

EFFECT OF GAMMA IRRADIATION ON TOURMALINE CHARACTERISTICS

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Received 24 July 2015; Revised 10 October 2015; Accepted 2 December 2015;
Available online: 15 January 2016

ABSTRACT

The effects of gamma irradiation on gem tourmaline samples were studied for quality improvement. Color change, the main effect, depended on the initial type of defects. The tourmaline samples were analyzed before and after gamma irradiation by using UV-Vis, FTIR spectrophotometers, and LCR meter. The UV-Vis spectra showed that in light pink tourmaline the Mn^{3+} absorption were increased after gamma irradiation yielding deeper pink color, whereas in green tourmaline there was almost no change of both Fe^{2+} absorption spectra and the green color. The FTIR spectra showed that OH-stretching band intensities were decreased, which were consistent with the decrease of dielectric values measured by the LCR meter.

KEYWORDS: *tourmaline, irradiation, UV-Vis, FTIR, dielectric*

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INTRODUCTION

Tourmaline is a complex borosilicate mineral whose general chemical formula is $XY_3Z_6Si_6O_{18}(BO_3)_3V_3W$, where $X=Na^+, Ca^{2+}, K^+$ and vacancies; $Y=Mg^{2+}, Fe^{2+}, Mn^{2+}, Al^{3+}, Fe^{3+}, Mn^{3+}, Cr^{3+}, Li^+, Ti^{4+}$; $Z=Al^{3+}, Mg^{2+}, Cr^{3+}, V^{3+}$; $V=O^{2-}, OH$; and $W=O^{2-}, OH, F$. There are names in series known as schorl ($Y=Fe, Mn$), elabaite ($Y=Li, Al$) and dravite ($Y=Mg$) [1].

Good quality tourmaline can be used as gem material; however, some of the raw materials need to be color enhanced for improving their quality. There are some trade names such as rubellite (red), pink tourmaline, green tourmaline, chrome tourmaline, indicolite (blue), and paraiba tourmaline (blue-green). However, these colors may not all be found in nature.

Because of the complex structure of tourmaline, the cause of color is not yet definitely clear. There are some known causes of color based on defects, such as, Fe^{2+} related to green tourmaline and Mn^{3+} related to pink tourmaline and rubellite [2]. The $Mn^{2+}-O-Ti^{4+}$ charge transfer and Mn^{2+} causes greenish yellow and yellow-green, respectively [3].

There were two methods normally used for tourmaline color enhancement. The methods were heat-treatment [4] and gamma irradiation [5-7]. In this work, we investigated the effects of

gamma irradiation on color change of tourmaline. The characteristics of the samples were analyzed by using UV-Vis spectrophotometer, FTIR and LCR meters before and after irradiation.

MATERIALS AND METHODS

Forty-eight tourmaline samples from Brazil were used in this study. The samples were analyzed by UV-Vis, FTIR, and LCR meters prior to being irradiated by Co-60 gamma source at room temperature. The irradiation dose was 600 kGy. After irradiation, the samples were analyzed again using the same instruments.

A grating type of UV-Vis absorption spectrophotometer (LAMBDA™ 900) was employed to study the optical characteristics of the samples. The measurements were carried out in transmission mode with wavelength ranging from 200 nm to 1200 nm. The colors of the samples were analyzed by means of CIE $L^*a^*b^*$ color index [8] calculated from the absorption spectra. Each of color indices can be interpreted separately. The L^* is the value of the brightness which ranged from 0 (black) to 100 (white). The a^* and b^* have no specific numerical limit. Positive a^* is red while negative is green, and positive b^* is yellow while negative is blue. The colors will deepen as the absolute values of a^* and b^* increases.

The vibration modes of tourmaline were studied using a FTIR spectrometer (NEXUS™ 470), which is based on Michelson interferometer. The measurements were carried out in transmission mode with wave number ranging from 500 cm⁻¹ to 4000 cm⁻¹.

Parallel plate contacting electrode method was used for dielectric constant measurements. The samples were inserted into a dielectric test fixture (HP™ 16451B). The capacitance of the electrode with samples was measured using a precision LCR meter (HP™ 4284A) with four-terminal pair connection technique. The magnitude and frequency of test voltage were kept constant at 1.0 V and 1 MHz, respectively. Dielectric constant of air was used to validate the instrument at room temperature. The typical accuracy of the instrument was ±0.05%.

RESULTS AND DISCUSSION

The samples were divided into two groups: group A consisted of 30 samples for studying the effects of irradiation on optical characteristics, and group B consisted of 18 samples for studying the effects of irradiation on electrical characteristics.

Group A can be characterized by CIE L*a*b* color indices into five types as shown in Table 1.

Pink tourmaline (P) is assigned by the value of a* > b* which were tm01-tm07, tm19, and tm29. The pink caused by absorption of the band positions at the 507 nm to 532 nm and 680 nm to 709 nm. There were no clear absorption edges at about 300 nm. Yellow tourmaline (Y) is assigned by the value of a* < b* which were tm09-tm17. The yellow color caused by absorption at the 706 nm to 716 nm, 637 nm to 645 nm, and below 472 nm. The absorption occurred at around 1080 nm to 1170 nm in some samples. There were no clear absorption edges at about 400 nm. Yellow-Pink tourmaline (YP) is the combination of yellow and pink tourmaline that was tm08. The absorption bands were 524 nm and 790 nm. Green tourmaline (G) is assigned by the value of a* < 0 which were tm18 and tm20-tm28. The green color caused by absorption at the 720 nm to 738 nm and about 1100 nm to 1200 nm. Colorless tourmaline (W) showed no absorption band in visible region. The only sample of this type was tm30. There were two absorption bands located at 850 nm and 1160 nm. There was no clear absorption edge at about 300 nm.

After gamma irradiation, CIE L*a*b* color indices were calculated again to compare the color change. The background absorption of the

UV-Vis spectra were increased that effect mainly on decreased of L* or brightness.

Table 1. Color and absorption bands of tourmaline samples

| Samples | Absorption bands | | | Color |
|---------|------------------|---------|----------|-------|
| Tm01 | 526 | | | P |
| Tm02 | 514 | | | P |
| Tm03 | 520 690 | | | P |
| Tm04 | 400 | 507 687 | | P |
| Tm05 | 393 | 527 680 | | P |
| Tm06 | 517 684 | | | P |
| Tm07 | 524 681 | | | P |
| Tm08 | 524 790 | | | YP |
| Tm09 | 450 | 713 | 1080 | Y |
| | 446 | | | |
| Tm10 | 487 | 537 | 706 1100 | Y |
| Tm11 | 709 1100 | | | Y |
| Tm12 | 714 1150 | | | Y |
| Tm13 | 455 | 637 | | Y |
| | 472 | | | |
| Tm14 | 645 | | | Y |
| Tm15 | 638 | | | Y |
| Tm16 | 638 1100 | | | Y |
| Tm17 | 716 1170 | | | Y |
| Tm18 | 720 1200 | | | G |
| Tm19 | 532 | 709 | | P |
| Tm20 | 726 1200 | | | G |
| Tm21 | 727 1200 | | | G |
| Tm22 | 737 1150 | | | G |
| Tm23 | 730 1200 | | | G |
| Tm24 | 738 1150 | | | G |
| Tm25 | 730 1200 | | | G |
| Tm26 | 726 1140 | | | G |
| Tm27 | 723 1200 | | | G |
| Tm28 | 728 1200 | | | G |
| Tm29 | 700 | | | P |
| Tm30 | 850 1160 | | | W |

Gamma irradiation produced three different effects on pink tourmalines. The first one was the increasing of pink colors, *i.e.*, a* increase, (tm01, tm03, tm04, tm07, and tm19). The UV-Vis spectra showed the increasing of Mn³⁺ content at 515 nm. The second one was the decreasing of pink colors, *i.e.*, a* decrease (tm05 and tm06). UV-Vis spectra showed the decreasing of Mn³⁺ at 515 nm. The last one was the turning of pink into yellow, *i.e.*, b* > a* (tm02).

For yellow tourmaline, there were two effects. The first one was the increasing of red component (tm08, tm09, tm11, and tm13-17). The second one case was the increasing of yellow component (tm10 and tm12).

Green (tm18, tm20-tm28) and colorless tourmaline (tm30) samples experienced almost no effects from gamma irradiation on UV-Vis spectra except increased of background absorption.

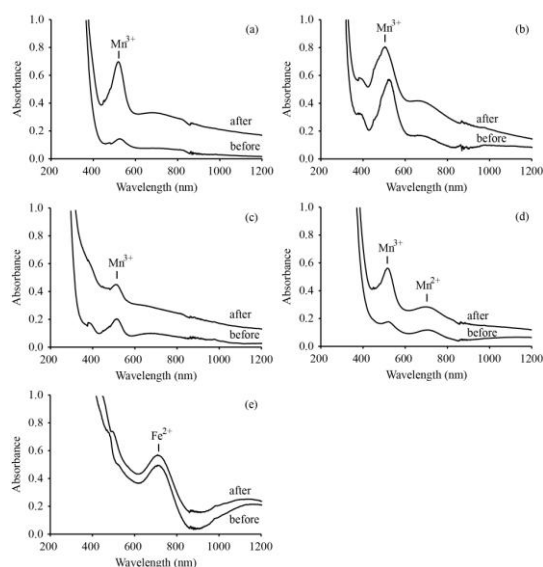


Fig. 1. Comparison of UV-Vis spectra before and after gamma irradiation of tm01 (a), tm05 (b), tm02 (c), tm08 (d) and tm12 (e)

Selected samples of tourmaline UV-Vis spectra before and after gamma irradiation are shown in Fig. 1.

After gamma irradiation, background absorptions of the FTIR spectra were increased. The spectra of all samples showed the reduction of OH-stretching band at wave number of 3000 cm^{-1} to 4000 cm^{-1} as shown in Fig. 2. The effect could be explained by the decomposition of an OH molecule in tourmaline according to the reaction $\gamma + \text{Al-OH-Al} \rightarrow \text{Al-O-Al} + \text{H}^0$ [9].

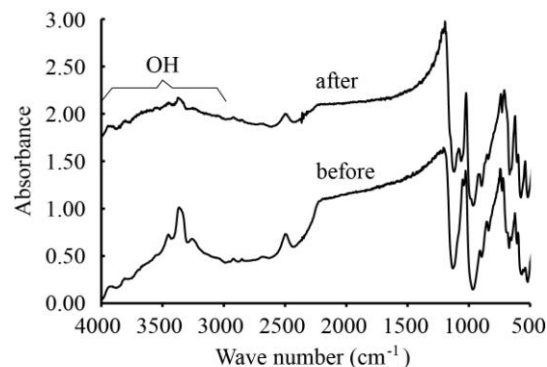


Fig. 2. FTIR spectra of tm13 showed the decreasing of OH-stretching band after gamma irradiation

Table 2. Comparison of dielectric constant before and after gamma irradiation of group B tourmaline samples

| Samples | Dielectric constant before gamma irradiation | Dielectric constant after gamma irradiation |
|---------|--|---|
| B1 | 4.453 | 0.948 |
| B2 | 4.665 | 0.987 |
| B3 | 3.330 | 1.130 |
| B4 | 3.755 | 0.628 |
| B5 | 5.015 | 0.566 |
| B6 | 4.286 | 0.415 |
| B7 | 3.873 | 0.722 |
| B8 | 4.023 | 0.682 |
| B9 | 2.318 | 0.987 |
| B10 | 4.168 | 0.291 |
| B11 | 4.334 | 0.719 |
| B12 | 5.131 | 0.994 |
| B13 | 3.987 | 0.702 |
| B14 | 3.706 | 0.493 |
| B15 | 5.420 | 1.053 |
| B16 | 4.868 | 0.700 |
| B17 | 4.863 | 0.760 |
| B18 | 4.493 | 0.794 |

The measurement results of group B samples are showed in Table 2. Dielectric constant after gamma irradiation clearly decreased for all samples. The decreasing of OH stretching band in FTIR spectra of group A samples was consistent with the decreasing of the dielectric constant of group B samples. However, this effect did not affect the color change of tourmaline. Dielectric constant

measurement could be a potential technique to identify gamma-treated tourmaline samples.

CONCLUSION

Tourmaline samples with different initial colors and shapes were divided into two groups for this study. Samples of different colors from the first group (group A) were cut approximately into the same size to study the effect of gamma irradiation using UV-Vis and FTIR absorption. The second group (group B) was flat to make them suitable for measurement of dielectric property. Effects of gamma irradiation, for group A samples, UV-Vis absorption spectra showed both increasing and decreasing of Mn^{2+} (710 nm and 1060 nm), Mn^{3+} (515 nm) and Fe^{2+} (450 nm). For most pink samples, the color intensities were increased. However, there were little or no effects on yellow, green and colorless samples. FTIR spectra clearly showed the decreasing of OH-stretching band of group A samples consistent with the decreasing of the dielectric constant of group B samples. Dielectric constant measurement may be used to identify gamma-treated tourmaline samples.

ACKNOWLEDGEMENTS

This project was funded by Kasetsart University Research and Development Institute (KURDI). L. Chaiyabutr would like to thank The Graduate School Kasetsart University for a scholarship. The authors would like to thank Thailand Institute of Nuclear Technology (Public Organization) for utilizing the gamma source.

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