

Transparent bright blue Cu-bearing tourmalines from Paraiba, Brazil

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Abstract

Physical, crystal-chemical and absorption spectroscopical properties of blue tourmalines from a new occurrence in the State of Paraiba, Brazil, are described. Refractive indices, birefringence and specific gravity have been determined as $n_e = 1.615\text{--}1.620$, $n_o = 1.632\text{--}1.640$, $\Delta n = -0.017$ to -0.020 and $3.04\text{--}3.07\text{ g/cm}^3$. Microprobe analyses proved the samples to be elbaïtes, which are relatively Mn-rich and contain 2.1 wt. % CuO and 0.5 wt. % Bi₂O₃. Lattice constants are $a_o = 15.854(4)$ and $c_o = 7.102(1)$ Å. The blue colour is due to pleochroic absorption bands of Cu²⁺ and Mn³⁺ with maxima at 700 and 520 nm respectively.

KEYWORDS: copper, tourmaline, optical properties, chemical composition, crystal chemistry, absorption spectrum, Brazil.

Introduction

BRAZIL is well known as a producer of gem-quality tourmalines in various colours. Since the summer of 1987 fine quality transparent bright blue tourmalines have become available. The material has been produced in a new occurrence near the village Sao Jose da Batalha in the Municipio of Salgado in Paraiba State. This bright blue colour of the tourmalines has never been observed before in any specimen of this important mineral group. Besides Brazil, occurrences of blue tourmaline—the so-called indicolite—have been found in Namibia, Madagascar, USSR, USA, etc., but the material from these localities shows only light to dark blue or greenish-blue colours.

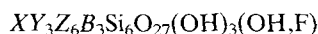
Optical data and specific gravity

Mineralogical data on refractive indices, birefringence and specific gravity have been determined as $n_e = 1.615\text{--}1.620$, $n_o = 1.632\text{--}1.640$, $\Delta n = -0.017$ to -0.020 and $3.04\text{--}3.07\text{ g/cm}^3$.

Crystal chemistry

Tourmaline is a complex boro-silicate with various isomorphous cation substitutions. The

general chemical formula is given by Deer *et al.* (1986):



X^{1+,2+} = Na, Ca etc. in irregular (3+6)-oxygen coordination.

Y^{2+,3+} = Mg, Fe, Mn, Li, Al, etc. in one-sided elongated octahedral oxygen coordination, producing brucite-like clusters, yielding together complexes of Y₃(OH)₄Si₆O₂₁ (with 3 oxygen atoms from BO₃-groups) with hexagonal rings of 6 SiO₄.

Z^{3+,2+} = Al, Mg, Fe³⁺, Cr etc. with 6 oxygen atoms in a distorted octahedral coordination.

The structural elements (SiO₄-rings and octahedral layers) are both shown in Fig. 1. Fig. 2 demonstrates a projection of the tourmaline structure parallel to [110].

The results of the microprobe analyses are compiled in Table 1, where the variation of six analyses and average contents are given. The average contents of B₂O₃, Li₂O, F and H₂O⁺ are added (from 15 elbaïte analyses published by Deer *et al.*, 1986). For the determination of the structural formula, these components are usually not detectable by microprobe, and there was not enough

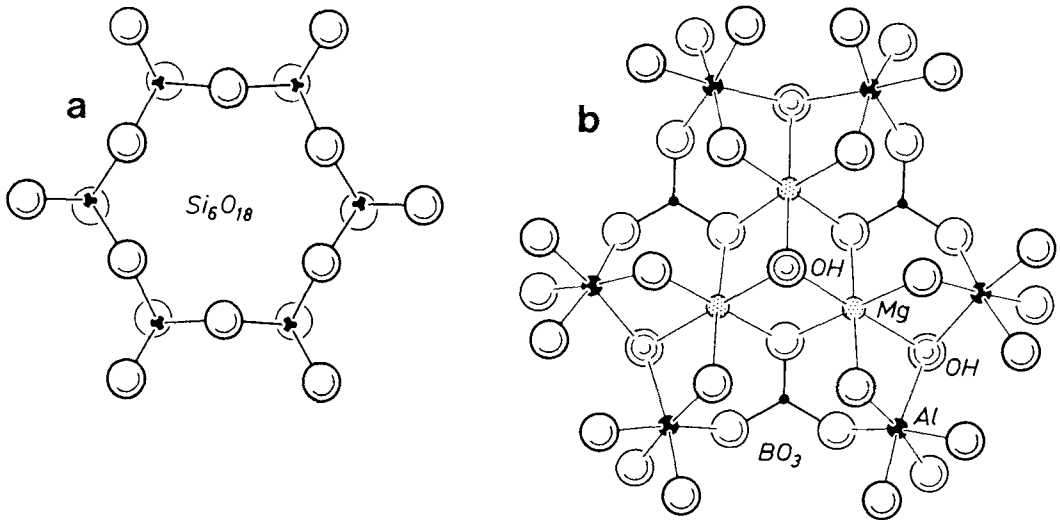


FIG. 1. The fundamental elements of the tourmaline structure (according to Weiner and Glas, 1985): (a) rings of 6 SiO_4 -tetrahedrons; (b) octahedron layers and BO_3 -regions.

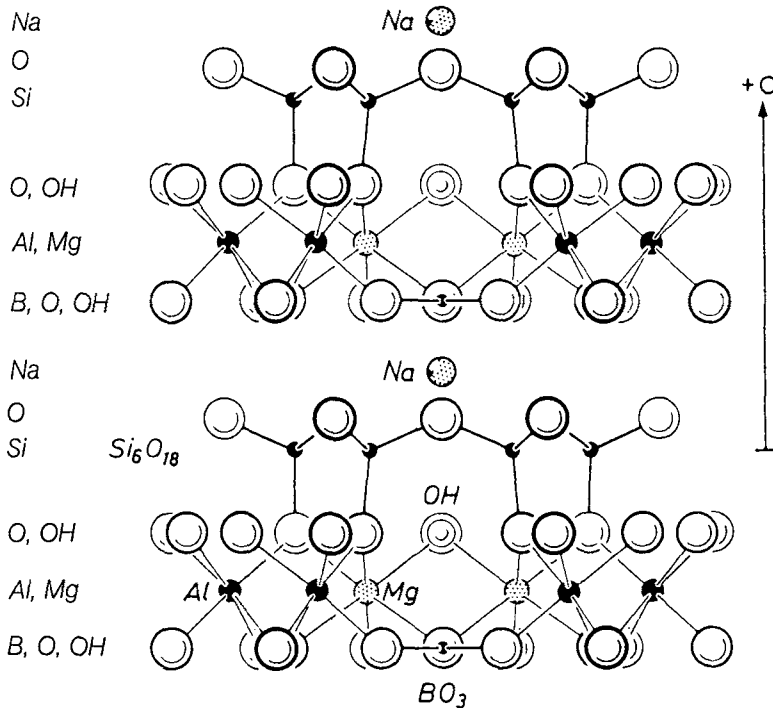


FIG. 2. Projection of the tourmaline structure parallel [110] (according to Weiner and Glas, 1985).

material available for other chemical analyses. In similar crystal-chemical conditions the B_2O_3 con-

tents as well as the sum of $(\text{H}_2\text{O}^+ + \text{F})$ scarcely show any variation, and the Li_2O contents should

Table 1. Electron-probe analyses of Cu-bearing tourmaline.

	Variation of 6 analyses in wt. %	Average values in wt. %	Number of atoms, calculated on the basis of 31 (O, OH, F)		
SiO ₂	37.04 - 37.21	37.12			
TiO ₂	---	---			
Al ₂ O ₃	39.50 - 40.50	40.20	Si	5.90	Si-position: 5.9 Si 0.1 Al
FeO	0.00 - 0.11	0.02			-0.1 charge
MgO	0.00 - 0.03	0.01	B	2.94	B-position: 2.94 B -0.18 charge
MnO	1.13 - 1.31	1.20	Al	6.0	Z-position: 6.00 Al ± 0.00 charge
CuO	2.11 - 2.21	2.14	Al	1.53	
CaO	0.36 - 0.40	0.37	Fe ²⁺	0.003	
Na ₂ O	2.16 - 2.25	2.20	Mg	0.002	
K ₂ O	0.01 - 0.04	0.03	Mn ²⁺	0.16	Y-position: 2.93 atoms + 0.41 charge
Cr ₂ O ₃	---	---	Cu ²⁺	0.26	
Bi ₂ O ₂	0.51 - 0.57	0.54	Li	0.97	
B ₂ O ₃ *		10.71	Ca	0.06	
Li ₂ O*		1.52	Na	0.68	X-position: 0.77 atoms -0.13 charge
F*		0.91	K	0.01	
H ₂ O**		3.06	Bi ³⁺	0.02	
			F	0.46	OH-position: 3.70 OH, F
			OH	3.24	
		100.03 wt. %			

*according to Deer, Howie and Zussman (1986)

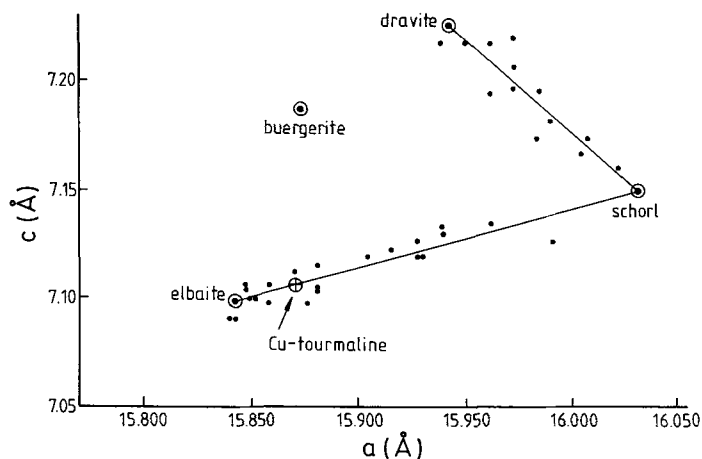


FIG. 3. Correlation diagram of the lattice constants according to Epprecht (1953) with the position of the Cu-bearing tourmaline from Paraiba, Brazil.

also correspond the true concentrations. So it is not surprising that the sum of the measured and averaged contents is close to 100 wt. %.

The chemical analyses prove the blue tourmaline to be an elbaites, having relatively high Mn contents, 2.1 wt. % CuO and 0.5 wt. % Bi₂O₃. The

Si₂O₂ and Al₂O₃ contents are in the known range for elbaites.

The number of atoms was calculated on the basis of 31 (O,OH,F) (see Table 1), which suggests that the occupation of the Si position is 5.9. This indicates a small analytical deficiency which

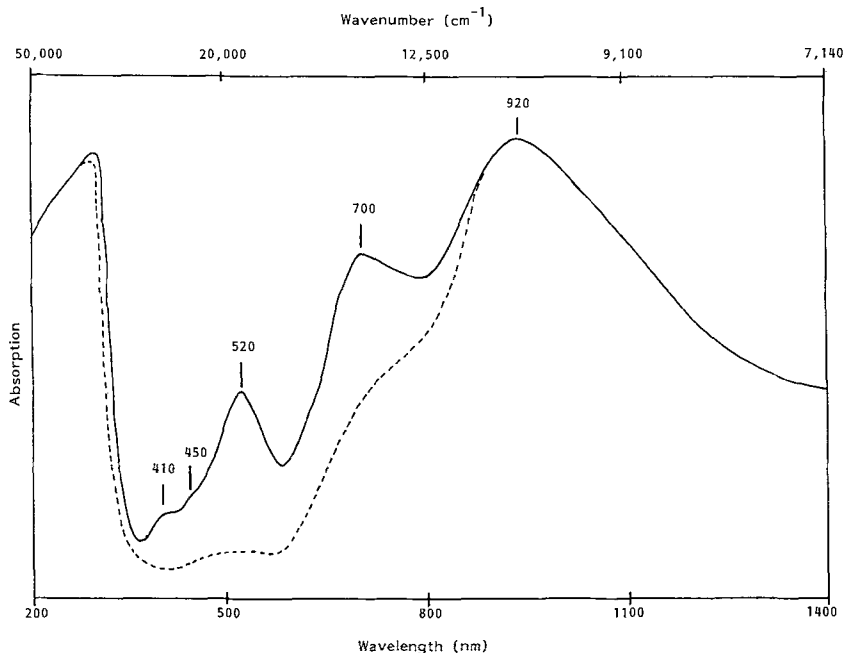


FIG. 4. Polarized absorption spectrum of the Cu-bearing blue tourmaline from Paraiba, Brazil (---E//c; —E⊥c).

is, however, completed here with 0.1 Al. The B position shows a similar effect with a lack of 0.06 B atoms in sufficiently close agreement with the theoretical formula. It is assumed, that all Z positions are occupied by Al, as is described for Al-rich elbaite (Donnay and Barton, 1972). The Y positions should be occupied by surplus Al as well as by Li and especially by Cu and Mn. Cu^{2+} and Mn^{3+} are supposed to show Jahn-Teller distortion of their oxygen coordination polyhedra, usually resulting in a more or less pronounced environment of four shorter and two longer bondings (Zemann, 1972). The crystal structure of Cu-free elbaite already shows a typical distortion of the Y-coordination octahedron favouring those cations with Jahn-Teller effects. A preliminary crystal refinement ($R_{\text{isotropic}} = 0.09$) of this Cu-tourmaline reveals the expected interatomic distance. Together with traces of Mg and Fe^{2+} , a lack of occupation of 0.17 atoms is indicated. Because of the relatively high content of Al, which is not compensated by Li, a charge surplus of 0.41 results. Similarities are found in the X position with Na, Ca, K and Bi showing a lack of 0.23 atoms and a charge deficiency of -0.13 . Bi^{3+} is expected to concentrate on the X position because of its large ionic radius. The mean interatomic distance for the X position ($X\text{-O} = 2.661 \text{ \AA}$) is

slightly less than a normal elbaite ($X\text{-O} = 2.671 \text{ \AA}$). This is probably due to the incorporation of Bi^{3+} . The balance of the formal charges at different cation positions yield a complete compensation.

X-ray diffraction data

Structural research was carried out on a single crystal of the same material. The data will be refined and Fourier syntheses will be carried out to locate the heavy metal positions. The lattice constants have been determined as $a_0 = 15.854(4)$ and $c_0 = 7.102(1) \text{ \AA}$, which is also typical for elbaite. A correlation with the a_0/c_0 diagram for tourmalines in Fig. 3 according to Epprecht (1953) shows that the presence of Mn, Cu (and Bi) affects the lattice constants in the same way.

Absorption spectra

Iron is usually described as the main cause of colour in blue tourmalines. According to Faye *et al.* (1968, 1974) and Smith (1978a, b), Fe^{2+} as well as $\text{Fe}^{2+}/\text{Fe}^{3+}$ -charge-transfer bands are present in the absorption spectrum. The Fe^{2+} -absorption band is located in the near infra-red region and for that reason it does not influence the colour. Therefore, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ -charge-transfer

process is responsible for the blue colour in the tourmaline, which causes a pleochroic absorption band with maximum at 555 nm with $E \perp c \gg E // c$. Deer *et al.* (1986) mention Mn as a colouring element in blue tourmaline in addition to Fe. Carobbi and Pieruccini (1947) ascribe the colour to Cu, but without publishing spectroscopical data.

The blue tourmalines from Paraiba possess quite different absorption spectra. A strong, broad absorption band is located in the near infra-red and red region of the absorption spectrum (Fig. 4). The band splits into two maxima at 920 and 700 nm. The 700 nm band is pleochroic with $E \perp c \gg E // c$. A second pleochroic absorption band is in the green region with the maximum at 520 nm with $E \perp c \gg E // c$. According to the absorption of various copper (II) minerals (Lehmann, 1978; Marfunin, 1979) the broad band in the near infra-red and red region is caused by a ${}^2E_g \rightarrow {}^2T_{2g}$ transition of Cu^{2+} in distorted octahedral sites and split by the Jahn-Teller effect. The 520 nm band is due to a ${}^4E \rightarrow {}^4A^1$ transition of octahedrally coordinated Mn^{3+} (Manning, 1969). The two weak bands with maxima at 450 and 410 nm are also caused by Mn^{3+} . Consequently, the bright blue colour in the *o* direction ($E \perp c$) is caused by the transmission of light in the range between the absorption edge at 300 nm and the 520 nm band. In the *e* direction ($E // c$) the 520 nm band is weakly developed. Therefore, the green region of the spectrum is transmitted and a greenish-blue colour is observed.

Acknowledgements

The authors thank Dr Malley and Dr Schulz-Dobrick for the microprobe analyses.

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[Manuscript received 4 January 1990; revised 10 April 1990]