

A notable Mn-rich gem elbaite tourmaline and its relationship to "tsilaisite"

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ABSTRACT

An unusual, slightly yellowish-green gem tourmaline when chemically analyzed was found to have the most Mn-rich composition yet reported for tourmaline (approximately 9 wt% MnO). This composition does not represent a new species of the tourmaline group, but does support the existence of a possible solid-solution series between elbaite and a hypothetical Mn analogue "tsilaisite." This elbaite tourmaline has refractive indices of $\epsilon = 1.621$ and $\omega = 1.649$, a birefringence of 0.028, a specific gravity of 3.13 (± 0.01), and unit-cell dimensions of $a = 15.951(2)$ and $c = 7.116(2)$ Å. Its origin is uncertain, but we believe it to be from Zambia. Investigation of additional material from this area may yet disclose a sufficiently Mn-rich specimen to define a new tourmaline species.

INTRODUCTION

Possible new varieties of minerals, distinguished by their unusual color or appearance, are often first seen in the gem marketplace because of their potential gem value. In January 1984 a gem tourmaline with a surprisingly intense slightly yellowish-green color was submitted by a gem dealer to the Gemological Institute of America for examination. This rectangular-cut faceted stone weighed 38.47 carats and measured $22.00 \times 17.32 \times 11.66$ mm. Previously we had not seen a gem tourmaline of this color. The stone exhibited physical properties significantly different from the hundreds of other gem elbaites of varying color we have examined that typically have refractive indices in the range of 1.624–1.644 and a birefringence of approximately 0.020. Although of unknown origin, we suspect this gem tourmaline to have come from a locality in Zambia that has recently produced tourmalines of rather remarkable chemistry and color (Thomas, 1982; Bank, 1982; Schmetzer and Bank, 1984a, 1984b). Electron-microprobe analysis of this tourmaline showed it to be an elbaite having the highest Mn content yet reported among the tourmaline-group minerals. The properties and mineralogical significance of this unusual tourmaline are the subjects of this note.

PHYSICAL AND CHEMICAL PROPERTIES

Gem tourmalines are typically elbaite, and to a lesser extent liddicoatite, uvite, and dravite (Arem, 1977; Webster, 1983). Measured refractive indices of the yellowish-green cut stone obtained with a GIA DUPLEX II refractometer and a filtered, monochromatic, Na-equivalent light source were $\epsilon = 1.621$ (± 0.001) and $\omega = 1.649$ (± 0.001). These values are typical of elbaites (Dietrich, 1985, cites 1.603–1.634 and 1.619–1.655, respectively). However, the stone's birefringence of 0.028 is higher than for most elbaites (0.013–0.024; Dietrich, 1985). The color of the

tourmaline can be denoted using Munsell color values as 5GY 7/10, or using the CIE notation as $x = 0.4212$, $y = 0.5641$, and $z = 31.2080$. The stone was distinctly pleochroic with ω (medium brownish yellow-green) greater than ϵ (very light green). Its specific gravity (hydrostatic method) of 3.13 (± 0.01), a value in good agreement with the calculated density of 3.144 g/cm³, is also greater than for other elbaites (2.84–3.10; Dietrich, 1985). A solid-solution series exists between elbaite and schorl (Epprecht, 1953), and with respect to these physical properties, this gem tourmaline corresponds more closely to the latter.

Electron-microprobe analyses (Table 1) indicate that the yellowish-green tourmaline is an Mn-rich elbaite with very little Ti and almost no Fe. Although of fairly uniform color, the cut stone displayed slight compositional inhomogeneity. We believe that the Mn is situated in the Y crystallographic site on the basis of the structure refinement of an Mn-bearing Zambian tourmaline reported by Nuber and Schmetzer (1984).

Visible absorption spectra obtained from the stone (Fig. 1) show an increasing level of absorption toward the ultraviolet end of the spectrum. Upon this are superimposed a broad absorption band centered at about 630 nm, a sharp band at 413 nm, and in the $E \perp c$ spectrum, an additional weak band or shoulder at about 480 nm.

An X-ray diffraction pattern, obtained using a Debye-Scherrer camera and $\text{CuK}\alpha$ radiation, yielded the following five strongest lines: 6.339(30), 4.217(50), 3.988(60), 2.944(60), and 2.573(100). The 29 measured lines are closely related in both position and intensity to those in the X-ray diffraction pattern of a representative elbaite (1980 JCPDS Mineral Powder Diffraction File 26-964). Least-squares refinement yielded unit-cell dimensions of $a = 15.951(2)$ and $c = 7.116(2)$ Å. On diagrams plotting axial ratio vs. unit-cell dimension for tourmaline devised by Epprecht (1953), this tourmaline falls close to the mid-

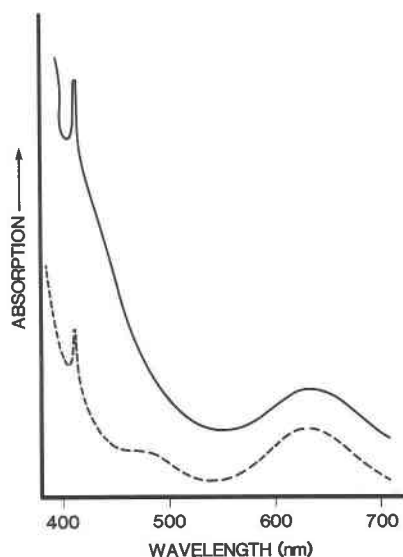


Fig. 1. Optical spectra of the yellowish-green gem elbaite. Path length approximately 11 mm. Bandwidth 2 nm. E || c spectrum solid line; E ⊥ c spectrum dashed line.

point of the line connecting elbaite and schorl, and is some distance away from the line connecting schorl and dravite.

As is often the case with gemstones, the exact source of this particular gem tourmaline is unfortunately not known. In the last few years, however, we have seen a number of gem-quality tourmalines from the Chipada region of Zambia. Some gem tourmalines from this area are heat treated to improve their color (Bank, 1982). We have heat treated some of the reddish- or yellowish-brown gem tourmalines from the Chipada area at 400°C and have produced various greenish-yellow colors. We do not believe, however, that the large yellowish-green cut stone underwent similar heat treatment because of the absence of any obvious damage to the numerous fluid inclusions it contains.

Schmetzer and Bank (1984a, 1984b) chemically analyzed yellow and greenish- or brownish-yellow tourmalines from this same area of Zambia and found them to also be high in Mn but low in Fe (see Rossman and Mattson, 1986). These tourmalines had 6–7 wt% MnO and were principally yellow or greenish yellow, but were otherwise similar to the yellowish-green cut stone we examined. The close correspondence between the properties of these Zambian tourmalines and our cut stone suggests that it too may be of similar origin.

DISCUSSION

While elbaite containing minor amounts of Mn (<1 wt% MnO) are common, more Mn-rich elbaite has only occasionally been described (Duparc et al., 1910; Kunitz, 1929; Agafonova, 1947; Epprecht, 1953; Slivko, 1961; Otroshchenko et al., 1971; Leckebusch, 1978). Mn has also been found in some schorls and dravites (e.g., Neiva, 1974; Ayuso and Brown, 1984). The Mn-rich elbaite has MnO contents from 2–6 wt% and the following phys-

Table 1. Microprobe analysis of the yellowish-green gem elbaite

	Chemical composition (wt%)*		Number of ions on the basis of (O,OH,F) = 31	
	Range	Average		
Na ₂ O	2.20–2.30	2.27	Na	0.716
CaO	0.17–0.20	0.18	Ca	0.031
K ₂ O	0.01–0.04	0.03	K	0.006
Li ₂ O**	—	1.05	Li	0.686
MnO†	8.60–9.18	8.86	Mn	1.221
FeO†	0.00–0.08	0.03	Fe	0.004
TiO ₂	0.10–0.14	0.12	Ti	0.015
			Al	1.039
Al ₂ O ₃	38.02–38.75	38.46	Al	6.000
B ₂ O ₃ **	—	10.47	B	2.940
SiO ₂	34.18–35.10	34.79	Si	5.661
			Al	0.339
H ₂ O**	—	3.62	OH	3.929
F	0.76–1.17	0.96	F	0.494
Subtotal		100.84		
–O = F		0.40		
Total		100.44		

* Range and average of four analyses. Analytical conditions—MAC microprobe, operating voltage 15 kV, beam current 0.05 μA; probe standards—(Na) albite, (Al) kyanite, (Mg) periclase, (Si) quartz, (K) microcline, (Ca) wollastonite, (Ti) rutile, (Cr) synthetic chromic oxide, (Mn) garnet, (Fe) fayalite, (V) Corning glass "W," (F) synthetic fluorapatite; data reduction carried out using the Ultimate correction program of Chodos et al. (1973); Mg, Cr, and V analyzed for but not detected.

** Not measured; values assumed for a tourmaline composition along the elbaite-"tsilaisite" solid-solution series of 59% elbaite and 41% "tsilaisite."

† Total Mn and total iron reported as MnO and FeO.

ical properties: refractive indices $\epsilon = 1.618$ – 1.636 and $\omega = 1.636$ – 1.662 ; birefringence 0.018–0.026; and specific gravity 3.01–3.19. These values are generally slightly higher than the corresponding values for common elbaite (compare Dietrich, 1985). The Mn-rich elbaite appears to be of pegmatitic origin. Interestingly, they are described in a wide range of colors including red, green, yellow, blue, brown, and black.

The highest Mn content (8.21 wt% MnO) noted previously in a tourmaline was reported by Kunitz (1929). To deal with the chemistry of such tourmalines, he proposed the name "tsilaisite" for a new hypothetical Mn endmember of the tourmaline group with the ideal chemical formula $\text{NaMn}^{2+}\text{Al}_6\text{B}_3\text{Si}_6\text{O}_{27}(\text{O,OH,F})_4$. No tourmalines approaching this composition have yet been found in nature. A synthetic tourmaline identified as "tsilaisite" was grown by Tomisaka (1968) but was not chemically analyzed.

Slivko (1961) made an extensive study of Mn tourmalines and documented the solid-solution series between Mn tourmalines and both elbaite and schorl. Because Mn tourmalines generally contain only 3–6 wt% MnO, he suggested an alternative ideal formula for "tsilaisite" of $\text{Na}(\text{Mn}^{2+}\text{Al}_2)\text{Al}_4\text{B}_3\text{Si}_6\text{O}_{27}(\text{O,OH,F})_4$ that requires a much lower Mn content and higher Al content in the Y site as compared to the original formula of Kunitz. In their study

of Zambian tourmalines, Schmetzer and Bank (1984a) identified this material as "tsilaisite" following Slivko's revised formula. The results of our work on the yellowish-green gem tourmaline, however, lend support to the existence of high-Mn tourmalines whose chemistry bears greater resemblance to the "tsilaisite" proposed by Kunitz. Calculation of unit-cell contents (Table 1) indicates that the composition of this yellowish-green gem tourmaline can be expressed in terms of ideal endmembers as 59% elbaite and 41% "tsilaisite." A tourmaline belonging to this series with more than 10.7 wt% MnO could properly be described as "tsilaisite."

Spectra of yellow and greenish-yellow Zambian tourmalines, similar to those shown in Figure 1, are illustrated in Schmetzer and Bank (1984a) and Rossman and Mattson (1986). Schmetzer and Bank ascribed the various colors of these tourmalines to differences in the absorption of the 633-nm band vs. the increasing level of absorption toward the ultraviolet portion of the spectrum, with the latter factor being more important. The sharp band at 413 nm is attributed to octahedral Mn^{2+} . Rossman and Mattson also suggested that the broad band at 633 nm is due to octahedral Mn^{2+} . They then proposed that the strong absorption in the ultraviolet centered at 325 nm results from Mn^{2+} - Ti^{4+} intervalence charge transfer. This mechanism has not previously been recognized as a cause of tourmaline coloration because the ultraviolet spectra of many colored tourmalines are dominated by Fe-Ti intervalence-charge-transfer bands.

Our cut stone has a much greener hue than the tourmalines examined by both groups of investigators Schmetzer and Bank (1984a) and Rossman and Mattson (1986). The 633- and 413-nm bands appear to be much stronger in intensity than is the case for the spectra of more yellow or greenish-yellow tourmalines. This is likely due to the higher Mn content of our stone. Rossman and Mattson's Mn^{2+} - Ti^{4+} charge transfer band at 325 nm is so intense in the spectra of the cut stone as to exceed the absorption range of our spectrophotometer. No spectral features that could be attributed to Fe were noted. Thus, our observations support the band assignments of Rossman and Mattson for the spectra of high-Mn, low-Fe elbaite tourmalines.

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