# Value Addition in Diamonds and other Gemstones by Nuclear Radiation, Phobias and Safety Considerations

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## ABSTRACT

Four Cs namely color clarity carat (weight) and cut primarily determine the price of a gem. Neutron irradiation, gamma rays and electron beam can be utilized to enhance the color and clarity of aquamarine, quartz, tourmaline, kunzite, topaz, pearls and most importantly of diamonds. Imparting color and clarity to these gems, otherwise devoid of these attributes, results in significant value addition. The enhanced gems may possess stable or unstable colors depending on the nature of color centre produced. This paper reviews the processes of enhancement of topaz and diamonds with special emphasis on neutron irradiation. In view of the radioactivity generated as a result of exposure to neutrons and the likelihood of undue exposure to radioactive gems, safety aspects have been discussed. From commercial viewpoint the aspect of detection of treated material has been documented. Related contender, the process of enhancement of gems by gamma rays has been described. The enhancement of gems by radiation (in synergy with heat) is a commercially viable technique and constitutes a peaceful application of nuclear technology .It has potential and future prospects in GCC member states.


## 1. INTRODUCTION

Lustrous and brightly colored objects have been worn since prehistoric times as personal adornment and as treasures by royalty. Luster or fire, iridescence opalescence, asterism, chatoyance, color or the lack of color are some of the characteristics that increase the beauty of a gemstone and consequently its value. Various methods, fraudulent or otherwise have been used over the centuries to enhance the appearance of gems. Some interesting examples include the practice of bleaching pearls by passing these through the intestine of a live cock, or by soaking these in slaked lime. Vinegar, oil and calves bile were constituents of a formulation or a process to produce emeralds.

Emeralds are oiled with green resins or plastic or special mixture to hide cracks and to deepen the color. To make opals and turquoise more lustrous, oil impregnation is carried out to fill the pores. A desirable brown color or red shade is obtained in agate and chalcedony by spraying an acid solution of iron oxide. Aniline, indigo and synthetic dyes are employed to improve the appearance of quartz, topaz and amethyst. Synthetic growth over quartz has yielded larger and much more valuable emeralds. Jewelers are known to increase their profits routinely by placing a metal foil cloth or butterfly wings at the back of gems that stud the jewelry. Pliny, in 50 A.D wrote “There is no fraud or deceit in this world which yields greater gain and profit than that of counterfeit gems”.

Fraudulent or otherwise, these practices were carried out in secretive fashion and without the adequate knowledge of reasons for color changes. Modern solid state physics and in particular high energy ionizing radiation has made it possible to carry out transformations which are comprehensible, reproducible and reliable. In the paper is reviewed briefly the enhancement of the gemstone in particular topaz and diamond by neutron irradiation and modern techniques.

## 2. RADIATION SOURCES

The irradiation sources can be classified into following types:

1. Electromagnetic radiation
2. Atomic particles

Electromagnetic radiation commonly utilized to change the color and clarity of the stones can be categorized as under;

i) Light or ultraviolet light which produces less pronounced coloration

ii) X Rays that cause non uniform color and changes are not so significant

iii) Gamma rays that produce uniform coloration accompanied by clarity in some cases. Assemblies or irradiators often comprise cobalt 60 or less commonly cesium pellets encapsulated in a thick lead shielding .These suffer from the drawback of need to replenish or reload the source periodically due to inherent decay. The 100000 curies source, designed to sterilize food and medical disposable may handle several hundred kilogram of load. The gamma ray power or intensity is averaged out around 1.25Mev and can’t be varied at will. At this intensity no radioactivity can be induced in gemstones.

Atomic particles that can be utilized in coloring gemstones are:

i) Charged hadrons namely protons neutrons and alphas. Due to their very limited penetration, less than tenth of a millimeter, these are not suitable for commercial use.

ii) Neutrons induce uniform color but could cause residual activity depending upon nature of metallic impurities. Certain kind of shielding and selection of the appropriate material can mitigate the generated activity. Neutrons, not being charged, transfer energy by direct collisions with the atoms of the gemstone. As the neutrons travel long distances, uniformly of color and depth is excellent. Out of the two types of neutrons emanating from the nuclear core, the desirable fast neutrons produce atomic displacements efficiently. Neutron energy of as low as 150eV is good enough to displace a carbon atom in diamond. These high momentum and massive neutrons kick out carbon atoms with so much energy that a cascading effect sets in. Slow neutrons are however a menace as these produce no displacement or color charges. These are absorbed by the atoms which become radioactive. The characteristics of the electromagnetic radiation and atomic particles are described in Table 1.

Often gemstones such as sapphire, ruby and quartz on turning radioactive are stored till they are safe to handle. Ideally the flux at the centre of 1 megawatt swimming pool reactor is around $10^{14}$ neutron/$cm^2$/second and the fast neutron ratio is high enough to color topaz, diamonds etc. in a matter of few minutes.

Irradiation with electrons has certain advantages beams can be made more uniform in density and spread over large areas, thus avoiding local heating. High energy electrons can displace atoms in the crystal so cause permanent changes. Topaz irradiation in this context has proved to be a commercial success as several tons are processed daily world over.

## 3. CAUSES OF COLOR

Irradiation can knock of electrons from the transition metal atoms. When the irradiation leads to a knockout of an electron, it generates a hole color centre or addition of an electron gives an electron color centre. To produce color centre, the crystal has to initially have hole centre or electron centre precursor. Thus the hole centre precursor is an ion or molecule or atom processing two electrons and removal or ejection of one electron by irradiation produces a hole centre. Likewise electron centre precursor traps the electron (generated by irradiation) and this leads to formation of an electron centre. Factually a neutral hole centre precursor gives a positively charged hole centre and a negatively changed electron centre. These absorb light and consequently produce colors. The explanation is pictorially shown in Fig 1.

Robert Weldon in an article published in Jeweler's circular-keystone, quotes from Gordon Austin Specialist at the US. Bureau of mines, "A very high grade ruby, perhaps no, but almost all else in ruby emerald and sapphire is treated. Close to 100%. Even beyond that aquamarine and other beryl and some tourmalines are all treated to clean up the color or hide the inclusion. One fine argument may be put forth i.e. it is fine to complete gems in areas where nature failed to do the job properly" (Weldon 1993).Most gem species undergo a wide range of treatments.

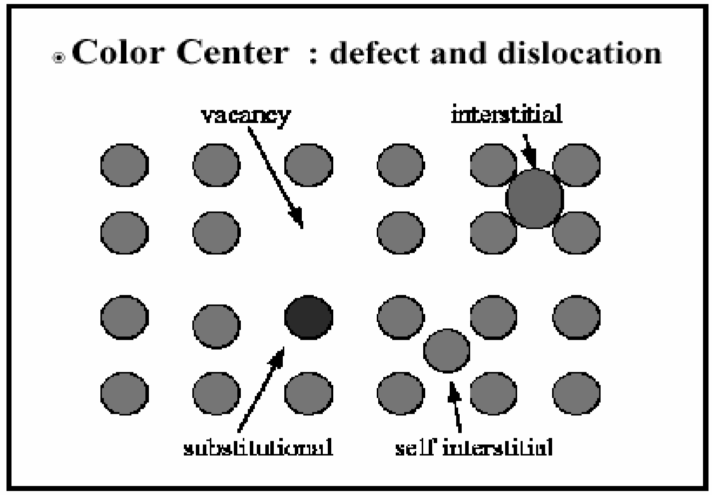


**Figure 1. Color centers responsible for color development**

## 4. NEUTRON IRRADIATION OF TOPAZ AND DIAMONDS

Where at one time or another, gemstones namely kunzite, aquamarine, colorless tourmalines have been neutron irradiated, here only those processes are described whose commercial irradiation is already well established. The nuclear reactors that have offered gemstone irradiation include Bhaba Atomic Research Centre in India, IRI Delft in Netherlands, Soreq Nuclear Research Centre in Israel, and the nuclear reactors in Thailand and Indonesia.

### 4.1 Enhancement of topaz

The enhancement of topaz is a commercial process whose economic viability has been established and well proven. Natural blue topaz is rare while irradiated and heated blue topaz abounds at gem shops and is seen every where. Typically topaz is processed in mass quantities by licensed linear accelerators, gamma commercial irradiators or research reactors that employ neutron irradiation. The stones are submitted as dull colorless pebbles and end up in strongly saturated colors ranging from slightly greenish to deep blue depending upon the type of treatment and irradiation used. Treated blue topaz is commonly available as California blue, sky blue, and London blue, a subtle reference to there depth of man induced color. It is author's experience that some colorless stones found in North Pakistan respond well to gamma irradiation Likewise there is certain kind of topaz transferred readily into blue on neutron irradiation. One problem encountered is the residual activity but this may be avoided to reasonable extent by choosing the right parameters for neutron irradiation and the right starting material.

| Radiation type | Typical energy (eV) | Coloration uniformity | Power Requirement | Induced radioactivity | Localized heating |
|---|---|---|---|---|---|
| **A. The electromagnetic spectrum** | | | | | |
| Light | 2-3 | Variable | Low | No | No |
| Ultraviolet, s.w. | 5 | Variable | Low | No | No |
| X-rays | 10,000 | Poor | Medium | No | No |
| Gamma rays | 1,000,000 | Good | None | No | No |
| **B. Particles** | | | | | |
| Neutral: neutrons | 1,000,000 | Good | Very High | Yes | No |
| Negative: electrons | 1,000,000 | Poor | High | No | Very Strong |
| Negative: electrons | 10,000,000 | Poor | High | Yes | Very Strong |
| Positive: protons, deuterons, alpha particles, etc. | 1,000,000 | Poor | High | Yes | Some |

**Table 1: Characteristics of the rays and particles use for irradiation**

| | |
|---|---|
| Type Ia: | Contain nitrogen in local platelet-like concentration. They from the majority of natural diamonds. |
| Type Ib: | Contain nitrogen only in most finely divided state (Almost all synthetic diamonds). |
| Type IIa: | These diamonds don't contain nitrogen |
| Type IIb: | Diamonds contain boron. All blue diamonds belong to type IIb: These are semi conductors of electricity. |

**Table 2: Diamonds Types**

Our experiments at PINSTECH (Ahmed 2006) using neutron irradiation have shown the presence of scandium-46 (half life 84 days), tantalum- 182 (115 days ), manganese- 54 (303 days) and iron- 54 (45 days) as impurities. Pronounced activity ensues from major emitter scandium – 46, that is quite penetrating, consisting of gamma rays with the relative high energy of 889000 and 1120000 electron volts.

To obtain deep London blue, fast neutron bombardment followed by electron irradiation is practiced, resulting in a brownish material which is heated around 400 $C^o$ to yield a deep blue. The residual activity is intense but this can be skillfully reduced. Very high doses of electron beam are required (around 400 Mrads) to achieve the right color. For bulk irradiation certain kind of containers made of aluminum appropriately shielded to reduce radioactivity have been designed by the author of the paper. The NRC (USA) monitors topaz treated in the USA and only licensed vendors deal in irradiated topaz. Neutron irradiation facilities in Indonesia and Thailand routinely produce large quantity of blue topaz.

## 4.2 Enhancement of Diamonds

Diamond combines a magnificent brilliance and durability with a wealth of differing colors, characteristics that make it unique among gemstones. In a diamond, carbon atoms are arranged in a cubic lattice that does not absorb visible light. A perfect diamonds is therefore colorless but most diamonds contain impurities of atoms ranging form the light boron to the massive uranium in rather low concentration of few parts per million. These impurities bring about distortion and defects of the lattice that absorb light imparting, consequently, colors to the diamond. These colors may range from light yellow to light brown. In trade these are named as cape diamonds. No wonder, about 80 % of the cut gems are light yellow to light brown in color and there worth is far less than a colorless stone. Consequently, large number of cheap cape diamonds lies unsold. On the other hand, stones of deep shades of yellow, green, red or purple or black are so rare in nature that these enjoy the status of expensive collector's item. This alteration of cape diamonds into a color diamond is thus a value addition of high order. For better comprehension , diamond types are shown in Table 2.

The treatment has been controversial due in part to the history associated with the nature of enhancement introduced at the turn of the century. The effect of radiation on diamonds was discovered when diamonds were embedded in radium salts (radium chloride or bromide) for a month or two by Sir William Crooks (Crooks 1904) to color them. Some gem dealers with a keen sense of profit than of caution were quick to exploit this discovery. However stones treated in this manner, although in great demand were never too satisfactory because of the surface contamination by radioactive material. Our neutron irradiation of cape diamonds coupled with heating has always resulted in deep colored green, blue, pink, yellow diamonds free from any radioactivity. ( Ahmed 2007).

A high energy electron of more than 500 KeV energy or a neutron of energy grater than 20eV (because it is more massive) can displace a carbon atom from diamonds lattice if there is a hard collision. A gamma ray on the other hand has to knock out an electron which in turn could produce a displacement only if it gains sufficient energy. This second order process therefore makes gamma radiation very inefficient is producing color in diamonds. Prolonged exposure to gamma rays merely increases the luster of the stones. When knocked out, the displaced carbon atoms may settle down between the rows of lattice atoms having a vacancy in its original site. This interstitial vacancy or point defect is responsible for absorption that's give blue color. Such diamonds were first found in large quantities in Jagersfontien mine in South Africa and were known as Blue Jagers. It is interesting to remark that totally colorless diamonds and those of deep color are very rare and so command a high price.A natural blue diamonds is type II b, which is a semi conductor of electricity. An artificially colored blue diamonds will not be type II b and therefore will be a non-conductor of electricity.

## 4.3 Identification or detection of irradiation

Irradiation is difficult sometime impossible to detect by conventional gemological techniques. This is especially true of greenish diamonds. A Geiger counter will detect radio activity but there is rarely any because of modern treatments which preclude treatment by radium salt. It may be easier to detect the treatment when irradiation and heating are combined. Naturally colored blue diamonds contain boron and are natural semi conductors of electricity whereas irradiated blue are non conducting. Electron spin resonance measurements may determine the origin of the color but as there measurements are expensive, it is not worth testing a diamonds weighing less than a carat (0.2 gm). In trade it is assumed that all small size colored diamonds has been irradiated, unless proven otherwise. There remains an ethical questions for the treatments, accepting that such discolor will detract something from the price.

If the diamond has been cyclotron treated through the table, a dark ring will be seen on looking down on the pavilion. If it has been treated through the pavilion, a shape like an opened umbrella will be seen looking down through the table. If treated through the side, there will be a zone of color near the girdle probably on both sides of the stone.

Diamonds treated in a cyclotron by protons, deuterons or alpha particles also lose their radioactivity after treatment. The color is only skin deeps because the charged particles can't penetrate deeply, it can be polished off but it is permanent as far as it is known. The subject of the identification of artificial coloration in diamonds has been discussed in detail by Scarratt (Scarratt 1982).

Interesting account of what must you disclose and price differential has been presented in an article by R. Weldon entitled, "How gem enhancement turns ugly ducklings into swans" (Weldon 1993).

# 5. SAFETY CONSIDERATIONS

As mentioned previously, the green diamonds obtained as a result of immersing in radium salt solution by Crooks, become trade favorite but the surface activity remained even when tested after 34 years. Activity was reported to originate from presence of $Pb^{216}$ and $Po^{210}$ as residual contaminants and one stone showed activity as high as 40 mr/hr. Though nuclear irradiation of gems may have been pursued by the gem community but two particular reports become well publicized. Crowningshield (Crowningshield 1981) reported that a parcel of topaz on examination showed that activity registered was 0.2mr/hr. A parcel of irradiated spodumene was reported to register 0.7 milliroentgens per hour (Rossman and Qui 1982). A statement from the nuclear regulatory commission to the effect that these would not be desirable for extended use was reported by Crowningshield. There are some investigators who contest that occasional exposure to such low doses does not pose a significant risk for health, others however contend that even low doses of radiation present a statistical risk of biological harm (Upton 1982). Prudence dictates that unnecessary exposures must be avoided as much as possible.

Naturally occurring radioactive elements produced an activity of approximately 0.04 Becquerel/gm, K- 40 gives out around 0.16 Bq/gm. In nature, cosmic radiation is considered responsible for the coloration of blue topaz and smoky quartz. The average individual gets from the environment a dose of about 360 mrem per year (1 mrem daily). Due to geographical situation, in some parts of the world, the dose may be ten times higher. Contributing to this, background radiation itself is about 36 mrem. Average human body contains about 200 nCi of potassium 400 and 100 nCi of carbon 14.

Health hazards from gemstones possessing radioactivity less than 2nc/gm are therefore practically ignorable. There is also a general agreement that any material having less than 2nCi/gm is harmless. In a documents published by "Nuclear Regulatory Commission (NRC)" are recorded the maximum permissible concentrations of radio nuclides in treated gemstones( Stello 1987). In a detector, 2nano-curies /gm is equal to 75 counts per second per gram. A liberal law in US allows that radiation workers can receive 1500 mrem over the whole body whereas in Europe, the permissible limit is 50 m Sieveret (5000 m rem) on a yearly basis. Applying this to jewelry would correspond to wearing of rings, bangles or watches of 8.5 mrem per hour per night and day for a year. To benefit from the enhancement, most regulation has been ignored particularly by insistence of the treator of the fact that the material released once it has gone below the background activity is safe. No wonder science 1981, United States, NRC began issuing licenses to irradiation facilities.

Ironically though concentrations of radioactive elements are present in some gemstones, most prominently zircon, ekanite, fergusonite, thoriantite and potassium feldspar. There are no government regulations to the knowledge of the author that control the sale and the distribution of naturally occurring gemstones though these may contain radioactive elements. Activity of some is recorded here.

a. Red, yellow and blue zircons contain $U^{238}$ from 0.03 to 0.3 nano curie per gram.

b. Green zircon has activity around 0.5 to 2.5 nCi/gm of $U^{238}$.

c. Ekonite contains Th $^{232}$ and $U^{238}$ from 26 to 6.5 nCi/gm.

d. Fergusonite contains $Th^{232}$ and $U^{238}$ from 40 to 3 nCi/am.

e. Feldspar has around 0.1 nCi/gm of $k^{40}$.

f. Thorianite contains $Th^{232}$ and $U^{238}$ in concentrations of 87 to 19 nCi/gm. This exceeds NRC limits by about 1700 times.

Due to radiation emanating from minerals in soil containing radioactive elements such as thorium, uranium, radium and potassium-40, changes in oxidation state of transition metals do transform colorless gems into colored ones. Radiation could affect a gem by interacting the vacancy and interstitial defects in the lattice. The intense radioactivity in some stones destroys the crystalline structure totally

## 6. GAMMA IRRADITION of GEMSTONES

Gamma irradiation of certain topaz, colorless tourmaline, quartz, spodumene, aquamarine and pearls and resultant transformation into value added colored gemstone is a value addition process, adopted particularly in countries where rough is mined in sizeable quantities. All the same, some contract facilities provide services by charging a few US dollars to several hundred dollars per kilogram. As no radioactivity can be induced, there is no licensing required. Color centre are implicated to be the origin of coloration. Colors imparted can be stable or unstable depending on the fact that the knocked off electron can be sent back to original site, a phenomenon triggered by light or heat. For a shallow or weak trap the electron gees back even at room temperature in darkness. Deep traps would require ultraviolet to bleach them. Smoky quartz, amethyst, blue topaz and stable brown topaz would not bleach in sunlight and need heating at temperatures above 400 $^oC$ to bleach these.

## 7. IMPLEMENTATION IN GCC COUNTRIES

Some neighboring countries in Africa namely Nigeria, Kenya, Ghana, Zimbabwe Tanzania abound in gemstones both precious and semi precious, namely rubies tourmaline topaz , aquamarines etc. Angola, Ghana, Zaire, Sierra Leone produce diamonds of good quality.11 million carats of proven reserves of diamonds are located near Accra in Ghana .In 1960s the state owned company Ghana Consolidated Company mined 2 million carats of diamonds per year. Nuclear reactors in GCC member states can provide contract services for irradiation of gems brought in from these countries or elsewhere and charge a handsome fee corresponding to the cost of the treated material. Gamma rays facilities and EB facilities in GCC member states may provide services for commercial irradiation of, tourmaline, topaz, aquamarine, kunzite, quartz and pearls etc and earn reasonable revenue. For the latter two techniques, no licensing or monitoring of radioactivity will be required. In addition to commercial gains and upgrading of quality of material, academic research will provide expertise in the advanced field of radiation and heat processing of gems. This surely will be a very rewarding peaceful application of nuclear technology in GCC member states.

## 8. CONCLUSION

Though the enhancement of the gems by the synergy of heat and radiation would benefit enormously the institutes and the nations that mine these gems, yet following impediments have hindered the ready acceptance and implementation of these technologies.

a. The phobia and fear relating to radiation, applying equally well to food irradiation.

b. Practically no links between scientists and gem dealer whose business in most cases is quite obscure.

c. Inaccessibility of radiation sources to the gemstones dealers.

d. Inability of the treator and the research institute to penetrate the gem trade.

Author of the paper had opportunity to visit China, Viet Nam, Sri Lanka, Kenya, Ghana, Morocco in connection with enhancement of rubies, sapphires, aquamarine tourmalines, topaz and diamonds employing processes including EB treatment , neutron irradiation and gamma rays in synergy with heat treatment. These countries have expressed deep interest in developing this technology at commercial scale particularly because mining operations are yielding higher quantities of all kind of gems including diamonds. Additionally it has been demonstrated that the associated value addition is high. The door is open for those who wish to turn ugly ducklings into swans and earn enormous profits as treators or sellers of these value added products. Under the appropriate guidance of an expert, the processes or technology can be learned also ensuring that under no circumstances the precious gems are destroyed in the course of enhancement or experimentation.

In conclusion gem enhancement by neutron radiation constitutes a peaceful application of nuclear technology that has enormous potential for implementation in GCC member states.

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