Origin of color in cuprian elbaite from São José de Batalha, Paraíba, Brazil

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Abstract

Gem-quality elbaite from Paraíba, Brazil, containing up to 1.4 wt% Cu has been characterized using optical spectroscopy and crystal chemistry. The optical absorption spectra of Cu²⁺ in these tourmalines consist of two bands with maxima in the 695- to 940-nm region that are more intense in the E ⊥ c direction. The vivid yellowish green to blue-green colors of these elbaite samples arise primarily from Cu²⁺ and are modified to violet-blue and violet hues by increasing absorptions from Mn³⁺.

Introduction

The color of elbaite has been extensively investigated. Most colors are determined by small amounts of transition elements (Dietrich, 1985). In particular, blue to green colors have been attributed to various processes involving both Fe²⁺ and Fe³⁺ ions (Mattson and Rossman, 1987) and Fe²⁺ → Ti⁴⁺ charge transfer (Mattson, as cited in Dietrich, 1985, p. 129). Cr³⁺ and V⁴⁺ have been identified as coloring agents in green dravite and uvite (Schmetzer and Bank, 1979) but never in elbaite. Several investigators briefly mentioned Cu²⁺ as a potential coloring agent in blue and green elbaite on the basis of emission spectroscopy analyses. For example, Warner (1935) observed that blue samples have a lower Cu concentration than yellow-green ones. On the contrary, Carobbi and Pieruccini (1946, 1947) found greater amounts of Cu in blue crystals. None of these investigators, however, proved that this ion actually acts as a coloring agent. Staatz et al. (1955) mentioned the presence of trace amounts of Cu in tourmaline but did not relate it to color.

A new find of gem-quality elbaite with unusually saturated shades of green and blue colors was made in 1988. This discovery took place at an undescribed locality called Mina da Batalha (“Mine of the Battle”) near the village of São José de Batalha, 4.5 km northeast of the town of Salgadinho, in the state of Paraíba, northeastern Brazil (G. Becker, B. Cook, and D. Epstein, personal communication, 1989). These elbaite samples are found in a range of color from violet-blue, not unlike the color of a blue sapphire, to green-blue, reminiscent of turquoise, and to yellowish green. The deep blue material is referred to locally as “heitotrite,” in honor of Heitor Dimas Barbosa, founder of COGASBRA, the mining cooperative working the deposit. Some of the complete crystals contain a deep pink core surrounded by a blue zone and a thin pink rim. Other color-zoning patterns have been observed.

Because of their attractive color, these elbaite samples have proved very popular as gemstones and have commanded prices up to ten times higher than those paid for other colors of gem tourmalines in the same size and clarity range. A brief gemological description of the Paraíba tourmaline locality is given in Fritsch et al. (1990).

Materials and methods

Three crystal fragments and two faceted samples, representative of the color range of the tourmaline found at São José de Batalha, were studied in detail. These five specimens were selected on the basis of their color and color homogeneity from several hundred fragments of this material. The crystallographic orientation of the crystal fragments was determined using striations (parallel to the c axis, or optic axis) on the prism faces. When striations were not present, the samples were oriented by X-ray alignment photography. Each specimen was cut with a microsaw to obtain a parallel-windowed section containing the optic axis. The sections were then ground to an appropriate thickness (0.2–5 mm) and polished with 1-µm
alumina powder. Optical absorption spectra were recorded using a Cary model 17 spectrophotometer with calcite polarizers. Chemical analyses were obtained from the same specimens with a JEOL model 733 electron microprobe. X-ray diffraction measurements to confirm the identity of the five specimens were performed with an automated Rigaku powder diffractometer operated at 35 kV and 15 mA.

The color of each of the five specimens appears homogeneous when the polished sections are viewed with the naked eye. Color descriptions are given in Table 1, using the terminology of the Munsell Book of Color (1979) and Kelly and Judd (1976). The color was visually determined on parallel-polished slices about 1.5 mm thick containing the c axis. Because of tourmaline’s strong pleochroism, the face-up color of faceted gemstones might be significantly different from the descriptions reported in Table 1. The colors of the slices range from light yellowish green to light purplish blue, the sample with the highest Cu content being brilliant bluish green.

**RESULTS**

**Physical properties**

The ranges of indices of refraction of the five specimens measured with a GIA GEM Instruments Duplex II refractometer and a filtered, near-monochromatic Na-equivalent light source are $\varepsilon = 1.618-1.621 (\pm 0.001)$ and $\omega = 1.638-1.646 (\pm 0.001)$. These values are typical of elbaite (Dietrich, 1985). All specimens have a uniaxial negative optical character. The birefringence ranges from 0.018 to 0.025; these values are toward the high end of the recorded range for elbaite (Dietrich, 1985). These elbaite samples are distinctly pleochroic, with the most saturated color seen along $\omega$ (see Table 1). Their specific gravity, measured by the hydrostatic method in H2O, ranges from 3.05 to 3.12 (±0.01), which is slightly higher than for most elbaite (2.84-3.10; Dietrich, 1985). None of the samples tested contained inclusions of foreign, possibly heavier minerals, as determined by microscopic examination at 80× magnification.

**X-ray diffraction**

Measured lines in the X-ray diffraction patterns of these tourmalines are closely related in both position and relative intensity to those from the pattern of a representative elbaite sample (1986 JCPDS Mineral Powder Diffraction File 26-964). Least-squares refinement of data for the most Cu-rich of the five specimens (sample R030) yielded unit-cell dimensions of $a = 15.883(4)$ and $c = 7.111(1)$ Å. The five strongest lines in this pattern are $3.978(56)(220)$, $3.445(76)(012)$, $2.938(100)(122)$, $2.567(90)(051)$, and $2.029(54)(152)$. No significant differences were noted between the diffraction patterns of this and the other elbaite specimens from this locality. The $a$ and $c$ dimensions of the other specimens were within 0.02 Å and 0.03 Å, respectively, of those for sample R030.

**Chemical analysis**

Electron microprobe analyses (Table 2) show that these five tourmalines contain little or no Ti, V, Cr, or Fe and have Cu and Mn as major transition element constituents. Analyses performed at three random locations on each specimen show only very slight compositional variation, as might be expected from the fairly uniform coloration. It is also interesting to note that small amounts of Bi, Pb, and Zn were detected in each specimen. Results of site occupancy calculations based on charge balance considerations (see Table 2) indicate that Cu is present in the $Y$ crystallographic site (using the site terminology of Correns, 1969, p. 406; Deer et al., 1986).

**Ultraviolet, visible, and near-infrared absorption spectroscopy**

Absorption spectra were obtained at room temperature in the range from 300 to 2000 nm. The spectra of all specimens are dominated by three features—an ultraviolet absorption edge beginning at about 400 nm (more intense in the E \perp c direction), a pair of broad bands in the 695- and 940-nm region (absorbing more strongly in the E \perp c direction), and a series of sharp bands in the 1400- to 1500-nm region strongly polarized in the E \parallel c direction (Fig. 1). Bands in the 1400- to 1500-nm region arise from the first overtones of the O-H stretching motion (Wickersheim and Buchanan, 1959, 1968; Gebert and Zemann, 1965).

The absorption rising toward the ultraviolet is more conspicuous in specimens that contain a larger amount of Ti (see Table 2). Because all specimens contain much

**TABLE 1. Properties of cuprian elbaite from São José de Batalha, Paraiba, Brazil**

<table>
<thead>
<tr>
<th>Specimen no.</th>
<th>Color*</th>
<th>Munsell notation</th>
<th>R.I.</th>
<th>Birefringence</th>
<th>Pleochroism</th>
<th>S.G.**</th>
</tr>
</thead>
<tbody>
<tr>
<td>R030</td>
<td>Brilliant bluish green</td>
<td>8 BG 7/9</td>
<td>1.621-1.646</td>
<td>0.025</td>
<td>$\omega = $ medium green-blue</td>
<td>3.117</td>
</tr>
<tr>
<td>R050</td>
<td>Light yellowish green</td>
<td>2.5 G 7/6</td>
<td>1.619-1.639</td>
<td>0.020</td>
<td>$\epsilon = $ medium bluish green</td>
<td>3.05</td>
</tr>
<tr>
<td>R052</td>
<td>Light blue</td>
<td>10 B 7/6</td>
<td>1.619-1.639</td>
<td>0.020</td>
<td>$\epsilon = $ light grayish green</td>
<td>3.11</td>
</tr>
<tr>
<td>R066</td>
<td>Light purplish blue</td>
<td>6.5 PB 7/55</td>
<td>1.620-1.638</td>
<td>0.018</td>
<td>$\omega = $ medium blue</td>
<td>3.04</td>
</tr>
<tr>
<td>R067</td>
<td>Light blue</td>
<td>10 B 7/65</td>
<td>1.618-1.638</td>
<td>0.020</td>
<td>$\epsilon = $ light greenish blue</td>
<td>3.065</td>
</tr>
</tbody>
</table>

* Color of a 1.5-mm slice containing the c axis.
** Average of three measurements.
Table 2. Electron microprobe analyses of cuprian elbaite from Paraiba, Brazil

<table>
<thead>
<tr>
<th>Weight percent</th>
<th>Specimen R030</th>
<th>Specimen R050</th>
<th>Specimen R052</th>
<th>Specimen R066</th>
<th>Specimen R067</th>
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<tbody>
<tr>
<td></td>
<td>Average</td>
<td>Range</td>
<td>Average</td>
<td>Range</td>
<td>Average</td>
</tr>
<tr>
<td>Na₂O</td>
<td>2.49</td>
<td>2.47-2.50</td>
<td>2.27</td>
<td>2.24-2.31</td>
<td>2.16</td>
</tr>
<tr>
<td>CaO</td>
<td>0.05</td>
<td>0.05-0.05</td>
<td>0.48</td>
<td>0.46-0.57</td>
<td>0.62</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.02</td>
<td>0.02-0.03</td>
<td>0.03</td>
<td>0.02-0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>MgO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.06</td>
<td>0.06</td>
<td>0.05</td>
<td>0.05-0.10</td>
<td>0.01</td>
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<tr>
<td>V₂O₅</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>MnO</td>
<td>1.48</td>
<td>1.48-1.49</td>
<td>1.47</td>
<td>1.35-1.55</td>
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<tr>
<td>FeO</td>
<td>0.07</td>
<td>0.06-0.10</td>
<td>0.22</td>
<td>0.22-0.23</td>
<td>0.15</td>
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<tr>
<td>ZnO</td>
<td>0.25</td>
<td>0.24-0.26</td>
<td>0.08</td>
<td>0.07-0.09</td>
<td>0.01</td>
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<tr>
<td>CuO</td>
<td>1.76</td>
<td>1.75-1.79</td>
<td>0.72</td>
<td>0.70-0.73</td>
<td>0.62</td>
</tr>
<tr>
<td>PbO</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01-0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>B₂O₅</td>
<td>10.94</td>
<td>10.94-10.94</td>
<td>10.94</td>
<td>10.94-10.94</td>
<td>10.94</td>
</tr>
<tr>
<td>SiO₂</td>
<td>36.53</td>
<td>36.47-36.63</td>
<td>37.27</td>
<td>37.20-37.34</td>
<td>36.97</td>
</tr>
<tr>
<td>Cl</td>
<td>0.01</td>
<td>BDL-0.01</td>
<td>0.01</td>
<td>BDL-0.01</td>
<td>0.01</td>
</tr>
<tr>
<td>O + Cl</td>
<td>97.02</td>
<td>97.95</td>
<td>97.60</td>
<td>97.35</td>
<td>97.48</td>
</tr>
</tbody>
</table>

Note: Electron microprobe analyses were performed on an automated, five-crystal JEOL 733 spectrometer operating at a beam accelerating potential of 15 kV, a current of 35 nA, and spot size of between 10 and 25 μm. Kα lines were analyzed for each element except Pb and Bi, for which Kr lines were analyzed. Standards include: (Na) = NaCl, (Mg) = MgO, (Al, Si) = kyanite, (K) = microcline, (Ca) = anorthite, (Ti) = TiO₂, (Cr) = Cr₂O₃, (Mn) = manganese olivine, (Fe) = synthetic fayalite, (Cl) = sodalite, (Zn) = ZnO, (Cu) = pure element, (Pb) = galena, and (Bi) = pure element. Entries indicated by “BDL” were below the detection limits of the instrument (less than 0.01 wt%). The data were corrected using the program CITZAF (Armstrong, 1988) employing the absorption correction of Armstrong (1982), the atomic number correction of Love et al. (1978), and the fluorescence correction of Reed (1965) as modified by Armstrong (1988). Each specimen was analyzed at three different locations; the range of oxide concentrations and an average analysis are shown for each of the five elbaite samples, along with a calculated chemical formula based upon the average analysis.

* Values of B₂O₅, Li₂O, and H₂O were calculated based on stoichiometry.

more Mn than Ti, this feature is attributed to Mn²⁺-Ti⁴⁺ charge transfer (Rossman and Mattson, 1986). In conjunction with the broad band at about 695 nm, this feature produces a greenish coloration.

The darker blue to violet specimens display an absorption band centered around 515 nm, attributed to Mn⁴⁺ (Manning, 1973). A weak, sharp absorption at about 415 nm, barely visible in Figure 2 but more apparent on spectra obtained from thicker samples, is attributed to Mn²⁺ (Rossman and Mattson, 1986). Figure 2 presents a comparison of the spectra of a variety of colors of cuprian elbaite from this locality to illustrate how slight differences in absorption spectra are related to differences in color.

**DISCUSSION**

We interpret the bands in the 695- to 940-nm regions as arising from absorption by the Cu²⁺ ion. Figure 3 shows that the two bands in both polarization directions correlate in intensity with the Cu content as determined with the electron microprobe. It is interesting to note that hydrothermally grown synthetic sodium-copper tourmaline spherulites also have a green to blue color (Taylor and Terrell, 1967). Recently, Taran and Lebedev (1990) re-
ported the spectrum of Cu-doped synthetic tourmaline that exhibited the same broad bands at about 695 and 940 nm. This pair of bands observed for the Cu\(^{2+}\) absorption results from the expected Jahn-Teller splitting in a distorted octahedral site (Marfunin, 1979) such as the Y site of elbaite.

The molar absorptivities \(\epsilon\) can be calculated for each of the Cu\(^{2+}\) bands from the formula absorbance = \(\epsilon \times \) path length \(\times\) Cu concentration, where the path length is in centimeters and the concentration is in moles per liter. The \(\epsilon\) values were determined using the average density of the samples and the best linear fit to the experimental points in Figure 3. The resulting values are listed in Table 3. These \(\epsilon\) values of about 13–50 are higher than the 7–10 values for Cu\(^{2+}\) in guildite (Wan et al., 1978) and the 4–5 values for Cu\(^{2+}\) in CuSO\(_4\)\(\cdot\)5H\(_2\)O (Holmes and McClure, 1957). Nevertheless, very little information is available regarding absorption intensity of Cu in materials that are more directly comparable with tourmaline. One should note that the \(\epsilon\) values of other transition elements often are over 10 in silicates with sites distorted from a regular octahedral coordination (Goldman and Rossman, 1977).

**CONCLUSIONS**

Our results indicate that Cu is the principal coloring agent in elbaite from São José de Batalha. The Cu\(^{2+}\) alone is responsible for two strong absorption bands around 695–940 nm, which result in a turquoise blue color. Additional absorption around 515 nm, attributed to Mn\(^{3+}\), produces a shift toward more violet colors (sapphire blue and even violet). A wide absorption centered in the ultraviolet and extending into the visible range, tentatively attributed to Mn\(^{2+}\)–Ti\(^{4+}\) charge transfer, produces a shift toward more greenish colors when combined with the Cu\(^{2+}\) absorptions.

Cu concentrations recorded for tourmaline from São José de Batalha are so high that they are significantly above the range of Cu content reported so far in natural elbaite (Staatz et al., 1955; Dietrich, 1985; and experience of the authors). Therefore, if a Cu content greater than...
0.1 wt% Cu can be detected in a gem-quality elbaite, this provides proof at this time that the tourmaline comes from São José de Batalha.

We believe that the Cu concentration found in these Paraiba tourmalines is among the highest reported in silicate minerals that otherwise do not contain Cu as a major constituent. This raises the question of why Cu occurs in these gem-quality tourmalines, since this element is not often concentrated in silicates. Furthermore, Cu concentration in a granitic pegmatite environment is also unusual. In absence of additional information on the mineral assemblage of this pegmatite, one can only hypothesize that tourmaline may have provided the most favorable site for Cu incorporation.

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TABLE 3. Spectroscopic data for Cu\(^{2+}\) in cuprian elbaite

<table>
<thead>
<tr>
<th>Polarization</th>
<th>E (\perp) c</th>
<th>E (\parallel) c</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band position (nm)</td>
<td>695 (+ 1) 905 (+ 2) 740 (+ 10) 945 (+ 6)</td>
<td></td>
</tr>
<tr>
<td>Value</td>
<td>24.2 50.5 13.2 15.5</td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. Correlations between the intensity of absorption bands in elbaite from Paraiba, Brazil, and the Cu content determined by electron microprobe analysis. The lines are linear fits to the data constrained to pass through the origin. Solid circles = 905 nm; open circles = 695 nm; solid triangles = 940 nm; open triangles = 740 nm.

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