

# Reinvestigation of the Causes of Colour in Natural and Irradiated Green Spodumene

## 天然和經輻照處理綠色鋰輝石的致色原因再探

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作者後續George Bosshart早前對鋰輝石的檢測，複檢並指出天然和經輻照處理鋰輝石的致色原因和導致顏色轉變的因素。

**Keywords:** Green spodumene, Colour centre, EPR, Fine structure

### Introduction

Green spodumene has long been of interest to mineralogists and gemmologists because of its “tenebrescent” behaviour, whereby the colour of some samples may fade under sunlight or heat, but may be restored with irradiation (Bosshart et al., 2011; Esther, 1953). This study is an extended work of the second author (George Bosshart) in investigating the causes of colour of stable and unstable shades of green in spodumenes.

### Samples and Experimental Methods

Six green spodumene specimens were selected from different localities with different colour origins (Figs. 1 & 2): two

natural hiddenites from Adams Mine, North Carolina (samples #1 and #2), three laboratory-irradiated yellowish green to green spodumenes from Afghanistan (samples #3-#5) and one naturally irradiated bluish-green spodumene from Northern Pakistan (sample #6). All samples were studied using conventional gemmological instruments. All features and colour distribution were examined under the microscope.



**Fig. 1** A green faceted spodumene from Afghanistan (sample #4)



**Fig. 2** Green spodumene specimens #1, #3 & #6 (from left to right), a) “as received” (upper row) and b) after strong light and UV exposure (lower row). Specimens #3 and #6 exhibit clear colour fading. Photos by Edward Liu.

The UV-Vis absorption spectra were obtained using a GEM-3000 UV-Vis Spectrophotometer in the range of 225-1100nm. Colour alterations of samples such as discolouration and modifying hues after exposure to strong visible light or x-ray were monitored and expressed in changing optical absorption spectra. Chemistry was determined using EDAX ENGLE III EDXRF Analyzer.

The single-crystal EPR measurements and spectra were recorded on a JES-FEIXG EPR spectrometer at room temperature. Magnetic field  $3350 \pm 1000\text{G}$  (or  $2550 \pm 2500\text{G}$ ), operating frequency  $9449\text{ Mc/s}$  (megacycles per second), response  $0.3\text{s}$  and sweep time  $4\text{ min}$ . Signals of different orientations of samples to the magnetic field were recorded for comparison.

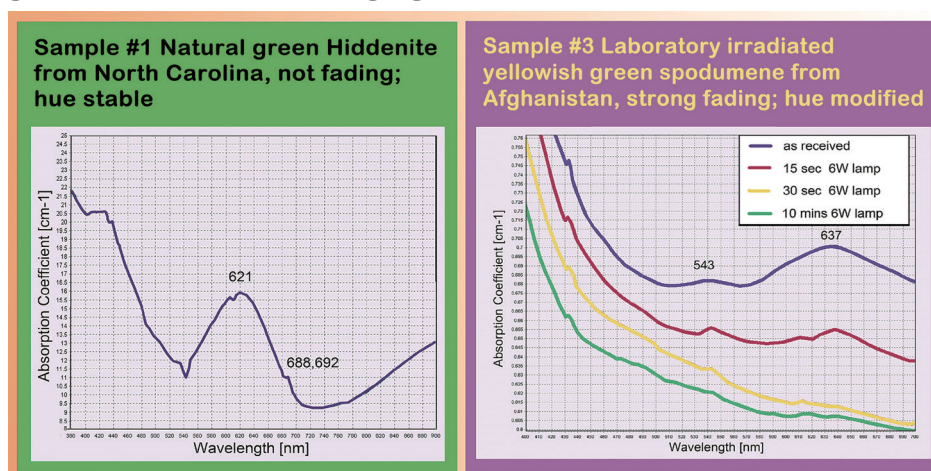
## Results

All North Carolina natural hiddenites showed stable green colour under strong light

without discolouration and tenebrescence. UV-Vis spectroscopy and chemical analysis by XRF revealed that they contain Cr and V (Fig. 3 & Table 1). The absorption band at  $621\text{nm}$  and a doublet at  $688$  and  $692\text{nm}$  can be assigned to the presence of  $\text{Cr}^{3+}$  (Bosshart, 2011).

Those irradiated (naturally and artificially treated) green spodumene samples showed similar absorption spectra which are related to colour centre(s). Their unstable colour can be easily bleached (from green to colourless) under daylight, ultra-violet, or moderate heat to  $\geq 250^\circ\text{C}$ , with a decrease in the corresponding (radiation-induced) absorption band at  $637\text{nm}$  (Fig. 3). Little change was found in the strength of the  $\text{Mn}^{3+}$  absorption band at  $543\text{nm}$  and sharp  $\text{Fe}^{3+}$  absorption bands at  $437\text{nm}$ .

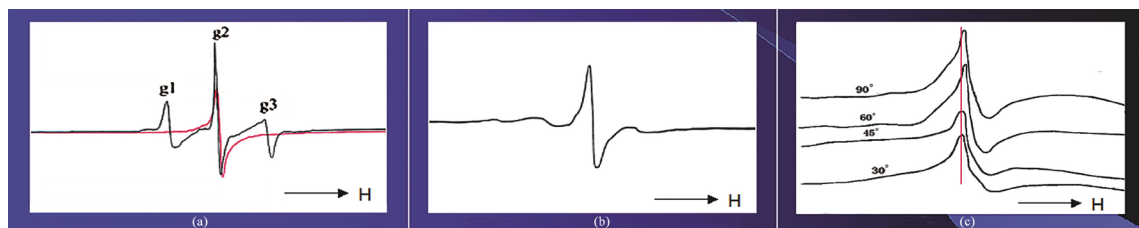
The laboratory-irradiated spodumene samples from Afghanistan appeared partially light purplish red with an increase



**Fig. 3** Visible spectra of (a) North Carolina natural hiddenite & (b) Afghanistan laboratory irradiated green spodumene. Diagrams by Edward Liu

**Table 1** ED-XRF analysis of the chromophoric trace elements of Spodumene samples

Trace Element	Natural Hiddenite #1 Oxide wt%	Yellowish green spodumene (laboratory-irradiated) #3 Oxide wt%	Light bluish-green spodumene (naturally-irradiated) #6 Oxide wt%
TiO <sub>2</sub>	0.014	0.010	0.017
V <sub>2</sub> O <sub>3</sub>	0.049	0.005	bdl
Cr <sub>2</sub> O <sub>3</sub>	0.057	0.036	bdl
MnO	0.035	0.126	0.091
Fe <sub>2</sub> O <sub>3</sub>	1.578	0.052	0.041



**Fig. 4** EPR spectra of:

- (a)  $\text{Cr}^{3+}$  fine structure of Hiddenite (sample #1) at different orientations ( $g_{\parallel}$ : black line;  $g_{\perp}$ : red line).  $g$ -factor (black line):  $g_1=3.671$ ,  $g_2=2.953$ ,  $g_3=1.595$  [H (Magnetic field):  $3350 \pm 1000\text{G}$ ];
- (b)  $\text{Cr}^{3+}$  fine structure overlapping with a related colour centre of laboratory-irradiated yellowish green spodumene (sample #4) [H (Magnetic field):  $3350 \pm 1000\text{G}$ ];
- (c) a simple signal of colour centre (with anisotropic  $g$ -factor) of naturally irradiated light bluish-green spodumene (sample #6) [H:  $2550 \pm 2500\text{G}$ ; at different orientations].

in the strength of the 536nm absorption band after exposure to x-ray. This colour faded rapidly within a few seconds under visible light.

EPR spectroscopic studies of all samples revealed that their colours were caused by different mechanisms:

1. EPR spectra indicated that the hiddenite sample from NC contained  $\text{Cr}^{3+}$  (in the 6-coordinated  $\text{Al}^{3+}$  site) with three fine structure lines (Fig. 4a). No signal of a colour centre could be observed. A  $\text{V}^{4+}$  fine structure lines signal was also detected.
2. The EPR spectra of laboratory-irradiated green spodumene specimen showed the  $\text{Cr}^{3+}$  signal overlapping with a related colour centre (Fig. 4b).
3. The naturally irradiated green spodumene sample displayed a different EPR spectrum, which contained a simple signal of colour centre (with anisotropic  $g$ -factor) only (Fig. 4c).

According to Hasson and Libib (1978) and Nassau (1983), the green colour of spodumene can be created by irradiation induced electron hole(s) to transform (oxidize)  $\text{Mn}^{2+}$  (colourless) to  $\text{Mn}^{3+}$  (purple) and further to rather unstable  $\text{Mn}^{4+}$  (green). XRF analysis also revealed that both irradiated green spodumene samples

had higher MnO contents than the natural hiddenite sample. However, no distinct Mn EPR signal could be observed in this study. The discovery of these colour centres revealed that the defects in the naturally- and artificially-irradiated green spodumene samples were different. EPR spectra may help to differentiate these two green versions.

## References

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