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Value Addition in Gemstones by Nuclear Techniques

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ABSTRACT

Northern areas of Pakistan are rich in minerals and different types of precious/ semi-precious gemstones. One of these gemstones called topaz is quite abundant in Gilgit-Baltistan, Skardu and Kashmir regions. Although, topaz is a semi-precious stone but pink topaz from Mardan district in KPK province has a high worth in its natural form because it is rare in the world. In general, topaz is a colorless transparent stone, which is not very expensive. These semi-precious stones can be made precious by adding colors using different treatments like thermal heating, electron beam exposure, gamma rays or neutron irradiations. Except for electrons and neutrons, all other treatments give brown, golden or light blue colors, which are of low worth. The colors are usually not stable and fade away with the passage of time. About 30-40 times value can be added if the color is persistent dark blue. This deep blue color in topaz can be produced by neutron irradiation from a nuclear reactor. At present, for semi-precious stones, the world market is in the hands of blue topaz; typically named as Sky blue, Swiss blue and London blue. Countries like Indonesia, Thailand and US are already in this business and making significant profit. Pakistan Research Reactor (PARR-1) at the Pakistan Institute of Nuclear Science & technology (PINSTECH) has the capability to produce these desirable colors. Therefore, handsome revenue can be generated by utilizing this methodology. Apart from this, the other benefits are the development of a useful technology, collaboration between public and private sectors and application of nuclear techniques for peaceful purposes, which is one of the objectives of Pakistan Nuclear Society (PNS).

Keywords: *Topaz, color formation, research reactors, neutron irradiations, radioisotopes, elemental analysis*

1. Introduction

History reveals that different types of gemstones were regarded as a status symbol. Since ancient times, kings and queens used to wear gems embedded in gold for their grandeur and beauty. The royal families had a hobby to collect attractive gems like diamonds, ruby, sapphire, emerald, tourmaline, aquamarine and topaz etc. People attach particular stones with their good fortune and believe that the use of these stones have impact on their lives. Therefore, the business of precious stones has always been considered as profitable one. Various types of such precious and semi-precious stones are found in different areas of Pakistan mainly in the metamorphic rocks of mountainous regions Fig. 1. These are found in Northwest Frontier Province (Deer, Swat, Mansehra and Peshawar), Federally Administered Tribal Areas (Mohmand Agency, Bajaur Agency, Khyber Agency and Waziristan Agency), Northern Areas (Chilas, Gilgit, Mardan, Hunza, Shigar, Baltistan, Kashmol etc.) and in Balochistan Province (Kharan and Chaman) [1]. Some of these gemstones have inherent worth in their natural form while others can be made valuable by various color enhancement processes. Such gemstones are labeled as 'treated stones'. In general, the value of gemstones depends upon 4 Cs': color, clarity, cut and carat. The utmost important is of color, which can be induced by thermal heating, diffusion, coatings, bleaching and irradiation methods that include X-rays, gamma rays, electrons and neutrons. Except for neutrons, the induced colors are usually temporary. The research reactor at PINSTECH can serve this purpose, as it is a huge source of neutrons.

For this study, topaz was chosen due to the interest of gemstone dealers and exporters. This is mainly due to the big difference in price of natural and treated gemstones. The name

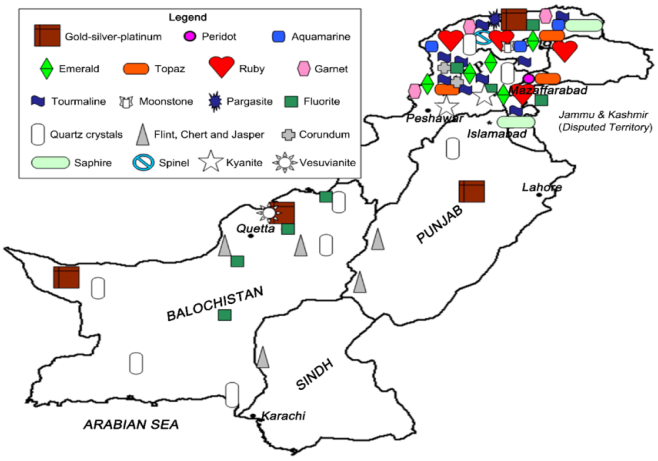

Fig. 1: Main areas of gemstones in Pakistan.

'topaz' is derived from the Greek Topázios (Topasos); old in the, which was famous for mining of yellow stone in ancient times. Alternately, it is believed that the topaz originates from Sanskrit word '*tapash*' due to the fire like appearance of golden topaz in sunshine. Worldwide, it is found in Afghanistan, Sri-Lanka, Czech Republic, Germany, Norway, Italy, Sweden, Japan, Brazil, United States, Mexico and Pakistan [2].

Topaz is an aluminum silicate with fluorine and hydroxyl ions having chemical formula $Al_2SiO_4(F,OH)_2$. Some general properties of topaz are given in Table-1 [3]. Both the main elements Al and Si do not cause induced activity problem but impurities with high capture cross sections may create problems when exposed to neutrons. Elemental analyses reveal that topaz from different mines may contain impurities like Mn, Sc, Co, Cs, Ta etc. Therefore, thermal neutrons are considered as undesirable as they activate metal impurities

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present inside the materials. To minimize their effect, strong absorbers like cadmium, indium and gadolinium is used to protect the material from thermal neutrons. Topaz changes its color due to formation of color centers (F-Centers) which are formed by bombardment with fast neutrons [4-8].

Table1: General Properties of Topaz

Chemical Formula:	$Al_2SiO_4(F,OH)_2$
Empirical Formula:	$Al_2(SiO_4)F_{1.1}(OH)_{0.9}$
Class	Silicates
Environment:	High temperature quartz veins and cavities in granites
Name Origin:	Named after its locality: Topasos Island in the Red Sea
Synonym:	Yellow stone

Most insulator crystals and pure alkali halide crystals are transparent to visible light. However, when irradiated, these crystals appear to be colored due to the selective absorption of some component of visible spectrum by certain imperfections, which are usually present in the crystal. Thus a color center is a lattice imperfection (or defect like vacancies) which absorbs visible light. The light of some specific wavelength gets absorb while the remaining part transmits through the material that causes the colored appearance. The transmitted beam received by our eyes contains only the remaining colors [9-16].

F-type color center formation is the reason of coloring in topaz. Fig. 2 is of a fluorite structure containing an 'F-center' where a fluorine ion has been replaced by an electron. The name F-center is from the German word for color, *farbe Farbenzenter'*, as crystals containing these point defects are highly colored. These defects have been investigated by various spectroscopic techniques. The F-centers are point defects and can be readily formed in alkaline halides with the help of ionizing radiation, such as a Tesla coil or X-ray source [17].

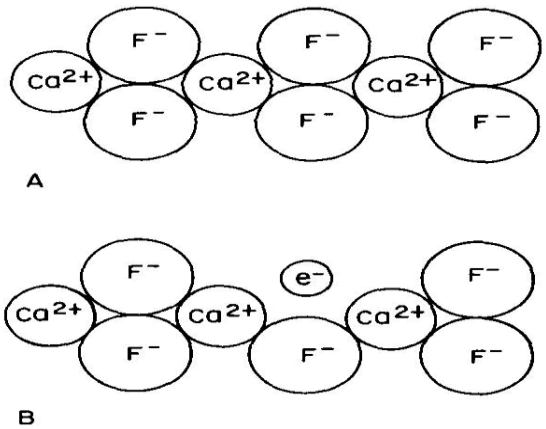

Fig. 2: Fluorite structure: (A) normal, (B) containing an 'F-center' where a fluorine ion is replaced by an electron.

2. Experimental

As pre-experimental arrangement, the surface of each stone was thoroughly washed in a standard decontamination soap solution, wiped with clean cloth and dried in air. First of all, raw topaz pieces were analyzed to see whether there was any radioactive element in the original material. For this purpose, gamma-ray spectroscopy system based on a high-purity germanium (HPGe) detector with associated electronics comprising of a Multichannel Analyzer was employed. The system was calibrated by using the standard Co-60 and Eu-152 sources from IAEA. The peak energies and the calibration spectrum of Eu-152 source is shown in Fig. 3.

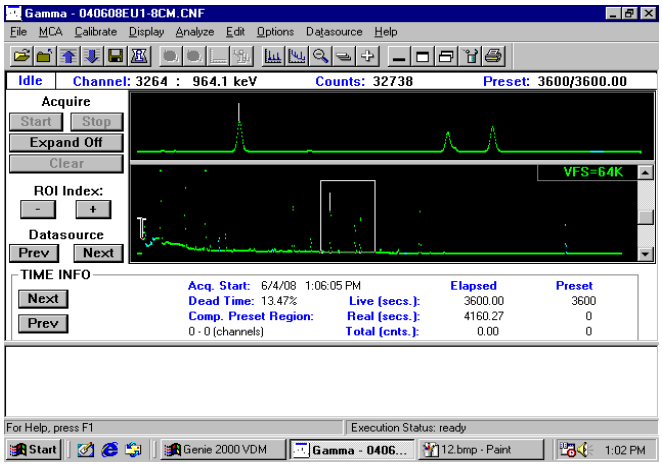

Fig. 3: Calibration of the detector using Eu-152.

The elemental analysis revealed that there was no radioactive impurity in any sample and its spectrum was the same as for background level of the laboratory where the analysis was performed Fig. 4.

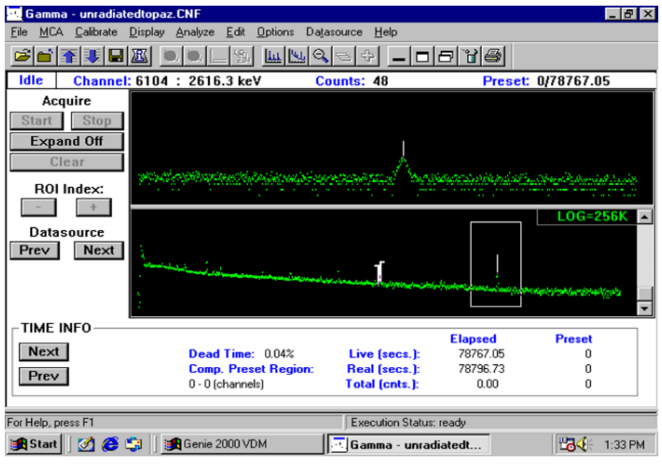

Fig. 4: The spectrum of raw topaz samples.

After that, a few pieces of topaz from Gilgit area, obtained with the courtesy of Gems and Gemology Institute, Peshawar were selected for irradiation inside the reactor core. For that initial attempt, two containers were used. A standard plastic (polyethylene) capsules for shorter time (less than one hour) used in pneumatic rabbit system of PARR-1 as shown in Fig.

5a and a high purity, reactor grade Al capsule for in-core irradiation as given in Fig. 5b.

Fig. 5a: Plastic capsule

Fig. 5b: Al capsule

A sheet of pure Cd (1mm thick) was placed inside the Al container to reduce the effect of thermal neutrons which were undesirable for this study. Similarly, the samples placed in the plastic container were wrapped with a thin sheet of Cd. The samples in plastic capsules were irradiated for 10 seconds and then 45 minutes whereas the samples in Al capsules were irradiated for 12 hours along with IAEA standard SL-1.

3. Results and Discussion

The main objective of this study is to analyze the changes that would occur in Pakistani topaz specifically from Gilgit area after irradiation with neutrons from PARR-1. These stones are originally transparent but can be colored with various treatments like electron beam heating, gamma radiations and neutron exposure. Prior to it, no work has been reported by utilizing neutrons. The study was carried out on topaz stones from different areas for different irradiation times.

3.1 Topaz irradiated for 10 sec

A few pieces of topaz stones (4-8 gm each) wrapped in 1 mm thick Cd sheet were put in plastic capsule and sent inside the reactor core through a pneumatic rabbit system. The neutron flux ~$5x10^{13}$ n/cm^2/sec turned colorless stones to brown. The overall doze on the lot was ~25 mSv. The plot of counts vs. energy is shown in Fig. 6. No residual activity was observed for irradiation of 10 seconds.

3.2 Topaz irradiated for 45 minutes

The same stones were reused in plastic capsule with Cd lining for 45 minutes. The neutron flux was the same. The sample kept in the pool for 2 days so as to reduce the induced activity. The capsule was opened in the hot cell by remote handling. It was found that there was not much activity in the stones (< 2 nCi/g). The color of all the samples changed to golden brown. The samples were taken to the analytical lab for elemental analysis. Negligible impurities were found in small concentrations. Fig. 7 is the plot of gamma ray spectra of topaz after irradiation for 45 minutes.

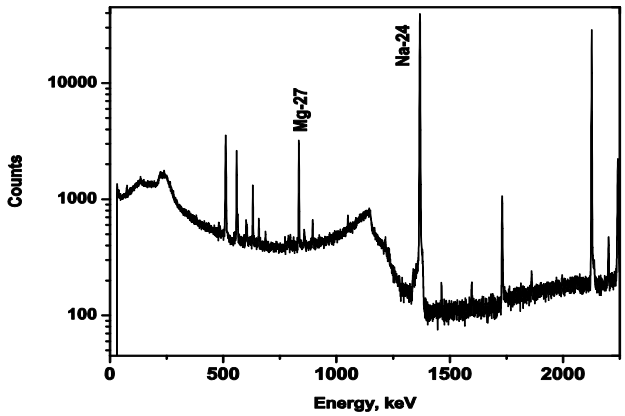

Fig. 6: Count verses energy plot for 10 sec.

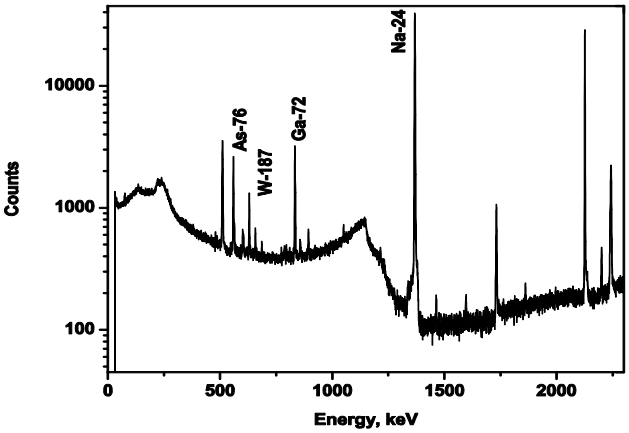

Fig. 7: Counts verses Energy plot for 45 min.

3.3 Topaz irradiated for 12 hours

Two pieces of topaz were packed in a standard Al capsule with Cd lining and sent for irradiation inside the core in a water-box channel where the neutron flux was quite high (~$2x10^{14}$ n/cm^2/sec). The samples were kept in the reactor pool for 2 days so that the induced activity went down. Capsule was cut in the hot cell by remote handling. It was found that there was not much activity in the stones. Some radioactive impurities (Cs-134, Ta-182 and Sb-124) were found in small concentration. Both the stones turned dark blue. The gamma ray spectrum and energy plot of topaz samples are presented in Fig. 8 and Fig. 9.

A detailed study on elemental analysis of topaz obtained from different places in the Northern areas of Pakistan was performed by Wasim et al [18]. They identified trace-level impurities of 22 elements after irradiation of topaz samples for different time intervals. Many of these were common impurities usually found in topaz depending upon the place from where these were obtained. Most of the impurities were the same as observed in this study. However, the focus was on long-live radioisotopes.

Ashbaugh [19] observed activity produced from the radionuclides of trace-element impurities such as Fe, Mn, Co, Zn, Sb, Ta, Cs, Sc and Tb. However, we did not find Mn, Co, Zn and Tb having longer half-lives.

A photograph of the stones irradiated for different times is given in Fig. 10. (Also provide photo of Topaz with no irradiation)

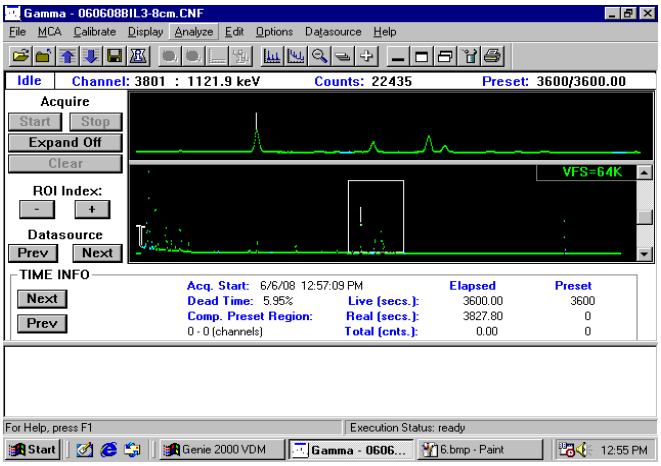

Fig. 8: The spectrum of topaz for 12 hours.

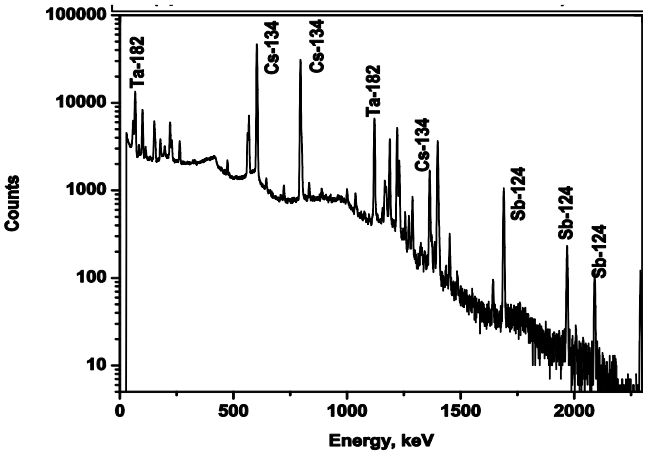

Fig.9: Counts verses Energy plot for 12 hours.

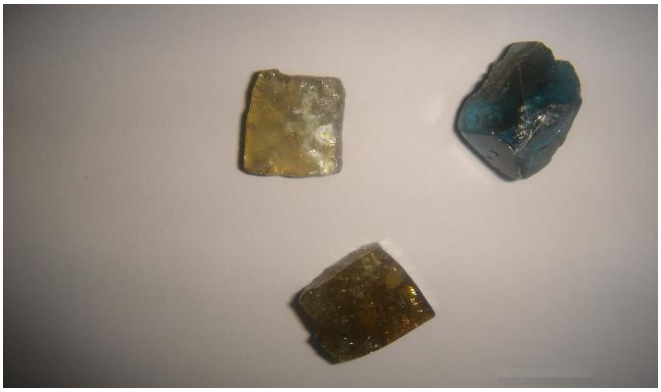

Table 2: Activity after 12 hrs irradiation

Radio-Isotopes	Half Half-life	Energy (keV)	Activity (Bq)
Sc-46	83.8 d	889	5.12E+03
Sb-124	60.2 d	1690	7.96E+05
Cs-134	2.06 y	603	3.72E+06
Ta-182	114.41 d	1120	1.49E+05

3.4 Irradiation of topaz in bulk

A visit to topaz mines was arranged with the logistic support from Pakistan Atomic Energy Commission (PAEC) and financial assistance from Pakistan Science Foundation (PSF). Hence, topaz stones in bulk quantity were purchased from the mining areas in Gilgit and Skardu. Actually, topaz is very similar to quartz and difficult to distinguish with naked eyes. Consequently, in the local markets it is sold mixed with quartz. To ensure its originality, the stones were purchased directly from the mines.

For large scale irradiations (material in kg), special containers of reactor grade pure aluminum sheets were designed and fabricated at the General Services Division (GSD) of PINSTECH. Pure cadmium sheet of 1 mm thickness was used as inside lining to minimize the effect of thermal neutrons. The container system called stringer is shown in Fig. 11. The material was then exposed to neutrons at a convenient position just outside the reactor core in high neutron flux. Generally, a high quality color enhancement in topaz occurs at a neutron fluence of 10^{17} n/cm^2, which can be achieved in 12-20 hours of reactor operation even if the fast flux is ~2x10^{12} n/cm^2/sec.

Zhang, et al [20] observed that the color centers in topaz were produced after 12 hours of irradiation at 1.2 × 10^{19} neutrons/cm^2/sec. They irradiated the samples in a light water nuclear reactor at China Institute of Atomic Energy in Beijing. The samples were placed in cadmium-lined containers to reduce the amount of thermal neutrons caused by absorption and also to increase the amount of fast neutrons. They obtained deep blue color (London blue) in this process. Most of the samples could be handled after 95 days.

The gemstones irradiated in this process could be handled ideally after 3 months but to release in the market may take two years. This is because the dose level must be less than 2nCi/g (74Bq/g) according to the international regulations set by International Air Transportation Agency (IATA).

Fig. 11: Aluminum containers with Cd sheet inside.

In the reactor run of 12 hours at 10MW, the stones were checked from a safe distance as the activity was much high

and it was observed that the color of the stones was not dark blue. Apparently, it was deep sky blue with olive green shade. Therefore, the stones were kept inside the reactor pool at the specified position for the next reactor run after one week.

It is to mention that the PARR-1 reactor mainly operates for the production of radioisotopes for nuclear medical hospitals in the country and not exclusively for gemstones coloring purposes. However, after the 2nd reactor run of 12 hours at full power of 10 MW, all the stones turned dark blue. Since the residual activity was quite high, therefore, the material was kept inside the reactor pool for 3 months. After that the stringer containing topaz gemstones was shifted to the hot cell where the stones were poured into another container. Two representative samples were taken to the analytical lab where the elemental analysis was performed. It was found that the results were exactly the same as for the samples previously irradiated for 12 hours in Al capsule inside the reactor core. Therefore, the experimental study revealed that London blue topaz can be produced in bulk quantities by neutron irradiations of about 20 hours.

4. Conclusion

Pakistani topaz purchased from mining areas in Gilgit region was originally transparent and was not radioactive in raw form. After 10 seconds irradiation, its color changed to light brown and no radioactivity was found. Samples irradiated for 45 minutes changed color to golden brown and negligible activity was observed. The 12 hours irradiated samples turned dark blue. The elemental impurities like Ta-182, Cs-134, Sb-124 and Ag-110 were identified by using elemental analysis system based on high precision gamma ray spectroscopy system. Due to the longer half-lives of some of these radioisotopes, sufficient time was given to decrease residual activity below the prescribed limits. The activity was in the range of micro-curies. In the case of bulk irradiation, the activity was too high. After two reactor runs of weekly 12 hours operation, it was observed that about 20 hours of exposure with neutrons is required to change transparent topaz to dark blue. Due to the formation of long lived radioisotopes, the material in bulk quantity had to be kept inside the reactor pool for about 3 months and subsequent cooling of many months to attain the permissible limits for taking into the market. However, a huge amount of foreign exchange can be earned by export of these treated gemstones. This can be achieved by taking all the stake holders involved in this business on board.

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