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Yellow, Mn-rich elbaite with Mn-Ti intervalence charge transfer

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ABSTRACT

The color of yellow-green to yellow-brown Mn-rich elbaite tourmalines from Zambia and Nepal is controlled by Fe^{2+}-Ti^{4+} (brown) and Mn^{2+}-Ti^{4+} (yellow-green) intervalence charge transfer. The proposed Mn-Ti interaction responsible for an absorption band centered at 325 nm is especially well developed in the Zambian tourmaline whose spectroscopic properties are discussed.

INTRODUCTION

Early in 1982, a small amount of tourmaline from Zambia appeared on the commercial gem market which was notable because of its unusual array of colors including nearly unprecedented greenish yellows and yellows. Both Bank (1982) and Thomas (1982) have described these unusual tourmalines which come from pegmatites described as either being near Chipata or from Lundazi, about 150 km north of Chipata. Schmetzer and Bank (1984) published a chemical analysis of a yellow Zambian tourmaline, which indicated that this material is unusually rich in Mn but low in Fe, and reported optical and spectroscopic data. Mn is a common constituent of pegmatitic tourmalines, but when it is the only transition element present, it normally is associated with pale pink to red color. The objective of this study was to better characterize the origin of the unusual color.

Sample descriptions

The tourmaline crystals used in this study are listed in Table 1. Our yellow Zambian tourmalines were mined from the outer margins of simple quartz pegmatites at the Kabelubelu mine in the Lundazi District of Zambia, west of the city of Lundazi (Marc Sarosi, pers. comm.). They consisted of 110 crystal fragments which ranged in color from yellow green to brown, and three faceted greenish-yellow to yellow stones. Additionally, we examined about 100 crystals from an unspecified Zambian mine(s) which ranged from bright green more typical of elbaite, to pink and yellow. These crystals had cores of generally homogeneous color and frequently had a rim of a darker color. Only crystals with a yellow component had exceptionally high Mn contents as judged by semiquantitative X-ray fluorescence analysis. The Nepal tourmaline consisted of three slabs apparently cut from different crystals zoned with bands that varied from dark brown to yellow. It was mined in 1979 uphill of the Hyakule mine, in the Chainpur area (Bassett, 1985; G. Moss, pers. comm.). The tourmaline from the San Diego mine, Mesa Grande, San Diego County, California, consisted of a near-colorless core section of a crystal with a light-pink rim. It is from the material documented by Foord (1976). Experimental details regarding chemical and spectroscopic analyses of these minerals are the same as those reported in Mattson and Rossman (1984).

Analytical results

Electron-microprobe analyses (Table 2) of yellow to greenish-yellow tourmalines indicate that they are elbaites. The analyses further indicate that they have high Mn content but no detectable Fe. The 0.3 wt% Ti content is unusually high for typical pale-colored elbaites (Deer et al., 1962). In regions of homogeneous color, the Mn content varies by less than 5% of the amount present. The composition with 6.76% MnO has only 60% of the Mn content necessary to fill one half of the Y site with Mn. If more than half of the Y site contained Mn, it could be called tsilaisite after the hypothetical end member, $NaMn_3Al_6B_3Si_6O_{27}(OH)_4$, proposed by Kunitz (1929). We specifically disagree with the proposal of Schmetzer and Bank (1984) to define the tsilaisite end member with only one half of the Y sites filled with Mn. Semiquantitative X-ray fluorescence (XRF) analyses of sample G5CT confirmed the high Mn content and minor Ti content and further indicated that with the exception of approximately 400 ppm Fe, no other chromophoric elements were present. XRF analysis of sample G8CT indicated only 80 ppm Fe, whereas XRF analysis of a brown, Mn-rich crystal indicated that it contained ~0.15 wt% Fe. Optical absorption spectra indicated that the Fe is present as Fe^{2+}. In an XRF survey of 35 Zambian tourmalines with a decided yellow component, the highest Mn content we observed was from a brownish-yellow crystal which had approximately 7.3% MnO. All the brown crystals had more Fe than the yellow ones. The Mn content of these tourmalines exceeds all other reported analyses of high-Mn tourmalines (Duparc et al., 1910; Epprecht, 1953; Slivko, 1959) with the sole exception of a partial analysis of a manganiferous elbaite with 8.21 wt% MnO (Kunitz, 1929).

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Table 1. Tourmaline sample descriptions

Sample	Color*	Locality	Archival Code
G5CT	yellow	Zambia	11/8/82-5
G8CT	greenish-yellow	Zambia	LACM 24347
NP	1=yellow 2=light brown 3=dark brown	Nepal	2/2/80-A
T10	yellow-green	Zambia	11/8/82-10
T11	yellow-green	Zambia	11/1/82-11
T12	brown-green	Zambia	11/1/82-12
T15	green	Zambia	2/11/83-16
SD	nearly-colorless	San Diego Mine	7/5/83-A2

* Elc color in thin section
LACM = Los Angeles County Museum of Natural History

Optical properties

The color of the yellow tourmalines is controlled by the tail of an absorption band rising toward the ultraviolet end of the spectrum (Fig. 1). Superimposed are absorption bands at 413 and 633 nm. Assuming that the 633-nm band is from Mn, its intensity expressed as the molar absorptivity, ϵ, is 0.04, a low value consistent with Mn^{2+} but not with Mn^{3+}. Because Mn^{2+} can produce yellow-green color when in tetrahedral coordination (e.g., Mn^{2+} in willemite from Franklin, New Jersey), it is worth noting that the intensity of the 633-nm band is about 100 times lower than tetrahedral Mn^{2+} usually produces and is at a much lower energy than is known for tetrahedral Mn. The sharper 413-nm band, actually a pair of bands at 412 nm and 414 nm, is at a wavelength at which absorption from the ${}^6A_g \rightarrow {}^4E_g,{}^4A_g$ transition of six-coordinated Mn^{2+} is commonly observed, as previously noted by Schmetzer and Bank (1984). The structural refinement of a Mn-rich crystal by Nuber and Schmetzer (1984) showed conclusively that the Mn is situated on the octahedral Y site.

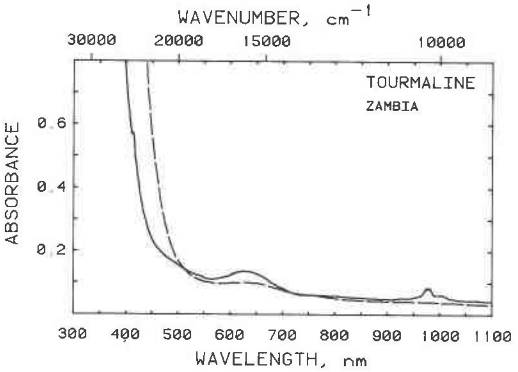

Fig. 1. Optical spectrum of greenish-yellow Zambian elbaite, T10, plotted for 2.00 mm thick. **E**∥**c**, solid line; **E**⊥**c**, broken line. Sharp features near 975 nm are overtones of the OH stretching vibration.

Table 2. Electron-microprobe analyses of tourmalines

Sample	Na_2O	CaO	MgO	FeO	MnO	TiO_2	Al_2O_3	ZnO	SiO_2	F
G5CT	2.81	0.33	BDL	BDL	6.18	0.27	38.2	NA	37.2	1.5
G8CT	2.77	0.25	BDL	BDL	6.76	0.34	38.5	NA	37.6	1.7
T10	2.61	0.26	BDL	BDL	6.85	0.33	37.8	NA	36.2	0.4
T11										
T12	2.65	0.25	BDL	0.29	6.50	0.31	37.5	NA	36.4	0.3
T15	2.45	0.47	0.21	2.10	1.06	0.05	39.4	NA	37.3	0.3
NP1	2.24	1.22	BDL	0.13	5.74	0.46	39.0	0.03	35.1	1.5
NP2	2.51	0.81	BDL	1.46	5.10	0.26	38.2	BDL	35.8	1.6
NP3	2.37	0.78	BDL	4.79	3.58	0.78	37.3	0.23	35.4	1.2
SD	2.17	1.08	BDL	0.03	3.57	0.02	40.4	NA	36.0	1.7

BDL -- below detection limits NA -- not analyzed

Formula proportions for T10:

$Na_{0.82}Ca_{0.04}Li_{0.94}Al_{7.22}Mn_{0.94}Ti_{0.04}Si_{5.86}F_{0.2}$

calculated assuming 1) charges in X + Y + Z + Si = 49
2) Li = 15 - Al - Si - Mn - Ti

The color of these tourmalines is controlled primarily by the absorption bands centered in the ultraviolet region. The two dominant bands in the ultraviolet are seen in the spectrum (Fig. 2) of elbaite NP which is zoned in Mn and Fe and Ti. A brown, Fe-rich zone exhibits a band at 415 nm which is associated with Fe^{2+}-Ti^{4+} charge transfer (Mattson and Rossman, in prep.). The Fe^{2+}-Ti^{4+} intervalence transition is the source of the green and brown color of many tourmalines. It is the cause of the variation from greenish yellow through yellow to brown color in the Zambian tourmalines which is correlated with increasing Fe content when Mn and Ti are nearly constant. It is important to note that the green color of typical pegmatitic elbaites such as from Maine, California, or Minas Gerais is associated with much higher Fe contents and lower Ti contents than is the case for the greenish-yellow color of sample T10. The analysis (Table 2) of Zambian elbaite T15 is more representative of common green tourmalines.

An additional band at 325 nm is evident in Figure 2 taken in a zone with an Fe:Mn ratio of 1:4. The band at

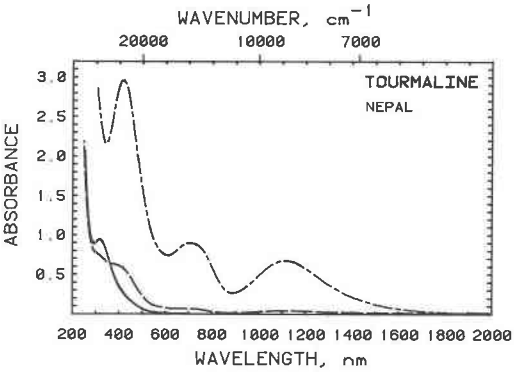

Fig. 2. Optical spectrum of zoned Nepal elbaite plotted for 150 μm thick. Solid line, zone NP1 (yellow); dashed line, zone NP2; dot-dash line, zone NP3 (brown). Absorption near 700 and 1100 nm arises from Fe^{2+}.

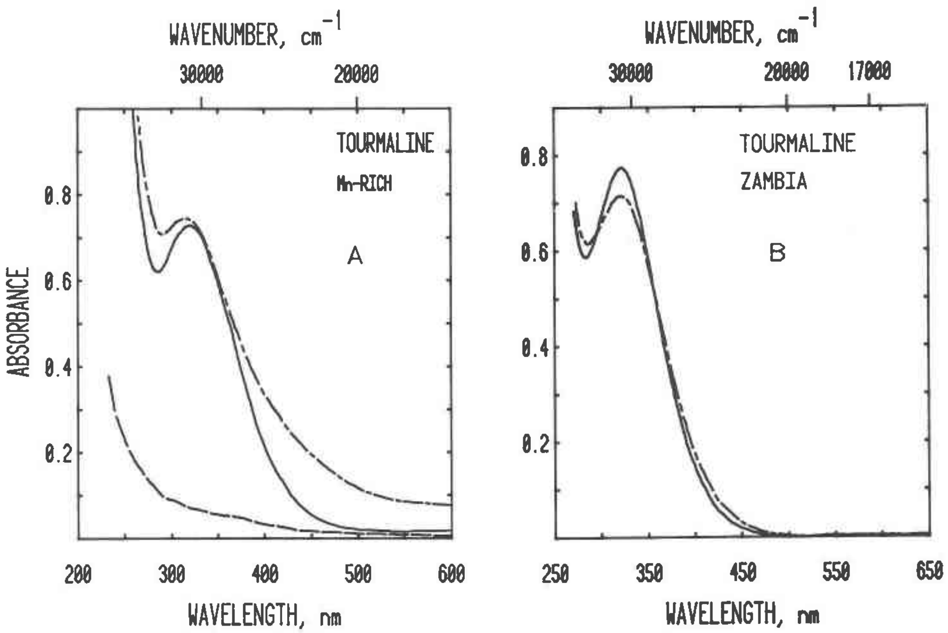

Fig. 3. (A) Comparison of the ultraviolet absorption of Zambian elbaite [solid line, T10 (greenish-yellow); dot-dash line, T12 (brown)] and San Diego mine elbaite SD, showing the absence of the proposed Mn-Ti IVCT band in the SD, low-Ti, manganian elbaite. All spectra $\mathbf{E}\perp\mathbf{c}$, 150 μm thick. (B) 23°C (dashed line) and −190°C optical spectrum of elbaite T10. Sample thickness, 150 μm; polarized $\mathbf{E}\perp\mathbf{c}$.

325 nm is clearly shown in a yellow zone with only trace amounts of Fe. Octahedral Mn^{2+} is unlikely to produce the intense 325-nm band. We propose that this band is Mn^{2+}-Ti^{4+} charge transfer.

Mn^{2+}-Ti^{4+} charge transfer

In addition to colors of the individual transition elements, color can be associated with pairs of transition elements such as the Fe-Ti pair. Mn can also be expected to participate in charge-transfer interactions. The high Mn content coupled with an appreciable Ti content makes it worth considering a possible Mn-Ti interaction in these tourmalines. There are a number of reasons for assigning the 325-nm band to Mn^{2+}-Ti^{4+} intervalence charge transfer.

First, it can be shown that the 325-nm band is not from just Mn alone. The spectrum of an elbaite from the San Diego mine (tourmaline SD, Table 1) which has a very low Ti content but 3.5 wt% MnO provides the comparison. The spectrum of this crystal is essentially devoid of absorption in the 300–400-nm region (Fig. 3a). Second, the intensity of the 325-nm band is approximately correlated with the product of the Mn and Ti contents, suggesting a mutual dependence on these two components.

The charge-transfer assignment is also based on characteristics which the 325-nm band shares with other charge-transfer bands. It is polarized along the direction between the ions of the pair—$\mathbf{E}\perp\mathbf{c}$ (in the plane of the Y sites)—and has a large half-width (7000 cm^{-1}). Additionally, this band shows a small intensity increase at low temperature (Fig. 3b), which is similar to the temperature dependence of the Fe^{2+}/Ti^{4+} charge-transfer band in tourmaline (Mattson and Rossman, in prep.).

The specific comparison of Mn^{2+}-Ti^{4+} and Fe^{2+}-Ti^{4+} charge-transfer transitions in tourmaline provides a confirmation of our understanding of the characteristics of charge-transfer bands related to polarization, half-width, and temperature dependence. However, the factors that govern the energy of charge-transfer transitions are poorly understood. The higher energy of the Mn^{2+}-Ti^{4+} charge transfer in tourmaline can be explained by one factor, however: charge-transfer energies can be related to the ionization potential of the donor ion and the electron affinity of the acceptor ion. Because Mn has a higher third ionization potential than Fe, the energy of Mn^{2+}-Ti^{4+} charge transfer is expected to be higher than that of Fe^{2+}-Ti^{4+} when all structural aspects are similar. This relationship was also observed in a reflectance study of Fe- and Mn-doped $MgTiO_5$ (Blasse, 1981). In contrast, there is an inadequate theoretical basis to compare the intensity of these two bands. The molar absorptivity of the 325-nm band (~450 $M^{-1}cm^{-1}$), derived under the assumption of statistical ordering of Mn and Ti in the Y sites, is much lower than that of Fe^{2+}-Ti^{4+} charge transfer in tourmaline (~4000 M^{-1} cm^{-1}).

The Mn-Ti intervalence charge transfer in tourmaline that we are proposing has not been reported before probably because the spectrum in the 300–400-nm region is normally dominated by the Fe-Ti intervalence charge-transfer bands. Its observation in this case is a direct result of the high Mn and low Fe contents of these yellow tourmalines.

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