a second after the ultra violet irradiation is halted.

Lasting some what longer is the phosphorescence or after-glow of substances such as some fluorites, some calcites, and some diamonds; this behavior can be viewed as derived from transient colour centers. This occurs when the colour-center trap is relatively shallow, show that the energy of the thermal vibrations at room temperature is enough to permit slow escape from the trap. The colour of phosphorescence may be the same as that of the fluorescence, as in the brief red phosphorescence of particularly iron-free rubies (mostly synthetics) or it may be different as in those diamonds which have a blue fluorescence followed by a yellow after- glow.

If substances in this group are cooled to a low temperature and then irradiated, this will frequently stabilize the colour center. On warming up, the colour center again will become unstable and emit its energy over a specific temperature range, an effect which is then called thermoluminescence. Liquid nitrogen or even lower temperatures may have to be used to observe this effect.

There are some materials which are easily coloured by low energy irradiation such as ultraviolet light and X-rays. One of these is the mineral hackmanite which can be coloured red by UV irradiation. This colour is perfectly stable as long as the specimen is kept in the dark, but will fade on exposure to visible light (or more rapidly on heating). Such materials are sometimes called photochromics. Photochromic sun glasses are now manufactured which turn dark from the UV present in strong sunlight and fade rapidly in the UV-free indirect light in the shade. These colours may be stable when cooled (arcticvear) and thermoluminescence may occur during heat bleaching. Several gemstones materials some naturally occurring , fall into this group.

There is some natural topaz which is brown as found but which fades rapidly when exposed to light. Similarly, almost any colourless or pale yellow topaz will colour brown on being irradiated by X-rays, gamma rays, etc. Two distinct component colours can occur, either separately or together : a pale yellow – brown and a dark cillamon-brown ; the former forms rapidly on irradiation and fades in a matter of hours in the sun; the latter forms more slowly and also fades more slowly in one or a few days in the sun. There are two additional radiation – related colours in topaz which are stable and are discussed in the next section. Details and colour illustrations have been published.Observation of the fading may be the only practical identification test for these transientbrown colours in topaz.

Pink kunzite will turn a deep almost imerald-like green upon irradiation. This colouration bleaches in an hour or so in sunlight and is quite distinct from the green of hiddenite. Colour illustrations have been published . Some pale tormalines turn red on irradiation, some turn yellow and some blues turn purple; all of these may fade in days to weeks in the sun (but see also the next section). Details and colour illustrations have been presented.

An important unstable colour in beryl is a magnificent deep blue, approaching the blue of tanzanite or sapphire, seen in Maxixe beryl and Maxixe-type beryl. The former was found in 1917 in the Maxixe mine in Minus Gerais, Brazil, while the latter has been produced in recent years by the irradiation of pale pink or othr pale colour beryl from certain localities in Brazil , Rhodesia, North Carolina , and probably elsewhere; UV , X-rays, gamma rays, and neutrons have all been used for this irradiation. This deep blue beryl has been called “ Halbanita “ and “aquamarine” , the latter being incorrect by customary gemological usage. A dark green colour can result if the starting beryl was yellow. Full details including colour illustrations, have been published.

Maxixe and Maxixe-type beryls fade in a matter of days or weeks on exposure to sun light.Identification and distinction from aquamarine is readily achieved by the

spectroscope (sharp lines near 7000A° not present in aquamarine) by examination is polarized light (the blue colour is carried by the ordinary ray, while in aquamarine it is carried by the extra ordinary ray), or by observing the fading. Both are hole colour centers and the rather small difference in the spectrum between Maxixe and Maxixe-type beryls has been attributed to different precursors, being small amount nitrate and carbonate, respectively. Irradiation removes one electron from these, leaving the hole colour centers NO and CO respectively. The displaced electron becomes trapped at a proton or a free carbon dioxide in the channels, producing H and CO, respectively.

Materials in this group generally need higher energy irradiation (atleast X-rays) and the resulting colours are stable to light at ordinary temperatures. The colours will fade if heat (or the combination of heat and light) is used. A report stating that irradiated blue topaz faded under a mercury lamp did not mention that the sample reached over 300°F under the fading conditions used undoubtedly, natural blue topaz also fades under such extreme conditions. Similarly, the investigation of reports of light-fading amethyst usually reveals that heat was also present. Thermoluminescence may occur during heat bleaching.

The colour of most natural brown topaz is stable to light, but heating will destroy this colour (if there is any chromium present, than pink or red " pinked" topaz result). Together with the two unstable brown colours discussed in the previous sections, this indicates the existence of atleast three distinct brown colourations in topaz.

When brown irradiated topaz is heated or exposed to light, the brown colour fades. Sometimes the fading does not return the material to the original colourless states but instead produces a blue topaz, which can be even darker than the blue of naturally occurring blue topaz. The accidental observation of this phenomenon in a specimen thought to be quartz explained the appearance on the gemstone market in the early 1970`s of quantities of unusually deep blue topaz without the report of the discovery of a new mine. The author found that the irradiation of old collections of colourless topaz produced a significant quantity of blue, while more recently obtained colourless topaz did not. From this one could deduce that essentially all colourless topaz is now irradiated and than heated so as to locate all blue-producing material. There appear no gemological-testing differences between the natural and the irradiated blue topaz, and both appear to have the same stability towards light and heat.

Almost all colourless quartz, whether natural or synthetic, turns into smoky quartz on being irradiated. This colour is stable to light and bleaches over a wide temperature range on heating, just as does natural smoky quartz; the last trace of smoky colour disappears anywhere from 140° to 400°C depending on the specimen. The colour can

vary from a yellowish or a reddish brown all the way to a pure black depending on the type of material and the irradiation dose used. There appear to be no gemological testing differences between irradiated and naturally- occurring smoky quartz. The colour center precursor consists of a few parts per million aluminum impurity (some alkali or hydrogen ions are also needed for charge compensating the Al^{3+} which substitutes for Si^{4+}).

If this heating to fade smoky quartz is carried out gradually in steps, much naturally occurring and irradiated smoky quartz will yield a greenish yellow colour, abbreviated G-Y quartz. This has been also called yellow quartz honey quartz, citrine, and radiation- produced citrine; the latter two terms are undesirable because of the absence of iron, characteristic of naturally-occurring citrine. G-Y quartz forms from smoky quartz at 140° to 300°C G-Y quartz loses its colour at 140° to 380°C. There is some naturally-occurring G-C. There is some naturally-occurring G-Y quartz, and some rare colourless quartz irradiates directly to G-Y quartz without the formation of any smoky colour. Full details of G-Y quartz, a reinterpretation of smoky quartz, and colour illustrations have been presented.

The detailed nature of the colour of natural amethyst was not understood until the achievements of its duplication by man. When synthetic quartz is grown with the incorporation of iron, the resulting colour is either yellow or green, depending on the growth conditions. If growth has occurred in certain crystallographic directions and if the iron concentration is in the correct range, than irradiation will result in the hole colour center of synthetic amethyst. Heating will restore the green or yellow colour, just as happe ns with natural amethyst, which gives either a citrine colour or the “greened amethyst”. Irradiation will once again restore the amethyst colour.

A colourless diamond is irradiated in four ways: proton and deuteron bombardment via cyclotrons; gamma ray bombardment via exposure to cobalt-60; neutron bombardment via the piles of nuclear reactors; and electron bombardment via Van de Graaff generators. These high-energy particles physically alter the diamond's crystal lattice, knocking carbon atoms out of place and producing colour centers. Irradiated diamonds are showing all some shade of green, black, or blue after treatment, but most are annealed to further modify their colour into bright shades of yellow, orange, brown, or pink. The annealing process increases the mobility of individual carbon atoms, allowing some of the lattice defects created during irradiation to be corrected. The final colour is dependent on the diamond's composition and the temperature and length of annealing.

The yellowish, brownish or colourless diamond when exposed to the radiations of radium salt alters to green colour Diamond. In this method diamonds are packed in direct contact with radium bromide or other radium salt and left for a period of several months. The result of this exposure to intense radio-activity is not only the change of colour of the diamond, but also a definite alteration of the material in certain localized areas. In these areas either the carbon is altered so that it becomes radio-active or a small amount of the radium salt penetrates into the diamond. The green colour in a radium-treated diamond is particularly strong in the vicinity of tiny pits in the surface which are apparently the result of this breaking down of the diamond.

RADIUM – TREATED DIAMONDS

Several methods of detection of radium-treated diamonds have been devised ; all depend on the above effects. The pits with green colour localized about them can easily be seen under the microscope and form quite definite proof of radium treatment. The radio-active nature of the transformed carbon or of the enclosed radium compound can also be detected by various means. The most common is, perhaps, the self-exposure of diamonds thus treated. Placed on a photographic plate in the dark room for a suitable period, some radium-treated diamonds will expose the plate, an effect which can be detected by developing the plate. Also the radio-activity may be detected by a delicate electroscope or by a spinthariscope. Still more delicate tests for radio-activity are also available.

Radium, in breaking down, produces three forms of energy. These are (1) alpha particles, which are positively charged atomic nuclei; (2) beta particles, which are negatively charged electrons ; and (3) gamma rays, which are light waves comparable to X-rays. Of these three forms of energy, the gamma rays are the most penetrating. A radium salt, as ordinarily used, is shielded by a thin metal container which absorbs the alpha and beta particles and allows only the gamma rays to pass. However, the only known method of altering the colour of diamonds by radium involves packing the stone in direct contact with the radium salt. In this contact, of course, the stone is under the influence of the alpha and beta particles as well as the gamma rays, and furthermore, has opportunity to pick up by contact some of the radium salt itself. It is not known whether the gamma rays alone have produced the alteration of the colour to green or whether alpha or beta rays are also necessary to produce the alteration.

If the alteration can be produced by the gamma rays alone, yellowish diamonds can be turned green by pure gamma rays or by intense X-rays (without the use of radium) ,and, therefore,can be altered without the resulting radio-activity in the diamond which

now is used as a distinguishing test. Research is desirable on this point, but both the necessary diamonds and the radium or intense X-rays are very expensive.

Fig. 5.1 Photograph showing irradiated colour in natural white Diamond.

Diamonds enveloped in radium salt slowly turned a dark green; this colour was found to be localized in blotchy patches, and it did not penetrate past the surface of the stone (Fig. 5.1). The emission of alpha particles by the radium was responsible. Unfortunately radium treatment also left the diamond strongly radioactive, to the point of being unwearable.

Cyclotroned diamonds have a green to blue-green colour confined to the surface layer: they are later annealed to 800°C to produce a yellow or orange colour. They remain radioactive for only a few hours after treatment, and due to the directional nature of the treatment and the cut of the stones, the colour is imparted in discrete zones. If the stone was cyclotroned through the pavilion (back), a characteristic "umbrella" of darker colour will be seen through the crown (top) of the stone. If the stone was cyclotroned through the crown, a dark ring is seen around the girdle (rim). Stones treated from the side will have one half coloured deeper than the other. Cyclotron treatment is now uncommon.

Gamma ray treatment is also uncommon, because although it is the safest and cheapest irradiation method, successful treatment can take several months. The colour produced is a blue to blue-green which penetrates the whole stone. Such diamonds are not annealed. The blue colour can sometimes approach that of natural Type IIb diamonds, but the two are distinguished by the latter's semiconductive properties. As with most irradiated diamonds, most gamma ray-treated diamonds were originally tinted yellow; the blue is usually modified by this tint, resulting in a perceptible greenish cast.

The two most common irradiation methods are neutron and electron bombardment. The former treatment produces a green to black colour that penetrates the whole stone, while the latter treatment produces a blue, blue-green, or green colour that

only penetrates about 1 millimeter deep. Annealing of these stones (from 500–900°C for neutron-bombarded stones and from 500–1200°C for electron-bombarded stones) produces orange, yellow, brown, or pink colour. Blue to blue-green stones that are not annealed are separated from natural stones in the same manner as gamma ray-treated stones.

Prior to annealing, nearly all irradiated diamonds possess a characteristic absorption spectrum consisting of a fine line in the far red, at 741 nm — this is known as the GR1 line and is usually considered a strong indication of treatment. Subsequent annealing usually destroys this line, but creates several new ones; the most persistent of these is at 595 nm. If however an irradiated diamond is annealed above 1000°C, the 595 line too is destroyed, but leaves two new lines at 1936 and 2024 nm in the infrared. These lines are detected in gemological laboratories using spectrophotometers: the lines are best detected when the stone is cooled to very low temperatures (below -150°C).

It should be noted that some irradiated diamonds are completely natural. One famous example is the Dresden Green Diamond. In these natural stones the colour is imparted by "radiation burns" in the form of small patches, usually only skin deep, as is the case in radium-treated diamonds.

Electron beam enhancement of colourless Topaz

Topaz is found on most continents of the earth. The colour varieties are; transparent colourless, red, pink, orange, brown, yellow, blue and green, with the cherry-red imperial and pink topaz from Brazil being the most valuable. The blue topaz coloured by radiation from natural radioactive materials in the ground during millions of years is also found. Its natural blue colour, in deposits found so far, is a pale light blue that is not given much attention. The most common topaz is the colourless topaz, which is found in abundance and for that reason is worth very little.

During the last two decades the technique of using radiation for colouring these colourless topaz into a more desirable and permanent blue colour, has been refined and today the electron beam enhancement is used for mass production of large quantities of blue topaz. This technique has made the blue topaz the most common of the topaz used in jewelries.

Colours of radiation treated Topaz

The most common colours of topaz resulting from radiation treatments are:

Sky Blue topaz (moderately strong light blue) is the result of treatment of colourless topaz with either gamma rays from Cobalt 60 sources or electrons produced by electron accelerators, followed by a heat treatment (Fig. 5.2).

Fig. 5.2 Photograph showing Topaz treated by high energy electrons from a linear accelerator results in the **Sky Blue** colour**.**

London Blue topaz (slightly grayish medium dark to dark blue) is the result of treatment of colourless topaz with neutrons produced in nuclear reactors, followed by heat treatment.

Topaz treated by neutrons from nuclear reactors result in the **London Blue** colour.

Swiss Blue topaz (strong to vivid medium to medium dark blue) is achieved by the use of a combination of neutron treatment followed by treatment with either gamma, or electron treatment and heating. Topaz treated by a two-step process, both with neutrons and electrons, result in the **Swiss Blue** colour

Colouring factors in Topaz

Most colours of topaz are caused by colour centers in the stones, except for the pink-to-

violet and the pink component of some orange, which are caused by chromium impurity (K. Nassau, 1984).

Almost all colourless topaz turns brown on irradiation, already at a very low dose (5 to 10 Mrad), and other colour varieties of topaz are affected by the brown component added. This became apparent when the US-Mail in 2001, started to irradiate mail in electron accelerators as a method to kill Anthrax spores, which could be distributed in mail by terrorists. Concerned jewelers and their customers realized that some gemstones could change colour with this treatment and wanted information whether alternative carriers, who did not use irradiation, should be used.

The very low dose brown colour intensifies with increased irradiation doses and is followed by a greenish-brown colour at medium doses (500 - 1,000 Mrad), a brownish-blue colour at higher doses (1,000 - 5,000 Mrad) and eventually to a blue colour at very high doses (5,000 - 20,000 Mrad). The brown colour derives from two different types of colour centers. One is of fading nature and the other of a more stabile nature (K. Nassau, 1984). Most frequently appearing brown colour centers is of the fading types, and exposure to light or heating it at around 200°C results in fading of the colour.

Type of irradiation methods

Topaz is as mentioned earlier most frequently treated by irradiation from Reactors, Cobalt 60 irradiators and Electron Accelerators. Electron irradiation from high-energy electron accelerators is today the most widely used process for colouration of Sky blue and Swiss blue topaz. The advantage over gamma irradiation is mainly the high dose rate, which allows the treatment to be carried out in a very short time. Neutron irradiation makes the topaz radioactive and in need of a cool-off time (from a few months to years) before they can be released for further processing such as electron treatment, annealing, cutting or polishing.

Accelerators used for irradiation treatment of Topaz

Electron Accelerators mostly used for colour enhancement of topaz are of the types, which produce a high energy 10 – 20 Million Volts (MeV), and has a high power 10 – 60 kilo Watt (kW). The accelerators power (kW) is important for the processing rate/time of the stones exposure to the electron beam. A 10 kW accelerator has the capacity to produce 15,000 ct to 45,000 ct per day and a 60 kW accelerator 100,000 ct to 300,000 ct per day.

The energy (MeV) is important for the penetration of the electrons through the stones, a higher energy will produce a higher penetration. If the electrons don’t penetrate the stone,

they will stop/get trapped in the stone and, due to the low electrical conductivity of topaz, the electrical charge in the stone will increase. If this charge becomes high enough, an electrical discharge in form of a lightning in the stone occurs, and an internal lightning/inclusion that looks like thin lines or, in case of a larger discharge, a small white cotton ball.

To prevent this damage the choice of energy, MeV, need to match the density of the amount of topaz that is exposed to the electron beam. The electrons need to pass through and out of the stone after they have induced their colouring effect. Suitable for small and medium stones is 10 MeV, and for larger stones energies up to 20 MeV is necessary. With higher energy levels (well above 10 MeV) some radioactivity can be induced in the topaz, with the level of radioactivity depending on quantity and nature of impurities present in the topaz (K. Nassau, 1984). A cooling off period from a few days to a few weeks is necessary until the radioactivity decays to acceptable/regulated level. Dose distribution in materials as a function of beam energy (MeV) (E. Svendsen, 2003).

Process of cooling

Because of the high power (the higher the kW - the higher the temperature) deposited in the stones during the electron beam processing, it is important to cool the stones. In most cases water is used for the cooling and the stones are either placed in running water or water is sprayed over the stones during the processing. Typical signs of insufficient cooling are thermal cracks surrounded by numerous lightning or small disc-like inclusions visible when the stone is tilted slightly. If the cooling fails the stones will rapidly be so hot that they will shatter and loose all colour, with a high economic loss as a result. The cooling system's water-flow must therefore be tightly controlled and interlocked so that the accelerator immediately stops the radiation if the cooling system fails.

Post irradiation annealing

After the electron beam treatment, changes in the topaz brown and blue colour centers occur. The brown colour fades already at temperatures around 200°C, while the blue colour is stable to temperatures up to 600°C. Heat treatment of the topaz for several hours at around 200° C is therefore performed in order to achieve strong blue colours.

Radioactivity in topaz

In most cases electron accelerators at 10 MeV is used for treatment of topaz and these facilities cannot produce radioactivity in topaz. Topaz treated with 20 MeV electrons can

be activated for days or a few weeks. Topaz treated with neutrons in a nuclear reactor turn radioactive for a longer time (the longer the exposure – the higher the activation), usually from a few months up to years. For this reason the health authorities have issued very strict rules for measuring of the activity in the topaz before they can be released from these facilities.

Identification of irradiated gemstone:

The identification of irradiated stones is not possible with conventional gem testing equipment.

i). In the case of stones which have just been irradiated or Those with residual radio activity, it may be possible To detect signs of activity with a Geiger Mueller Counter (measures radio activity).

ii). Structural imbalances which are caused as a result of irradiation can be identified in some cases with The help of spectroscopy-infrared and Raman Spectrums. In irradiated diamonds the characteristic absorption exists. Spectrum for yellow to brown irradiated stones are 594nm, 498nm : Brown : 498nm, 504nm (both of equal intensity) ; Green : 504nm, 741nm.

iii). In the case of Cyclotron treated diamonds, under Magnification those irradiated from the crown, Show a dark ring within the girdle. Those irradiated from the pavilion show an " umbrella effect" or a Number of dark shadow lines around the culet. If treated through the side, there will be a zone of Colour near the girdle.