

Spectroscopic characteristics of topaz: The impact of electron beam irradiation and heat treatment

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The natural topaz having the chemical formula of $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ exhibits lots of varieties in color and composition. Most of the natural topaz has been mined in colorless. In the work we performed a spectroscopic characterization of natural colorless topaz. The samples were irradiated with 2.5 MeV and 10 MeV electrons to fluencies of $2 \times 10^{17} \text{ cm}^{-2}$ for 1 h and were heated at 150 °C and 1 h in air. From the experiments, the spectra investigated by UV-visible spectroscopy (UV-Vis), electron paramagnetic resonance (ESR), and wavelength dispersive X-ray fluorescence spectroscopy (WD-XRF). Changes in the colorless sample after irradiation resulted in brown color, which had absorption peaks at 420 and 460 nm. These samples become light blue color after subsequent heat treatment. The samples EPR lines occurred two peaks, a peak near at $g = 2.012$ substitutional Al^{3+} ion in a Si^{4+} site and a peak near at $g = 3.5 \sim 4$ substitutional Fe^{3+} in an Al^{3+} site. After irradiation, the observed that while the peak at $g = 3.5 \sim 4$ related EPR line are decrease, but the perk at $g = 2.012$ related defect line show increase.

Key words: Topaz, Electron beam, WD-XRF, UV-Vis spectroscopy, ESR

Introduction

The color of gemstones is very important in trade. One of the important factors is that value of gemstones is evaluated by their color. In order to enhance the value of gemstones, various attempts have been made over the years to improve the color gemstones, such as dyeing, coating, heating, irradiation treatment and so on. As early as in the year 1974, K. Nassau reported that much colorless gemstones material can be turned in yellow-brown color on irradiation, such as quartz and topaz [1]. In a detailed study, the irradiation-induced color change in the topaz has been discussed, since the changes are complex, up to now the reason is not clear, but one major outline involves a color center theory. A color center involves on electron missing from a normally occupied position, leading to a hole center, while the presence of on extra electron leads to an electron center. The natural colorless topaz usually changes color by irradiation-induced color center.

Topaz occurs as an accessory mineral in some granites and associated hydrothermally altered rocks, as well as in pegmatites, and aluminous rocks. The crystallographic, optical, and chemical properties of topaz can vary with chemical composition, which reflects the petro genesis of the rocks in which the

individual crystal formed [2]. As a alumino-silicate mineral, topaz has the chemical formula $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ in which up to 30% of F may be substituted by OH. The structure of topaz consists of SiO_4 groups linking parallel to the crystalline c-axis. Four of the six anions surrounding the Al^{3+} ion belong to SiO_4 tetrahedral and the remaining two are both an F^- and OH^- group as shown in Fig. 1. [3] For more than 30 years, electron, gamma ray and neutron irradiations are commercially applied for color enhancement in topaz with the objective to get different shades of blue. In general, neutron irradiation turns colorless topaz immediately

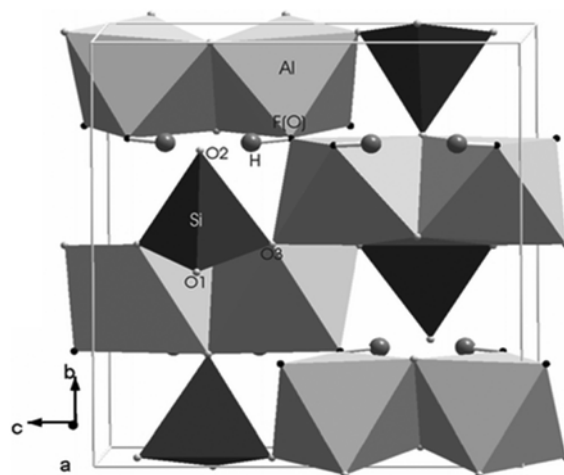


Fig. 1. Crystal structure of Topaz.

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blue, whereas gamma irradiation leads to grayish or brownish colors. The latter can be bleached out by heat treatments at about 150–200 °C, resulting in pale to medium blue colors [4].

The treatment with X-and gamma ray-induced paramagnetic centers using EPR was reported in Dickinson and Moore 1967 [5]. In 1990, the topaz by neutron irradiation was studied by EPR and optical absorption at room temperature [6, 7].

In this study, the color center formations in electron beam irradiated colorless topaz samples are investigated by EPR and UV-Vis. EPR and UV-Vis spectra of radiation induced defects are measured as accumulated electron beam does.

Experimental Methods

For this study, we selected faceted samples of untreated colorless natural topaz to examine in detail. The faceted samples were cleaned by immersing in beaker distilled water in and ultrasonic bath for 10 min. The chemical composition of the samples were measured with X-ray fluorescence using a Shimadzu XRF-1700. The size of the samples were about $6 \times 5 \times 4$ mm. The samples were irradiated in an electron accelerator with energy of 2.5 MeV to fluencies of $2 \times 10^{17} \text{ cm}^{-1}$ for 1 hour. And samples were practiced in an electron accelerator with electron energy of 10 MeV to fluencies of $2 \times 10^{17} \text{ cm}^{-1}$ for 1 h. After irradiation, the samples

underwent heat treatment. The samples were heated in a horizontal alumina tube furnace at 150 °C for 1 h in air. The UV-Vis and EPR spectra were taken before and after irradiation and subsequent heat treatment. The UV-Vis spectroscopy analysis was performed from 300 to 800 nm using a Jasco co., JASCO V-650. EPR spectra were observed from samples cut to less than 2 mm using a JEOL JES-FA200.

Results and Discussion

The chemical analyses of natural topazes were listed in table 1. All of the samples contained. Fe concentration is shown to be contained Fe_2O_3 .

Fig. 2 shows UV-Vis absorption spectra of the colorless topaz before and after irradiation. The non-irradiated colorless topazes exhibited no absorption band. After electron beam irradiation, the samples showed absorption band between 420 and 460 nm. As shown in Fig. 2a, for low energy condition, the sample changed light brown showing a broad absorption band at the about 420 nm together with a strong increase of absorption in the UV spectral range. High energy condition, on the other hand, the sample changed dark brown with an intense absorption band showed at about 460 nm as shown in Fig. 2b.

As shown in Fig. 3, the EPR spectrum of electron beam irradiated topaz for the magnetic field parallel to the c-axis. Two different paramagnetic defects are

Table 1. Chemical composition of colorless topaz by WD-XRF.

No	Al_2O_3	F	SiO_2	CdO	GeO_2	Fe_2O_3	K_2O	Cr_2O_3	CaO	Cl	CaO	P_2O_5
# 1	53.711	28.442	17.765	0.011	0.001	0.048	0.011	nd	nd	nd	nd	nd
# 2	38.302	49.258	12.343	0.018	0.004	0.051	0.012	nd	0.018	nd	nd	nd
# 3	48.670	29.28	19.382	0.011	0.009	0.082	0.009	nd	0.021	nd	0.028	nd
# 4	37.660	51.248	10.980	0.008	0.014	0.061	0.012	nd	0.006	nd	0.009	nd

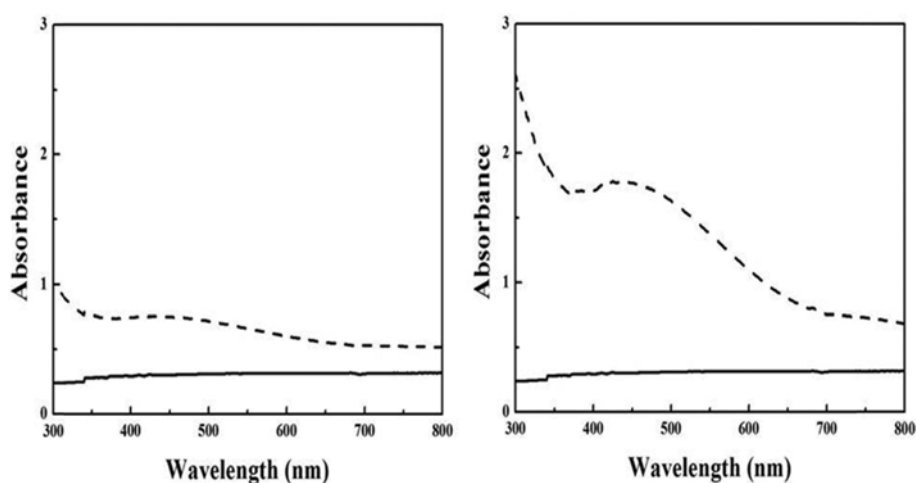


Fig. 2. UV-Vis absorption spectra of colorless topaz sample before (solid line) and after irradiation (dashed line) in the region of 300 to 800 nm.

(a) Low energy condition (2.5 MeV to fluencies of $2 \times 10^{17} \text{ cm}^{-1}$), (b) High energy condition (10 MeV to fluencies of $2 \times 10^{17} \text{ cm}^{-1}$).

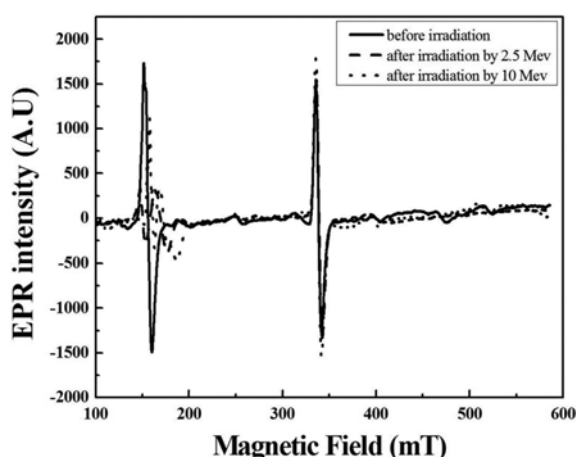


Fig. 3. EPR spectrum of electron beam irradiated topaz for the magnetic field parallel to the c-axis.

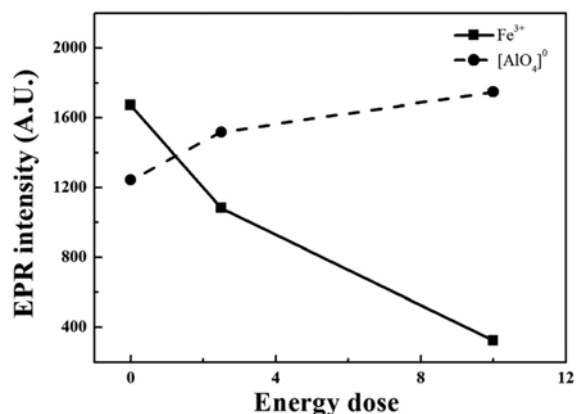


Fig. 4. EPR line intensities plotted as a function of electron beam dose.

observed after electron irradiation. First the most intense line occur at $g = 2.012$, where was identified by Petrov as a hole localized at a substitutional Al^{3+} ion in a Si^{4+} site, here designated a $(\text{AlO}_4)^0$ defect.[8] Second the three groups line occur at $g = 3.5 \sim 4$, where was identified as a substitutional Fe^{3+} in an Al^{3+} site, here was natural defect, were clearly identified in a series of reports [9, 10].

It is observe that some of the EPR lines presented in fig. 3 changed the intensity when the radiation dose. The inset in Fig. 4 shows the normalized EPR line intensities plotted as a function of electron beam dose. While the line at $g = 2.012$, for the $(\text{AlO}_4)^0$ line, increases in intensity as dose increase. But the Fe^{3+} line are decrease [11].

When the samples were heated at 150°C for 1 h in air, the samples that had changed to light brown to dark brown after irradiation reverted and become light blue. This change was the result of reduction of hole centers. It is showed that the hole centers are correlated with the absorption band about at 620 nm causing the light blue color, as shown in Fig. 5.

According to Schimer, the brown color caused by the

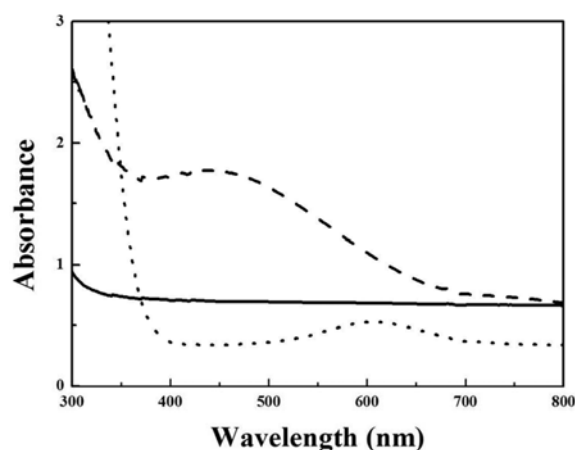


Fig. 5. UV-Vis absorption spectra of colorless topaz sample in the pristine state (solid line), after irradiation (dashed line), and after heat treatment (dotted line) in the 300 to 800 nm region.

absorption band about at 420 to 460 nm is typical for a tetrahedral bond polaron, where the acceptor defect charge is at least onefold negative as it in the case of an Al^{3+} ion substituting for Si^{4+} in the topaz lattice. On the other hand, the peak at 620 nm is more typical for a sixfold coordination, consistent with our defect model for the O^- center at $(\text{OH})^-$ sites, which is responsible for the light blue color, da Silva *et al.* [12].

Some previous studies have reported results different from ours. Nassau [3] observed that much colorless gem material can be turned in yellow-brown color on irradiation, such as quartz and topaz. E.G Yukihara [13] reported that gamma radiation induced defects in topazes were investigated $(\text{AlO}_4)^0$ line increased. Wang Ying [14], reported that low energy electron beam was employed to change the colorless topaz under heating.

The alteration of color may occur differently depending on the following conditions. First the dose and type of irradiation, second procedure of irradiation and heat treatment, and third the quantity of impurities present in the mineral. K.Krambrock reported the differences according to the above conditions [15]. In the experiment of topaz, fast neutrons create for paramagnetic O^- hole centers. The O^- centers have the same thermal stability as the optic absorption band at 620 nm. It is conformed that the absorption due to the O^- center is responsible for the blue color topaz.

Conclusions

In this study, we evaluated colorless topaz using samples prepared in two ways (i.e., electron beam irradiation, and after heat treatment).

Colorless topaz changed to a brown color after irradiation. Therefore, absorption bands were observed at 420 to 460 nm. After heat treatment, the sample showed new absorption band at 620 nm. This band is correlated with the creation of an hole center. The EPR

results presented two main signals were observed about at $g = 2.012$, designating $(\text{AlO}_4)^0$ line and about $g = 3.5 \sim 4$ for Fe^{3+} .

It is observed of the analogy between topaz and quartz. In both of them, Si sites are tetrahedrally coordinated with the oxygen anions, suggesting that some defects can be similar in both materials. The EPR lines of the $(\text{AlO}_4)^0$ line defect were in fact observed in quartz. This EPR line and the brown color are rated to an absorption band at 450 nm, similarly to the results that presented.

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