Role of natural radiation in tourmaline coloration: Discussion

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In a study of optical absorption spectra (300–900 nm) of elbaite, a Li-bearing tourmaline, Reinitz and Rossman (1988) suggested that irradiation-induced color in this mineral is due to oxidation of Mn^{2+} to Mn^{3+}. Using the intensity ratio of the bands of Mn^{2+} at 414 nm (~ 24150 cm^{-1}) and Mn^{3+} at 515 nm (~ 19400 cm^{-1}), it was concluded for a selected sample exposed to a controlled dose of gamma rays that 24.3% of Mn^{2+} was oxidized to Mn^{3+}. However, previous studies imply that the color-producing processes in this mineral are of a more complex nature. It is most important that all available data are considered before reaching quantitative conclusions.

De Camargo and Isotani (1988) studied optical absorption spectra (4000–30000 cm^{-1}) of natural and gamma-irradiated pink and green tourmalines. A sharp band at 7000 cm^{-1} was observed to be present in all spectra. It was ascribed to vibrations of H_2O. Moreover, bands at 8500 cm^{-1} and 14800 cm^{-1} were assigned to d-d transitions of Fe^{2+} at distorted octahedra of XO_4 $(OH,F)_2$ (b sites) and YO_5 (OH) (c sites), respectively, where X refers to Li and Al and Y refers to mainly Al as structural cations. The bands at 7000 cm^{-1} and 8500 cm^{-1} were not considered by Reinitz and Rossman (1988). Additional bands at 19500 cm^{-1} and 25500 cm^{-1}, also reported by Reinitz and Rossman (1988), were assigned by De Camargo and Isotani (1988) to $^5E \rightarrow {}^5A_1$ and $^5B_2 \rightarrow {}^5A_1$ d-d transitions of Mn^{3+} in b sites, respectively. De Camargo and Isotani (1988) observed that the pink color may increase in intensity by gamma irradiation and eventually adopt a yellow tint, mixed with the original pink. Heating at 500 °C eliminated the pink color, but the yellow was not affected. When heated at temperatures above 600 °C, the crystals became colorless. Green tourmaline became pink after irradiation.

Using defined gamma-ray doses (1–200 MGy) yielded two steps in the growth of absorption intensity of A_α and A_β for the 19500 cm^{-1} and 25500 cm^{-1} bands, where A_α and A_β are the absorbances measured for $\mathbf{k} \parallel \mathbf{c}$ and $\mathbf{k} \perp \mathbf{c}$, respectively, and $\mathbf{k}$ is the wave vector. These observations were interpreted in terms of at least two different color centers.
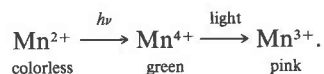
The bands at 8500 and 14800 cm^{-1} became more intense with increasing doses of radiation (De Camargo and Isotani, 1988). It is not yet certain whether this is due to a reduction of Fe^{3+} to Fe^{2+}. The origin of the yellow color, stable up to 500 °C, is also not clear. A possible interpretation would be coloring by Fe^{3+}. This, however, is inconsistent with the increase of the Fe^{2+} bands with increasing doses of radiation. In green beryl, Blak et al.

(1982) found two first-order processes of reduction of Fe^{3+} to Fe^{2+} by heat treatment between 200 °C and 600 °C, yielding two different activation energies. The possibility of two or more different processes for $Fe^{3+} \leftrightarrow Fe^{2+}$, e.g., at the X and Y positions of elbaite, are, therefore, quite likely and should be investigated by correlated optical absorption (Fe^{2+}) and electron paramagnetic resonance, EPR (Fe^{3+}). The X and Y positions refer to two edge-sharing octahedra. In green tourmaline, the lower-energy Fe^{2+} band is located at 13800 cm^{-1}, but in pink tourmaline, it is shifted to 14800 cm^{-1} by the strong Mn^{3+} band at 19500 cm^{-1}. Thus, quantitative intensity studies of the Mn^{2+} band should take this into account.

The sharp band at 23000 cm^{-1}, i.e., the band assigned to Mn^{2+} by Reinitz and Rossman (1988), was not interpreted uniquely in terms of crystal-field consideration by De Camargo and Isotani (1988) because of its low intensity. EPR, however, did not reveal Mn^{2+} signals.

De Camargo and Isotani (1988) suggested two possible mechanisms for producing the color: (1) oxidation of Mn^{2+} to Mn^{3+} and (2) reduction of Mn^{4+} to Mn^{3+}. Mechanism 1 was also proposed by Reinitz and Rossman (1988). However, De Camargo and Isotani (1988) considered that possibility as unlikely since the typical hyperfine splitting of Mn^{2+} could not be detected by EPR. It is to be expected that irradiation according to mechanism 2 will produce conduction electrons and valence holes that can be trapped by Mn^{4+} in b sites, yielding an electron trap for Mn^{4+} and a hole trap for Li^+. Thus, De Camargo and Isotani (1988) assigned the precursor center for the color-producing 19500 cm^{-1} band to Mn^{4+} in b sites.

Lehmann (1978) suggested that in the case of spodumene, $LiAlSi_2O_6$, irradiation may produce a green color of rather weak stability due to oxidation of Mn^{2+} to Mn^{4+}. After heating or exposure to daylight over some time, the green color changed to pink. This is associated with thermoluminescence, which is indicative of rearrangement of electrons and holes. The change of color may be explained by the processes

$$\underset{\text{colorless}}{Mn^{2+}} \xrightarrow{h\nu} \underset{\text{green}}{Mn^{4+}} \xrightarrow{\text{light}} \underset{\text{pink}}{Mn^{3+}}.$$

Thus, the natural pink color of spodumene is generally not produced by irradiation directly; it results from destruction of an intermediate, metastable state of Mn^{4+}. The two rather broad optical absorption bands of apparently tetrahedral Mn^{4+} in green spodumene (~ 10000 and ~ 15200 cm^{-1}) are about in the same region as those of

Fe^{2+} in elbaite. The possibility of superposition of the rather broad bands of Fe^{2+}, Mn^{3+}, tetrahedral Mn^{4+}, and a forbidden band of octahedral Mn^{4+} in elbaite is still open.

Nassau (1975) studied more than 500 tourmalines, including 85 elbaites from various localities all over the world. Gamma-ray irradiation and heat treatment revealed three main groups of color change: colorless ↔ pink, pink ↔ yellow, and colorless ↔ yellow. This result is in accord with the observations of De Camargo and Isotani (1988). Many of the colors produced by irradiation can be destroyed by heating the sample to temperatures of 260 °C or 400 °C. Similar bleaching temperatures were also found by Reinitz and Rossman (1988), e.g., for samples 614 (250 °C) and 565 (500–600 °C). It should be noted that the colors often fade at room temperature after exposure to light for a few weeks. In general, bleaching temperatures below 600 °C and bleaching due to exposure to light are typical for metastable electron centers or electron hole centers (e.g., O^{1-} ions) activated by irradiation, e.g., with gamma rays; they are destroyed by subsequent heat treatment.

Bradley and Bradley (1953) reported data on color changes in elbaite crystals from the San Diego mine, California, at high temperatures. The color remained stable up to 800–1000 °C.
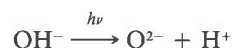
The relatively broad optical absorption bands of minerals that change color reversibly after heat treatment at temperatures below 600 °C (bleaching) and subsequent irradiation (reactivation of color) are of a complex nature in most cases. They are produced by superposition of bands due to electron and/or hole centers at crystallographically distinct anion positions.

For example, the many different colors of natural and irradiated topaz could be interpreted by a combined study of optical absorption, EPR, and thermoluminescence (Petrov, 1977, 1983). It could be shown that only the violet color is due to the d-d transition of Cr^{3+}. That color cannot be bleached even at temperatures of 1000 °C and higher. All other colors induced by X-ray, gamma, electron, and/or neutron irradiation are the result of distinct hole centers. Many of these colors may, of course, be superimposed on the color due to Cr^{3+}. In gamma-irradiated topaz (Petrov, 1983) and microcline (L. V. Bershov, personal communication), Mn^{3+} is commonly reduced to Mn^{2+} by formation of a Mn^{2+}-O^{1-} center. The bleaching temperatures of topaz are very similar to those reported by Nassau (1975) and Reinitz and Rossman (1988): 220 °C, 400 °C, and 450 °C.
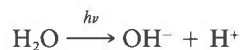
Bershov et al. (1968) studied elbaite crystals at 290 and 77 K using EPR, optical absorption, and luminescence. EPR measurements of irradiated, bleached elbaite crystals showed the typical 11-line superhyperfine (SHF) splitting of ^{27}Al-O^{1-}-^{27}Al hole centers. The EPR pattern, the broad optical absorption band at 515 nm, the broad luminescence band at 570 nm, and the color of the crystals decreased gradually after heating up to 500 °C where they disappeared simultaneously. The EPR pattern, optical ab-

sorption band, luminescence band, and color appeared again simultaneously after gamma or X-ray irradiation. These studies show clearly, that the 515-nm band is due to metastable ^{27}Al-O^{1-}-^{27}Al hole centers and not to d-d transitions of Mn^{3+} ions.
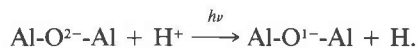
Using EPR, Bershov (1970) observed two hyperfine signals of atomic H in natural and irradiated elbaite crystals, in addition to O^{1-} lines. The H signals were split to SHF doublets by ^{19}F. The H atoms were assigned to octahedrally coordinated interstitial positions, H being located near the oxygen that is in *trans* position to the F^- ion. After irradiation, the intensity of the signals of H and color were increased. They disappeared simultaneously with subsequent heat treatment. From the studies of Bershov et al. (1968) and Bershov (1970), the following color-producing mechanisms in elbaite may be inferred:

$$OH^- \xrightarrow{h\nu} O^{2-} + H^+$$

and/or

$$H_2O \xrightarrow{h\nu} OH^- + H^+$$

and

$$Al\text{-}O^{2-}\text{-}Al + H^+ \xrightarrow{h\nu} Al\text{-}O^{1-}\text{-}Al + H.$$

According to the data now available, the optical absorption band at 515 nm and the color-producing processes in elbaite are composed of several quite different phenomena: (1) metastable O^{1-} centers, (2) $Mn^{4+} \rightarrow Mn^{3+}$ electron centers, and (3) electronic transitions of transition-metal ions, e.g., Mn^{3+}. The pink colors that are stable up to about 250 °C (e.g., sample 614 of Reinitz and Rossman) are apparently due to (1). O^{1-} centers stable below 250 °C are known to exist in quartz, topaz, feldspars, etc. Pink colors stable up to 500–600 °C (e.g., sample 565 of Reinitz and Rossman and the pink samples of De Camargo and Isotani) result most likely from a combination of (1) and (2), which are both reducing processes. Colors stable up to 800 °C or higher (e.g., the samples of Bradley and Bradley) may be due to (3).

For unambiguous interpretation of the optical absorption band at 515 nm in elbaite, thermoluminescence and EPR spectra at low temperatures are mandatory.

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