The Impact of Electron Beam Irradiation in Topaz Quality Enhancement

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Abstract. Most of the natural topaz is found as colorless. Variety attempt have been used to change its color. In this study, the process of enhancement by electron irradiation be carefully taken by consideration on the optimization of power and energy of electron, efficient cooling system, annealing process and radioactivity occurring and remaining. Electron irradiation was performed on topaz originated from Yen Bai province, in Vietnam. The two of topaz sample were irradiated by 20 MeV electron beam (e-beam) with different fluences of $1.34 \times 10^{16}$ cm$^{-2}$ and $2.64 \times 10^{16}$ cm$^{-2}$, respectively. The characteristic spectra obtained from the investigation compared to the natural topaz sample afterwards. Interaction of radiation with impurity ions in topaz sample during irradiation resulted in changing of colorless to sky blue topaz, which had the broad absorption band of UV-Vis spectroscopy at 620 nm. The ESR spectrum of topaz sample showing a single broad isotropic line with $g = 2.012$ that are correlated with an O-center in the topaz structure. FTIR spectra indicated that sky blue color may originate from the decomposition of hydroxyl group (OH) by the electron beam irradiation.

Keywords: topaz, electron beam, enhancement

1. Introduction

Natural topaz is most commonly found in colorless, but can usually formed in the other colors such as red, pink, orange, brown, yellow, blue and green. The most valuable are the cherry-red imperial and pink topaz from Brazil. Topaz is most commonly irradiated with a variety of radiations. London blue and Swiss blue color, the dark shades of blue color, can produce by exposure the white topaz to neutrons in a research reactor and/or electrons in a linear electron accelerator. On the other hand, if exposure the white topaz to gamma rays and/or electrons and continue by heating it to burn off undesired brown overtones that appear during the exposure process receiving a lighter pure blue color we know as Sky blue color. The detailed process of produce the blue topaz is complicated, especially for sky blue topaz.

Topaz is an aluminum fluoro-silicate with general formula $\text{Al}_2(\text{SiO}_4)(\text{F,OH})_2$, in which OH$^-$ may substitute for up to 30mol% of the F$^-$. The OH/F substitution turns its symmetry into triclinic (P1) [2]. The crystal structure of topaz is belong to the orthorhombic with space group Pbnm ($D_{2h}^{16}$) [3] and four molecules per unit cell. It structure consists of chains of a pair of edge-shared $\text{AlO}_6\text{F}_2$ octahedra and corner-shared $\text{SiO}_4$ tetrahedra that linking octahedral chains in a zigzag fashion parallel to the
crystalline c-axis. The coloration of topaz is frequently governed by transition metal impurities or by irradiation. Many authors have been attributed the blue color to an O\(^{-}\) defect, produced by irradiation and located in OH\(^{-}\) positions of topaz structure, interacting with two equivalent structural Al ions \([4]\). The O\(^{-}\) defect is related to the absorption band at 620 nm. Some authors have been ascribed this absorption band to the presence of Cr\(^{3+}\), Fe\(^{2+}\) and Mn\(^{2+}\) impurities \([5]\). Irradiation treatment caused exchange interaction between these impurities and radiation defect. The chemical composition, different valence states, and occupancy in each site of the topaz structure appear to be associated with one another in the color change caused by irradiation treatment. However, disagreement exists over the detailed origins of the colors. Specifically, the reason for the color changes after e-beam irradiation is still unclear and not well understood.

In this study, we used Ultraviolet–visible Spectroscopy (UV-Vis), including Wavelength Dispersive X-ray Fluorescence (WDXRF), Electron Spin Resonance (ESR) measurement and Fourier-transform infrared (FTIR) spectroscopy analyses to investigate the chemical behaviors in electron beam (e-beam) irradiated colorless topaz samples by two different fluence levels. We also discuss the detailed process of produce sky blue topaz by e-beam irradiation in terms of the initial point of the jewellery manufacturing process.

2. Materials and Methods
Natural colorless topaz of originated from Yen Bai province, in Vietnam was investigated. The natural sample was cleaned by immersing in beaker containing distilled water and sonicated in ultrasonic bath before cutting in perpendicular to the crystallographic c-axis in to 3 pieces. Subsequently, all samples are polished by silicon carbide abrasive paper to be a faceted sample. After cutting and polishing, each faceted sample size was about 6 × 6 × 2 mm.

2.1. E-beam irradiation and annealing
Electron accelerators which produce a high energy 10-20 Million Volts (MeV), and has a high power 10 – 60 kilo Watt (kW) are mostly used for color enhancement of topaz. The electron accelerator used in this study is located at the Irradiation Center, Thailand Institute of Nuclear Technology (TINT), and can produce high-energy 8-25 MeV and a high power 10-16 kW.

2.1.1. Power and energy of electron. The accelerators power in kW is an important parameter for the processing rate/time of an e-beam exposed to topaz samples. All samples were irradiated a 10 kW for 48 hr. and 96 hr. to get electron fluences of 1.34×10\(^{16}\) cm\(^{-2}\) and 2.64×10\(^{16}\) cm\(^{-2}\), respectively. Another important parameter is the energy in MeV, which indicates the penetration of the electrons passing through the topaz; a higher energy will generate a higher penetration. The electrons need to pass through and out of the topaz after they have induced the coloring effect. Topaz has very low electrical conductivity. If the electrons don’t penetrate the topaz samples, the electrical charge in the topaz will increase. If these charges have accumulated high enough, an electrical discharge in form of a lightning and/or a small white cotton ball inclusion in the topaz occur. A suitable energy range for small and medium topazes are 8–10 MeV, and 20 MeV is suitable for larger topazes. All our small samples were irradiated by using 20-MeV electrons. The dose distribution in aluminium as a function of beam energy using in this study is shown in figure 1.

2.1.2. Process cooling. The higher power (kW) creates the higher temperature deposited in the topaz during the e-beam processing. The cooling system is most important to prevent occurring of thermal cracks. In our case, water was used for the cooling process. The topaz samples were either placed in moving water or sprayed with water during the processing.

2.1.3. Annealing. After treated the topaz by e-beam, the unwanted grayish and brownish overtones caused by the brown color center and the pale blue color originated from the blue color center have occurred. The brown color is bleached out by thermal treatments at temperatures about 200°C, while
the blue color is stable to temperatures up to 600 °C. Therefore, the heat treatment of the topaz for several hours at around 200 °C was performed after finished the e-beam irradiation process in order to achieve strong blue colors.

![Figure 1. Dose distribution in aluminum as a function of beam energy at TINT's electron accelerator facility.](image)

2.1.4. Radioactivity after e-beam irradiation. The electron accelerators at lower 10 MeV energy cannot produce radioactivity in topaz after treatment. Topaz treated with 20 MeV electrons can be activated the short half-life radioactive isotope which requires a just few day to allow the residual radioactivity to reach a safe level of less than 74 Becquerel per gram (Bq/g) [6]. After e-beam irradiation, the topaz samples have lie down in safety room to radioactive decay for 3 weeks. Gamma ray spectroscopy has used to monitor the radioactive levels which the final level before further to next process is equal to background level.

2.2. Chemical composition
The chemical composition of the samples was carried out with a S8 TIGER high-end wavelength dispersive X-ray fluorescence (WDXRF) spectrometer. The spectrometer was installed at the TINT’s Service Center in Ongkharak Branch, Thailand. The measurements were done at room temperature with a sample excitation by an X-rays (Rh tube) using 75 μm Be window, 4 kW generator and eight maximum position crystal changer.

2.3. Optical absorption
Optical absorption measurements were done at room temperature using a PerkinElmer Lambda 750 UV/Vis/NIR spectrophotometer located at the Irradiation Center, Ongkharak Branch, Thailand. The recorded spectra were measured on the topaz platelets oriented perpendicular to the c-axis before and after irradiation in wavelength ranging from 300 to 800 nm by setting a spectral resolution of 2.2 nm with a scan speed of 200 nm/ min.

2.4. ESR measurement
The ESR measurements were carried out at room temperature on a Bruker ESR spectrometer (ESP 300 series) operated at an X-band microwave frequency at the Office of Atoms for Peace, Bangkok, Thailand. The spectrometer operating conditions adopted during the experiment were a 350.0-mT central magnetic field, a 10- to 100-mT scan ranges, a 1.0-mW microwave power, a 100-kHz field modulation frequency, a 0.1-mT field modulation amplitude and a 5.10-ms time constant. The stable free radical 1, 1-diphenyl-2-picrylhydra-2l (DPPH) with a g factor of 2.0036 was used as an internal
standard for g-factor calculations. After the spectra had been measured, the positions of the ESR signals were labelled by using their effective g ($g_{eff}$) values.

2.5. FTIR spectroscopy

The mid-infrared spectra of the samples were carried out with a Bruker ALPHA spectrometer equipped with a Globar lightsource, a KBr beamsplitter, and a high sensitivity DLATGS detector at the Ministry of Natural Resources and Environment, Thailand. The measurements were recorded in the region of 4,000 and 400 cm$^{-1}$ with a resolution of 1 cm$^{-1}$. The recorded spectra were averaged over 100 scans. Gauss- Lorentz functions were chosen for band fittings by using the fitting program OriginPro 2015.

3. Results and Discussion

Table 1 shows the chemical compositions analysis of a given sample as measured by using WDXRF. The major oxides in the sample from the WDXRF analysis are Al and Si. It contains significant amounts of Na and Mg, and minor quantities of Fe, Br, Rb and Cs. Other contents, such as Cr, Ti, Ni and Cu, were detected in subordinate concentrations. These concentrations indicated that the sample was topaz pegmatite [7]. This colourless given sample have contended. The correlation of color is may related to this chemical composition [8].

| Oxide: wt%       | Topaz from Yen Bai province |
|------------------|----------------------------|
| Al₂O₃            | 59.49                      |
| SiO₂             | 37.40                      |
| Na₂O             | 1.44                       |
| MgO              | 1.30                       |
| Fe₂O₃            | 0.04                       |
| Br₂O             | 0.01                       |
| Rb₂O             | 0.03                       |
| Cs₂O             | 0.27                       |

| Oxide: wt ppm    |                             |
|------------------|-----------------------------|
| CuO              | 40                          |
| Cr₂O₃            | 33                          |
| Ni₂O₃            | 33                          |
| TiO₂             | 52                          |

| Total            | 99.98                       |

The optical absorption spectra of the given topaz samples were measured in the spectral range from 300 to 800 nm at room temperature. Figure 2 shows the UV-Vis absorption spectra of the colorless topaz before irradiation (solid line), after e-beam irradiations at 1.34x10$^{16}$ cm$^{-2}$ (dashed line) and 2.65x10$^{16}$ cm$^{-2}$ (dotted line). The spectra of the samples show high absorption edge in the UV (below 400 nm) region as can be noticed from the figure 2. All irradiated and heating samples spectra found that the absorption edge shifted to below 400 nm. The natural state sample exhibited no absorption band while after e-beam irradiation at 1.34x10$^{16}$ cm$^{-2}$ increasing of the spectra intensity over the whole wavelength range (380-800 nm). Moreover, after add the level of e-beam irradiation up to 2.64x10$^{16}$ cm$^{-2}$, increasing of the spectrum intensity was highest and appearing of a broad band with maxima at
620 nm was found. Simultaneously, the sample crystal obtained the zoned brown color. After annealing at 200 °C for 1 hr, the colorless zones turned to pale blue and brown color zones turned to sky-blue. Annealing reduced the spectra intensity to original level as before e-beam irradiations but remained apparently a broad band at 620 nm. This band originated for blue color in topaz.

**Figure 2.** The UV-Vis spectra of topaz sample: natural state (solid line), after e-beam irradiations at 1.34x10^{16} cm^{-2} (dashed line) after e-beam iradiations at 2.64x10^{16} cm^{-2} (dotted line) and after annealing (short dashed line).

**Figure 3.** ESR Spectra of topaz sample: after e-beam irradiation 1.34x10^{16} cm-2 (circle-symbol line) and 2.64x10^{16} cm-2 (filled square-symbol line).
The blue color in topaz can be produced by leading the natural colorless topaz to irradiate with neutron, electron and gamma ray. The neutron irradiation can directly produce blue color but in case of electron and gamma ray irradiation, the pale brown color appeared first consecutively with blue color using annealing. The detail origin of blue color in topaz produced by each irradiation method is difference. In e-beam irradiation leaded to appearing of broad band at 620 nm was ascribed to the presence of Cr$^{3+}$, Fe$^{2+}$ and Mn$^{2+}$ impurities [5, 9]. However, the topaz sample in this study has no Mn ions (table 1) including none of any other absorption peak for Cr$^{3+}$ and Fe$^{2+}$. Therefore, one possible reason for the appearance of the absorption band at around 620 nm was the O$^-$ defect [10]. The e-beam irradiation produced this O$^-$ defect in hydroxyl sites which substitutes for fluorine in topaz structure.

The ESR spectra of e-beam irradiated topaz for the magnetic field perpendicular to the c-axis are shown in figure 3. The paramagnetic defects of both e-beam irradiated topazes are observed in identical position of before irradiated topaz sample. The spectra of these samples displayed a strong broad resonance signal with peak-to-peak linewidth of 14.20 mT at $g = 2.012$ which did not show in the natural state sample. Moreover, this ESR line increased the intensity when the electrons fluence levels grow up to $2.64 \times 10^{16}$ cm$^{-2}$. These response is the O$^-$ hole center [11], which has been identified as an O$^-$ ion on an (OH)$^-$ site having interactions with two nearest equivalent Al$^{3+}$ ions. The electron by e-beam irradiation creating the peroxy radical [12, 13] in texture of topaz responded to the broad isotropic resonance line. The ESR intensity of this line slightly decreased after annealing the topaz meaning that the radicals were reduced by heat.

![Figure 4](image)

**Figure 4.** Mid-infrared spectra in the 3300 – 4900 cm$^{-1}$ region of topaz sample: natural state (solid line), after e-beam irradiations at $1.34 \times 10^{16}$ cm$^{-2}$ (dashed line) and $2.64 \times 10^{16}$ cm$^{-2}$ (dotted line).

Figure 4 shows the Mid-IR spectra of the topaz sample. The spectra of the natural state sample (solid line) showed slightly low spectra intensity than irradiated state sample in some range of the Mid-IR region. Normally, the Mid-IR spectra of topaz responded in three region as 600-1200 cm$^{-1}$, 2500-3800 cm$^{-1}$ and 4700-4900 cm$^{-1}$ for the OH stretching and bending modes. The OH bending mode in crystal together with OH stretching mode have occasionally appeared at the 600-1200 cm$^{-1}$ region [14]. However, the absorption peaks of this region in minerals are difficult to assign, due to the wavenumber has overlapped by Si-O or Al-O fundamental mode of minerals. In the next region defined at the 2500-3800 cm$^{-1}$ region which has produced strong absorption of the OH stretching mode [15]. The final region, 4700-4900 cm$^{-1}$, has determined to a combination of OH stretching and bending modes [16]. In the samples appeared the weak bands in range from 4780-4830 cm$^{-1}$ with the intense
peak at 4800 cm\(^{-1}\). While, the strong intensity bands appeared in range from 3610-3690 cm\(^{-1}\) with the intense peak at 3650 cm\(^{-1}\). The 4800 cm\(^{-1}\) absorption band has defined as combination of OH-stretching and bending modes, while the 3650 cm\(^{-1}\) absorption band has assigned to OH stretching modes. In the low wavenumber region, 600-1200 cm\(^{-1}\), which referred to OH bending mode cannot be observed in the spectra. Moreover, the decreasing in the intensity of absorption bands at 3650 cm\(^{-1}\) and 4800 cm\(^{-1}\) after e-beam irradiation (dashed and dotted line) have also exhibited in the both irradiated samples. The E-beam irradiation have decomposed the OH\(^{-}\) groups into O\(^{-}\) (hole trap) and H\(^{+}\) (electron trap) generated the decreasing in the intensity of those absorption bands.

4. Conclusion
The natural colorless topaz with complicated chemical composition changed to the shaded blue color by the complicated e-beam irradiation process. The zoned brown color appeared first continually with blue color using annealing. Therefore, the UV-Vis absorption bands at 620 nm were observed. After annealing, this band show decreasing in their intensity. The band at 620 nm is correlated with the creation of O\(^{-}\) defect by electron which supported by ESR spectra. The ESR signal at g ~ 2.012 which has been identified as an O\(^{-}\) ion on an (OH\(^{-}\))\(^{-}\) site increased the intensity when the electrons fluence level rising up. Moreover, the ESR intensity of this line show a little decreasing after the topaz was annealing. Decomposing of OH\(^{-}\) groups are occurred after e-beam irradiation from evidence of Mid-IR spectra. Furthermore, decomposing of OH\(^{-}\) groups are occurred after e-beam irradiation from evidence of Mid-IR spectra. The absorption bands at 3650 cm\(^{-1}\) and 4800 cm\(^{-1}\) after e-beam irradiation indicated OH stretching modes and combination of OH stretching and bending modes, respectively.

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6. References
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