

Gamma Ray Irradiation Induced Changes in the Color of Tourmalines

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Abstract

Color changes were observed on gamma ray irradiation of over 500 colorless, pink, blue, and green tourmalines. The only significant changes observed were the development or intensification of pink or the development of yellow superimposed on the preexisting color. Irradiation and heating indicates the possibility of at least seven causes of pink and two causes of yellow colors in tourmaline; some of these colors are stable to heat, and some are not. This complexity may explain the diversity of previous assignments for the origin of the pink color.

Introduction

There is in the literature an occasional mention of experiments on the effect of penetrating radiation on the color of tourmaline. For example, Lind and Bardwell (1923) observed no change in pink and green tourmaline exposed to radium salts; Pough and Rogers (1947) noted a dark rose purple resulting from the X-ray exposure of pink and dark green tourmaline and a yellowing of light green, but stated that the results obtained were not marked ones; Bershov *et al* (1969) reported that the color of pink tourmaline (elbaite), if destroyed by heating, can be recovered by gamma or X-ray irradiation.

For the brown, green, blue, and black tourmalines of the elbaite-schorl and dravite-schorl series, Faye *et al* (1974) have outlined the role of iron and titanium, particularly involving charge transfer processes. In addition to the many references given by them on this subject, some additional studies are relevant (Townsend, 1970; Triche, Leckebush, and Recker, 1973) as well as the successful synthesis of green and blue tourmalines containing Fe by Voskresenskaya and Grum-Grzhimailo (1967).

The causes of the color in pink elbaite (rubellite) are much less certain. A low iron content is essential, and Mn^{3+} is usually the assigned cause of the color. However, Mn^{2+} and/or Fe^{3+} (Wilkins, Farrell, and Naiman, 1969) and $Mn^{2+}-Mn^{3+}$ or $Mn^{2+}-Fe^{3+}$ charge transfer (Manning, 1969) have also been suggested. Because pink color as well as an ESR spectrum identified with it were removed by heating above 400° but restored by X-ray or gamma-ray irradiation, Bershov *et al* (1969) attributed the pink color to a color center, possibly a trapped electron at an oxygen vacancy. Wilkins *et al* (1969) also noted an almost

complete loss of color in rubellite after two hours at $650^{\circ}C$; some specimens, however, lose color only at 800° to $1000^{\circ}C$ (Bradley and Bradley, 1953).

In view of the wide variety of elements which can be present in the tourmaline structure and the equally wide number and types of localities where it occurs (Deer, Howie, and Zussman, 1962), some variety in the behavior on irradiation was to be expected, but not the extreme complexity that was actually found in the survey here reported. In view of this complexity, the present report is intended to be a guiding framework within which future, more detailed, investigations will be able to take their bearings.

Experimental

A wide variety of tourmaline specimens were irradiated at room temperature in a cobalt-60 gamma ray cell for 14 to 72 hours. This corresponds to a dose of 10 to 50 megarads of approximately equal amounts of 1.17 meV and 1.33 meV gamma rays.

Color changes were recorded separately for each segment if a specimen was bi- or tri-color; counting each such section as a distance unit, a total of 542 entries in Table 1 were recorded on the more than 500 specimens examined. Designations of origin, if available, are given in Table 1.

Results

The observed color changes (Table 1) can be summarized rather simply in three groupings containing a total of seven entries:

- A: Development or intensification of a pink to red color:
- (i) colorless or pale colors \rightarrow pink or red (165)
 - (ii) pale green \rightarrow grey (18)
 - (iii) yellow \rightarrow peach (3)

(iv) blue → purple (7)

B: Development of yellow, usually at the expense of pink:

(v) pink → yellow or orange (55)

(vi) pale green → yellow green (15)

C: No significant change:

(vii) any color (279).

The numbers in parentheses refer to the number of observations for each color change. Considerable variation occurred even within individual specimens. For example, one green pencil from Topsham, Maine, turned into a green-pink bicolor, while another such pencil turned gray (a combination of pink and green); a green-pink bicolor from San Diego, California, turned to a uniform pink, and so on. Some additional details, and color reproductions of some of these changes have been published elsewhere (Nassau, 1974).

Some of these irradiated specimens with pronounced color changes were tested for their color stability by heating to 260°C and 400°C for up to 24 hours and by exposure to sun/daylight for five weeks. There was a wide variation of stability. Some deep pink to red tourmalines (originally very pale color) survived all these tests, while others faded rapidly and returned to their original color after as little as two hours at 260°C, or faded significantly after five weeks light exposure.

In the central experiment of this survey, 85 specimens which were originally pale to medium pink in color, all from Brazil, were classified (Fig. 1) according to their colors after irradiation with 10 megarads gamma rays and after subsequent heating for 24 hours at 400°C. The designations P₁ to P₇ and Y₁ and Y₂ in Figure 1 refer to seven types of pink and two types of yellow which appear to be quite distinct from one another in their behavior with respect to color change on irradiation and heating. The reversible P₃ to P₅ and P₆ to Y₁ changes could be repeated on successive irradiations and heatings but the others could not.

Examination in polarized light indicated that all specimens showing any pink or red component, either before or after irradiation and/or heating, showed a much stronger pink or red coloration for light vibrating perpendicular to the *c* axis of the crystal.

Chemical analyses by X-ray fluorescence spectroscopy were performed on three specimens each of the five columns in Figure 1. From these data (Table 2) it would appear that Cr, V, and Ti are at concentrations too low to explain significant direct

TABLE 1. Color Changes in Tourmaline on Gamma Irradiation

Original Color	Color After Gamma Treatment*	Number of Observations	Origin**
Colorless	NSC	5	M,U
	pink to red	4	M,S,U
Very Pale (pink, blue, green)	NSC	10	B,U
	pink	36	B,T,U
	red	45	B,U
Pale Yellow	peach	3	S,U
Yellow to Tan	NSC	120	B,O,U
	pink	5	B,S,U
Pink (pale to medium)	NSC	67	B,O,S,U
	darker to red	50	B,M,N,S,U
	yellow to orange	55	B,S,U
Dark Pink	NSC	6	B,C,U
Green (pale to medium)	NSC	56	B,C,N,O,S,U
	yellow-green	15	S,U
	paler (grey) green	18	B,N,T,U
	pink	25	S,U
Dark Green	NSC	12	S,U
Blue (pale to medium)	NSC	3	S,U
	Purple	7	B,S,U

* NSC indicates no significant change with 50 megarads of Cobalt-60 gamma rays.

** B = Brazil
C = Chrome Tourmaline, Tanzania
M = Mozambique
N = Newry, Maine
S = San Diego Co., California
O = Tefelo Otoni, Brazil
T = Topsham, Maine
U = Unknown, probably Brazil

coloration in some members of each group and that the same is true of Fe in all except possibly the P₃;P₅ type. Mn is, however, present in quite significant amounts in all except perhaps the P₆;Y₁ type. In itself, chemical analysis data like this can be merely suggestive.

These results reveal why different investigations have ascribed the pink colors to different causes, e.g., to Mn and/or Fe or to a color center; no exhaustive

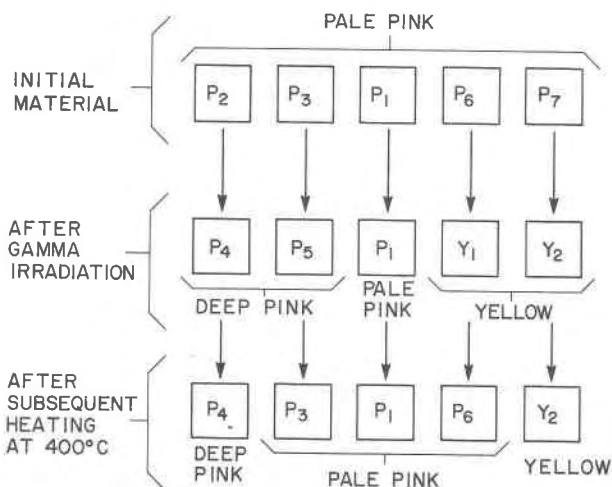


FIG. 1. Color changes observed in 85 pale pink elbaite tourmalines on irradiation with 10 megarads gamma rays and subsequent heating for 24 hours at 400°C. This illustration has been published in color by Nassau (1974).

TABLE 2. Impurities in Pale Pink Tourmalines from Brazil

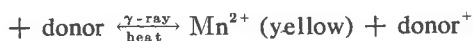
Type of Pink Tourmaline from Fig. 1		Concentration in %*				
Type	Changes**	Fe	Mn	Cr	V	Ti
P ₂ :P ₄	pink/darker/same	nd-0.02	0.3-0.36	nd-0.04	nd	nd
P ₃ :P ₅	pink/darker/pink	0.05-0.12	0.8-2.0	nd	nd-0.003	nd
P ₁	pink/same/same	nd-0.015	0.08-0.17	nd	nd-0.0004	nd
P ₆ :Y ₁	pink/yellow/pink	nd-0.015	0.01-0.07	nd-0.016	nd	nd
P ₇ :Y ₂	pink/yellow/same	nd-0.015	0.3-1.0	nd	nd-0.01	0.004-0.014

* Range observed in three specimens for each entry by x-ray fluorescence spectroscopy; nd: not detected below the detectability limit of 0.001% for Mn and Cr and 0.002% for the other elements.

** First change is on gamma irradiation with 10 megarads, second change is on subsequent heating to 400°C for 24 hours as in Fig. 1.

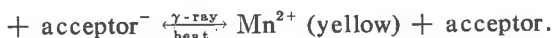
survey had been made of the various types of pink colors, and the results were based on data from a few crystals only. In the case of kunzite, Cohen (1973) has found that Mn²⁺ produces a yellow and Mn³⁺ a pink color, and that the color change can depend on other impurities. He suggests (unpublished) that in tourmaline some of the variability may involve different electron acceptor or donor impurities together with Mn. Consider electron transfers such as

Mn³⁺ (pink)



or

Mn³⁺ (pink)



Depending on which sides of these equations are thermodynamically more stable, heat may or may not reverse the color change produced by irradiation for any given acceptor or donor impurity. A similar set of equations may be written with either electron or hole type color centers (and their precursors) replacing Mn³⁺ and Mn²⁺. Additional equations can be written for color centers *together* with Mn.

The color changes, colorless \longleftrightarrow pink and colorless \longleftrightarrow yellow, may also occur independently, and their simultaneous occurrence in the pink \longleftrightarrow yellow change may be due to a fortuitous combination in which either Mn²⁺ or Mn³⁺ is colorless, and a color center provides the second color.

It is also possible that O²⁻ \rightarrow M and M \rightarrow M charge-transfer processes may be involved here as they are in the green and blue specimens (Faye *et al*,

1974) and that irradiation could change these processes. It appears likely that these color changes involving pink, yellow, and colorless, when combined with the blue and green and brown colors produced by Fe and Ti (Faye *et al*, 1974), can explain all the irradiation-induced color changes observed in tourmaline.

In view of the large diversity of behavior, it is clear that extensive work will be needed to identify and characterize these and other possible color-forming mechanisms in pink elbaite tourmalines. Concurrent polarized optical spectroscopic and ESR experiments before and after both irradiation and heating, coupled with impurity analyses, will be required for each of the various types of materials. It is hoped that this survey will provide a guide to the manifold variety of behavior to be expected in future detailed studies.

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References

- BERSHOV, L. V., V. O. MARTIROSYAN, A. S. MARFUMIN, A. N. PLATONOV, AND A. N. TARASHCHAN (1969) Color centers in lithium tourmaline (elbaite). *Sov. Phys.-Crystallogr.* **13**, 629-630.
- BRADLEY, J. E. S., AND O. BRADLEY (1953) Observations on the coloring of pink and green zoned tourmaline. *Mineral. Mag.* **30**, 26-38.

- COHEN, A. J. (1973) Color variation of natural green spodumenes. Abstr. V127, *Trans. Am. Geophys. Union*, **54**, 504.
- DEER, W. A., R. A. HOWIE, AND J. ZUSSMAN (1962) *Rock-Forming Minerals*. John Wiley & Sons, Inc., New York, Vol. 1, p. 300-319.
- FAYE, G. H., P. G. MANNING, J. R. GOSSELIN, AND R. J. TREMBLAY (1974) The optical absorption spectra of tourmaline: Importance of charge transfer processes. *Can. Mineral.* **12**, 370-380.
- LIND, S. C., AND D. C. BARDWELL (1923) The coloring and thermophosphorescence produced in transparent minerals and gems by radium radiation. *Am. Mineral.* **8**, 171-181.
- MANNING, P. G. (1969) An optical absorption study of the origin of colour and pleochroism in pink and brown tourmalines. *Can. Mineral.* **9**, 678-690.
- NASSAU, K. (1974) The effect of gamma rays on tourmaline, greenish-yellow quartz, pearls, kunzite, and jade. *Lapidary J.* **28**, 1064-1084.
- POUGH, F. H., AND T. H. ROGERS (1947) Experiments in X-ray irradiation of gem stones. *Am. Mineral.* **32**, 31-43.
- TOWNSEND, M. G. (1970) On the dichroism of tourmaline. *J. Phys. Chem. Solids*, **31**, 2481-2488.
- TRICHE, C., R. LECKEBUSH, AND K. RECKER (1973) Quantitative Nachweise von Ti, V, Cr, Mn und Fe in Turmalinen mittels Spektrochemischer Methoden. *Neues Jahrb. Mineral. Monatsh.* **1973**, 63-69.
- VOSKRESENSKAYA, I. E., AND S. V. GRUM-GRZHIMAILO (1967) Color of synthetic tourmaline crystals containing iron. *Sov. Phys. Crystallogr.* **12**, 311-312.
- WILKINS, R. W. T., E. F. FARRELL, AND C. S. NAIMAN (1969) The crystal field spectra and dichroism of tourmaline. *J. Phys. Chem. Solids*, **30**, 43-56.

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