

CHARACTERIZATION OF COLORED TOURMALINES OF UVITE / DRAVITE SERIES FROM BRUMADO DIS- TRICT, BAHIA, BRAZIL

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ABSTRACT

Green, reddish brown, orange and red tourmalines from the uvite / dravite series were investigated by electron microprobe analysis, optical absorption, photoluminescence spectroscopy, Raman scattering and electron paramagnetic resonance (EPR). The related color or impurity centers are not known. Some of the uvite samples present strong dichroic effects ranging from pale pink (along *c*) to green (along *a*, *b*). In the present work seven uvite / dravite samples from metamorphic rocks of the famous magnesite deposit of Serra das Éguas, Brumado district Bahia, Brazil, were studied.

Keywords: tourmaline, color, EPR

INTRODUCTION

Tourmalines from the uvite and dravite series form a complete solid solution with trigonal space group symmetry $R\bar{3}m$ and three molecules per unit cell ($Z = 3$). The end member chemical compositions of uvite and dravite are $[\text{CaMg}_3(\text{Al}_5\text{Mg})(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_3\text{F}]$

and $[\text{NaMg}_3\text{Al}_6(\text{BO}_3)_3\text{Si}_6\text{O}_{18}(\text{OH})_4]$ with unit cell parameters $a = 15.973 \text{ \AA}$ and $c = 7.231 \text{ \AA}$ and $a = 15.941 \text{ \AA}$ and $c = 7.201 \text{ \AA}$, respectively. Figure 1 shows the projection of the tourmaline structure on the (0001) basal plane. Little is known about the colors and related impurities as well as dichroic effects.

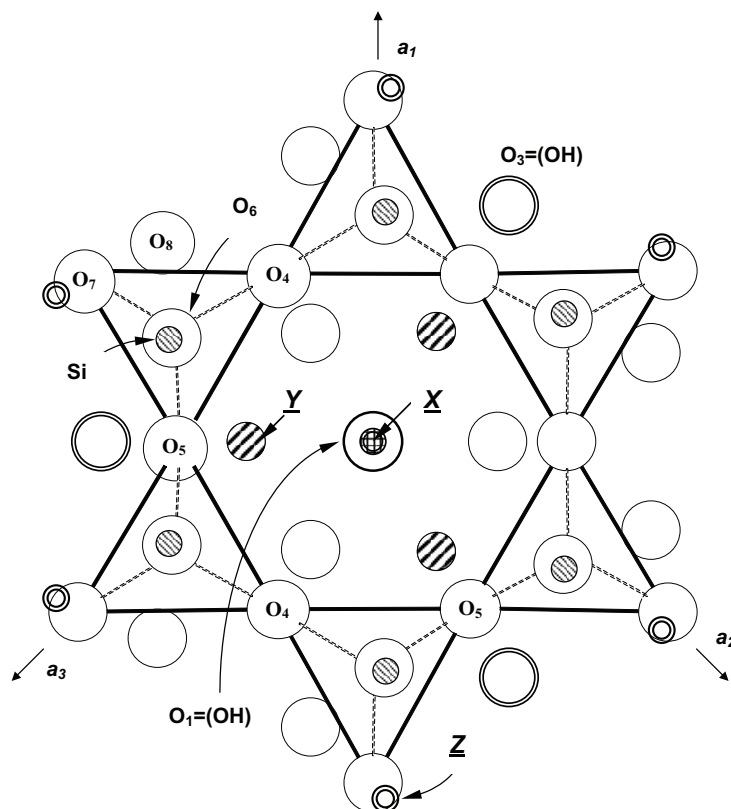


Figure 1- Tourmaline structure projected on the (0001) basal plane. The figure indicates the different cationic sites: X (center), 3 Y sites (within the rings) and 6 Z sites (border), as well as the two different O sites: 1 OH_1 site (center) with C_{3v} symmetry and 3 OH_3 sites (border) with C_s symmetry. The octahedral Z sites are smaller than the octahedral Y sites. Most substitutions of transition metal ions are found in the Y and Z sites. In dravite the X sites are in general occupied by Na^+ and Y sites by Mg^{2+} , whereas in uvite the X site by Ca^{2+} and Y sites by Mg^{2+} and Fe^{2+} . In dravite the Z sites may be substituted by trivalent cations as V, Cr, Fe or Al and in uvite by Mg, Fe and Al.

EXPERIMENTAL RESULTS

Different tourmalines from the uvite / dravite series were investigated in this work. They originate from the region of Serra das Éguas, Brumado, Bahia, Brazil, from the famous magnesite deposits and are found within metamorphic rocks (dolomite and quartzite) of about 450 m thickness. The uvite crystal specimens (~ 1 cm long)

are found in cavities grown on crystals of magnesite, quartz or dolomite and are considered of best quality worldwide. Associated minerals are: hematite, chlorite, rutile, topaz, kyanite, enstatite, apatite, barite and gypsum. In the majority the tourmalines from Brumado present prisms with short faces and rhomboedral terminations. The most common colors are reddish brown; the most valued colors

are green and red. Tourmalines with long prism faces are in general dravites with higher Na contents.

Natural green and red to brown dravite as well as green and red uvite, some with dichroic effect were investigated. The two dichroic uvite samples are pink for looking on *c*-axis and strong or weak green on *a* and *b* axes. All samples were analyzed by electron microprobe in the wavelength dispersive mode with operating potential of 15 kV and 10 nA on a JEOL JXA8900RL spectrometer. The results are listed in table 1 in wt. %. From the table it can be noticed that the analyzed samples are in

between the end member compositions of dravite and uvite (webmineral 2009). Main impurities are iron impurities in the red and orange dravite and red uvite. For the green samples vanadium impurities are detected. Chromium content was below the detection limit for all samples. Interesting to note is the high titanium and magnesium content and low Al content in the uvite samples. Titanium (Ti^{4+}) and magnesium (Mg^{2+}) may substitute for Al (Al^{3+}) in pairs (Fonseca-Zang et al. 2008). Highest concentration of titanium was found in the dichroic pink/green uvite sample.

Table 1: Electron microprobe analyses of seven samples of uvite / dravite series from Brumado district, Bahia, Brazil (in wt. %). Reference values are from webmineral (2009). B_2O_3 , H_2O and F have not been determined.

Sample	Color	Na ₂ O	CaO	MgO	Al ₂ O ₃	SiO ₂	FeO	TiO ₂	V ₂ O ₃
Dravite	Green	1,020	0,793	10,545	34,023	38,878	0,047	0,095	0,093
Dravite	Orange	0,844	0,566	10,808	32,491	37,434	1,533	0,025	0,017
Dravite	Red	1,689	0,705	10,944	31,076	36,081	2,501	0,126	0,015
Uvite	Pink/green s	0,406	4,607	14,436	27,380	36,985	0,062	0,461	0,854
Uvite	Pink/green w	0,369	4,732	14,541	27,632	37,089	0,091	0,621	0,303
Uvite	Green	0,625	4,040	14,024	28,299	37,440	0,070	0,417	0,601
Uvite	Red	0,336	4,835	14,036	25,388	36,104	4,119	0,427	0,008
Dravite	Ref.	3.23	0.00	12.61	31.19	37.60	0.00	0.00	0.00
Uvite	Ref.	0.80	4.33	9.35	26.27	37.16	0.00	0.00	0.00

Figure 2a shows the optical absorption spectra of the green dravite and uvite sample measured at room temperature. The optical absorption bands of green uvite and dravite samples are described by two broad absorption bands centered at 16400 cm^{-1} (607 nm) and 23140 cm^{-1} (432nm). The dichroic uvite samples show a color change from pale pink along *c* direction and weak to strong green on *a* and *b* directions. For the strong dichroic uvite sample the absorption valley is shifted from 505 nm to 487 nm when looking on *a* (*b*) axis and *c* axis, respectively. In the strong dichroic uvite sample photoluminescence spectra excited with Ar^+ ion laser at 514.5 nm reveal three sharp bands centered at 14532, 14635 and 14697 cm^{-1} or 688, 683 and 680 nm.

The intensity of the sharp bands depends strongly on the orientation.

The two broad strong absorption bands in the green samples and the sharp photoluminescence bands are explained by $^4A_{2g} \rightarrow ^4T_{1g}$ and $^4A_{2g} \rightarrow ^4T_{2g}$ and $^2E \rightarrow ^4A_{2g}$ transitions, respectively, of a transition metal ion in 3d³ configuration. The 10 *Dq* and Δ splitting parameters are 16400 cm^{-1} and 6740 cm^{-1} , respectively, similar to that of Cr^{3+} in emerald and euclase (Krambrock et al. 2008). Because Cr^{3+} , a strong coloring element in many minerals, was not observed by electron microprobe analysis we tentatively attribute these bands to V^{2+} (3d³) ions. However, other experiments are in progress to confirm these conclusions.

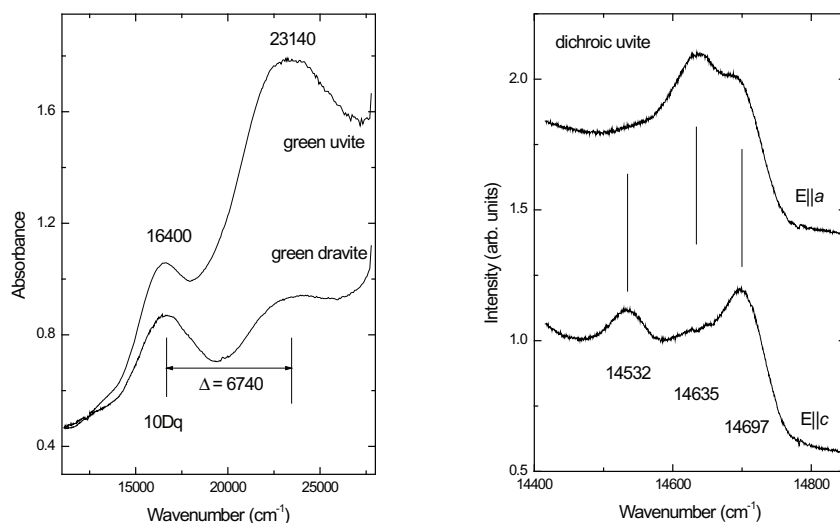


Figure 2 - (a) Optical absorption spectra of green uvite and dravite from Brumado district, Bahia, Brazil measured at room temperature and (b) photoluminescence spectra of dichroic pink/strong green uvite measured at room temperature.

Red uvite samples show a strong absorption band centered at 21275 cm^{-1} (464 nm) with a shoulder at 18345 cm^{-1} (544 nm). These bands are related to high Fe concentrations which are about 4.1 wt. % in the red uvite samples and about 2.5 wt. % in the dravite samples.

Polarized Raman scattering measurements show that all samples contain hydroxyl ions, OH^- that show preferential orientation along c direction, probably on O1 sites within the center of the channel formed by $\text{Si}_6\text{O}_{18}^{4-}$. From Raman measurements it seems that in the dichroic samples hydroxyl ions may be bond to some of the impurities. From electron microprobe no simple correlation between the dichroic effect and impurity ions could be established. The pink/weak green uvite sample shows the highest Ti impurity concentrations followed by

the pink/strong green sample, however, all uvite samples including the red one show high concentrations of Ti.

Figure 3 shows the EPR spectrum of the green uvite sample for the magnetic field along c axis measured at room temperature with microwave frequency of 9.39 GHz. The spectra are explained by vanadyl molecule, VO^{2+} , because of the following reasons: (i) the spectrum is easily measured at room temperature; (ii) the spectrum does not show electronic fine structure splitting, therefore $S = \frac{1}{2}$; and (iii) the spectrum shows 8 lines due to the hyperfine interaction with ^{51}V isotope ($I = 7/2$ with 99.75 % natural abundance). It should be noted that the intensities of the hyperfine lines are not equal due to spin relaxation mechanism which depends on the nuclear quantum number involved in the transition.

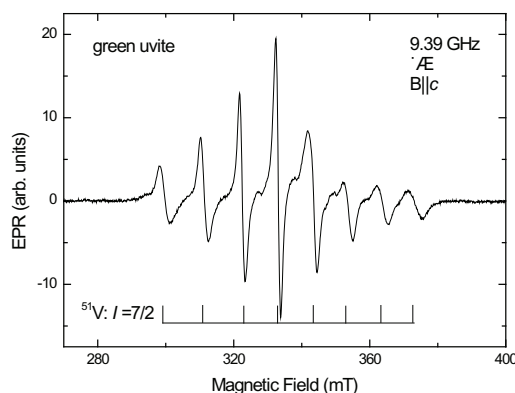


Figure 3 - EPR spectrum of green uvite sample measured at 300 K with microwave frequency of 9.39 GHz for $B||c$ showing 8 hyperfine-split lines. The spectrum is due to the vanadyl ion which has $S = 1/2$. The hyperfine splitting is due to the ^{51}V isotope ($I = 7/2$, 99.75 % natural abundance).

Detailed analysis of the EPR angular dependencies will be published elsewhere. For arbitrary magnetic field direction three magnetically inequivalent sites are observed which coincide when the field is along c axis. All green samples, uvite and dravite, show the same VO^{2+} EPR spectra. However, highest concentration of vanadyl is found in the strongly dichroic sample.

SUMMARY

The green color of tourmaline samples of uvite / dravite series from Brumado district, Bahia, Brazil, is due to a transition metal ion in the $3d^3$ electronic configuration. Because Cr^{3+} , a strong coloring ion, was not observed by the different experimental techniques, we tentatively attribute the color to the V^{2+} ion. Although V^{2+} is paramagnetic its EPR spectrum may be masked by the high intense EPR spectrum of the vanadyl ion, VO^{2+} . The explication of the strong

dichroic effect observed in some uvite samples is still an open question.

Acknowledgements

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