Revision 1. Crystal chemistry of Cu-bearing tourmalines

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Abstract

The crystal structures of two elbaites from the Paraiba deposit with copper contents of 3.51 and 1.61 wt. % CuO (a=15.881(1), 15.840(3); c=7.112(1), 7.1028(9), respectively), as well as a synthetic Cu-bearing olenite with CuO content 8.39 wt.% (a=15.840(4), c=7.091(1)) have been refined to R-indices of 2.2, 3.1 and 4.1 % using X-ray single-crystal method. On the basis of original and published data (for six structures) the crystal-chemical relationships of copper-bearing tourmalines were analyzed. It was shown that copper cations and cations of other 3d elements (Mn, Zn, Fe) almost occupy only Y site. Such ordered distribution results in a change in size of the Y-octahedra. There is an inverse correlation between the content of 3d elements (firstly Cu^{2+} cations) and Al^{3+} cations in the Y-octahedron and also between the value of <Y-O> and the content of Al^{3+} cations in the Y site. The direct correlation between values of <Y-O>-distance in the structures of Cu-bearing elbaites and the parameters (a, c) of the unit cell have been found. Distortions of polyhedra in the structures of Cu-bearing elbaites are similar, and significantly higher than those present in the structure of the synthetic Cu- bearing olenite.

Keywords: Cu-rich elbaite, Cu-bearing olenite, Paraiba, crystal chemistry, tourmaline, X-ray structure refinement

Introduction

Copper ions in a tourmaline were first found (in the ppm range) in the middle of the 20th century in occurrences in Tanganyika and South-West England (Bassett et al., 1953; Power et al., 1968). The first traces of tourmaline with a concentration of CuO up to 2 wt. % were found in 1980s in the Batalha occurrence, state of Paraíba, northern Brazil (Koivula and Kammerling, 1989; Bank et al., 1990). Tourmalines found in this deposit were sapphire-blue, neon-blue, indigo, or bluish-violet in color, and were valuable jewelry materials. The price for some samples was higher than $ 20.000/ct. At the present time, copper-bearing elbaites are also found in Namibia: the Khan pegmatite close to Rossing (Haughton et al., 1969); Nigeria: the Edeko mine near Ilorin in the state of Ojo (Zang and Da Fonseca-Zang, 2001) and in the occurrence situated near Alto Ligonha, Mozambique (Abduriyim et al., 2006; Laurs et al. 2008).

Synthetic copper-bearing tourmalines were first produced by I.E. Voskresenskaya at the Institute of Crystallography of the USSR Academy of Sciences (AS) (Voskresenskaya, 1968). The largest tourmaline crystals, which reached a size of 1–2 mm, with up to 14 wt. % CuO, were synthesized at the Institute of Mineralogy and Petrography, Siberian Branch (SB) of Academy of Sciences, Novosibirsk (Lebedev et al., 1988).

Over the past thirty years, Cu bearing tourmalines have been the subject of several dozen articles, most of which have been related to their unique jewelry properties, the features of their chemical composition, and geological conditions of their occurrence (Koivula et al., 1989; Shigley et al., 2001; Wilson, 2002; Abduriyim et al., 2006; Breeding et al., 2007; Furuya & Furuya, 2007, etc.).

The crystal chemistry of copper-bearing tourmaline has received less attention. To date, there exists data on just three refinements of tourmaline crystal structures, which contain less than 1 wt. % CuO (MacDonald & Hawthorne, 1995; Ertl et al., 2002).

The aim of our work was to define the crystal structures of three tourmalines with different copper contents, and analyze the crystal chemistry of copper bearing tourmalines on the basis of original and published data.

Materials and methods

Two natural and one synthetic tourmaline with different copper contents were chosen for research (Table 1).

Synthetic tourmaline (Sample 1) was grown in the Institute of Mineralogy and Petrography AS, in Novosibirsk. Synthesis was conducted by the hydrothermal method at a temperature of 650 °C and a pressure of 1.5 kbar in solutions 0.05 (H, Na) - 0.05 H_3BO_3-0.9 H_20 (mole fraction). Mixture consisting of powdered $A1_20_3$, α-quartz (fraction 1-2 mm) and copper oxide was used. The Al/Si/Cu mole ratio was about 1/1/0.3, the solution/solid molar ratio about 25. The tourmalines were grown on seed plates of natural tourmaline (size 5x2x1 mm, the composition of the seed is close to pure elbaite), placed between the silica source (above) and alumina source (below), in sealed gold tubes (V= 150 cm^3). The charged gold tube and pure water as a pressure medium were filled and enclosed in a Bridgman type steel vessel with capacity of 200 cm^3 and then heated during 30 days. Total variations and uncertainty were estimated as ±10 ºC in temperature and ±0.1 kbar in pressure (Taran et al., 1993, Lebedev et al., 1988).

Both of the natural Cu-bearing elbaites studied (Samples 2 and 3) were found in the State of Paraiba, Brazil. The Paraíba tourmalines occur in northeastern Brazil in four deposits of highly fractionated and zoned granitic pegmatites of the Borborema Pegmatitic Province. “The Borborema Pegmatitic Province covers an area of 150×75 km^2 in the eastern part of the NNE-striking Seridó

Foldbelt in the Northern Domain of the Borborema Tectonic Province. Paraíba tourmaline bearing pegmatites are rich in spodumene or lepidolite, and are emplaced in iron-poor quartzites or metaconglomerates of the Neoproterozoic Equador Formation. The Paraíba tourmaline occurs at the transition between the albite-rich inner intermediate zone and the quartz core of the pegmatites, in primary wedge-shaped crystals of near-end-member color-zoned elbaite, arranged in fan-like, radial or comb-textured groups of crystals. This color-zoned tourmaline most commonly forms the intermediate growth-zone of color-zoned elbaite crystals having a pink to red core and a green to dark green rind" (Beurlen H. et al., 2011)

Chemical studies

The elemental compositions of all single crystals used for the refinement of crystal structure were analyzed with a wavelength-dispersive Link AN-10000 using an automated CamScan 4-DV electron microprobe at the V.G. Khlopin Radium Institute (analyst Yu.L. Kretser). The conditions of the experiment were: accelerating voltage - 20 kV, beam current- 4 nA, data collection time - 60 sec (excluding dead time). The following standards for Kα X-ray lines were used: Na - albite, K - orthoclase, Ca – diopside, Si - almandine, Al - kyanite, Ti – rutile, Fe – iron, Mn - manganese; Zn - zinc; Mg – augite, Cu-copper. The fluorine content was analyzed with a wavelength-dispersive INCA Energy 450 using an automated CamScan MX2500 electron microprobe at the VSEGEI (analyst A.V. Antonov). Each grain was analyzed at a minimum of 15 points to obtain good counting statistics.

Calculations of preliminary crystal-chemical formulas on the basis of microprobe analysis data were carried out on 15 cations (Zolotarev et al., 2007). In Samples 2 and 3, Li being estimated by iteration as 49 minus ($O_{18}(BO_3)_3V_3W$), suggesting that the V and W positions were only populated by monovalent anions (OH, F) (Burns et al. 1994, Henry & Dutrow 1996). The copper valence was determined by the Electron paramagnetic resonance (EPR) method. The EPR spectra were recorded on a Radiopan SE/X 2543 spectrometer, with a working frequency of about 9.3 GHz. To determine the g-factor and spin amount, a powdered sample of 2,2'-diphenyl-1-picrylhydrazyl (DPPH) with g = 2.0036 was used.

Crystal structure refinement

X-ray data collection was carried out with X-ray single-crystal automatic diffractometers (Table 2) in one-sixth of the reciprocal space (Samples 1 and 3) and a full sphere (Sample 2) using MoKα radiation ($\lambda = 0.71073$ Å).

The intensities were corrected for Lorentz and polarization factors. The refinement of crystal structures was carried out in a space group typical for tourmalines, R3m, on the basis of unequivalent reflections with $F>4\sigma F$, alternating least squares (taking into account the anisotropy of the displacement parameters of atoms), and analysis of difference Fourier syntheses by means of the CSD software package (Akselrud et al., 1989). The coordinates of atoms in the structure of aluminum-rich elbaite (Gorskaya et

al., 1982) were used as initial conditions. Aluminum atoms were placed at Y and Z octahedral sites, and a sodium atom was positioned at the alkali cation site. X-ray scattering at these sites was actually determined by refining the occupancies on the basis of the small-angle reflections ($Sin\theta/\lambda \leq 0.5$) that are slightly affected by uncertainties in temperature factors. The absorption correction was made with program DIFABS (Walker and Stuart, 1983), after refinement of the anisotropy displacement parameters of the atoms.

After the crystal structure refinement, a procedure of cation distribution optimization over crystallographic sites was performed by minimizing the differences between the results of chemical analysis, the scattering of the cation sites, bond lengths and valence balance (Wright, 2000). The optimized formula minimizes the differences between the formula obtained by chemical analysis and that obtained by structure refinement. The coefficients in the final crystal-chemical formula were obtained from chemical analysis, site scattering, and bond-lengths. The final lithium contents of Samples 2 and 3 were calculated from site scattering, site bond-lengths, and balance of charges, with the use of flame-photometry data.

Chemical deformations

The chemical deformations of Cu-bearing tourmaline structures studied and described in the literature were analyzed on the basis of variations of the unit cell constants and the sizes of the polyhedra. Polyhedra distortions were estimated using equations (Ertl et al., 2002):

$$\Delta X = \frac{1}{9}\sum_{i=1}^{9}\left[\frac{(X-O)i - \langle X-O\rangle}{\langle X-O\rangle}\right]^2; \quad \Delta_{oct}Z = \frac{1}{6}\sum_{i=1}^{6}\left[\frac{(Z-O)i - \langle Z-O\rangle}{\langle Z-O\rangle}\right]^2;$$

$$\Delta_{oct}Y = \frac{1}{6}\sum_{i=1}^{6}\left[\frac{(Y-O)i - \langle Y-O\rangle}{\langle Y-O\rangle}\right]^2; \quad \Delta T = \frac{1}{4}\sum_{i=1}^{4}\left[\frac{(T-O)i - \langle T-O\rangle}{\langle T-O\rangle}\right]^2.$$

Results

Chemical composition

The copper content of the investigated tourmalines varied from 0.17 to 1.08 apfu (from 1.46 to 8.39 wt. % CuO, respectively, Table 3), which is much greater than the content of the element in previously structure studied samples (MacDonald & Hawthorne, 1995; Ertl et al., 2002). The elemental composition of the natural tourmalines investigated (Samples 2 and 3) is typical for elbaites from the Paraiba occurrence, Brazil (Table 4) and is much more diversified than the synthetic tourmaline (Sample 1). For all samples studied, the main cation in the X-site was Na^+. In natural samples, a trace of calcium and significant part of vacancy was also found in that site. In addition, in all cases the content of Al^{3+} was greater than 6 apfu, which indicated this cation was not only present in Z-octahedra. The content of Al^{3+} cations in the synthetic tourmaline reaches 7.92 apfu, which indicates it is as a synthetic analog of olenite according to the tourmaline nomenclature (Henry et al., 2011). In the composition of elbaites, besides Cu

cations, other 3d element cations (Mn, Zn and Fe) were also found at trace levels (from 0.03 to 0.27 apfu). Another important feature of the studied tourmalines' chemical composition was a low silica content (which also evident in variation of the Si / Al ratio). In the synthetic sample the Si content equals 5.26 apfu, compared to natural samples, where it varies from 5.87 to 5.93 apfu (Table 3). Both natural tourmalines contain relatively low amounts of F (Table 3).

EPR-data

The central EPR spectrum of the synthetic tourmaline (Sample 1) consisted of four poorly resolved lines of hyperfine structure at g_c =2.021, with splitting between the two central lines similar to 9.3 mT, the line width between inflexion points ΔH_{pp} ~ 7 mT. In previous work (Bank & Henn, 1990; Rossman et al. 1991) it has been shown that such spectra are related to the Cu^{2+} ion, and the magnetic parameters (principal values and principal directions of **g** and **A** matrices) of the EPR spectrum were determined to be due to narrow EPR lines ($\Delta H_{pp} \approx 1.5$ mT) observed in African elbaite with a low copper content. The magnetic parameters suggest that Cu^{2+} ions enter elongated Y-octahedra (Mashkovtsev et al., 2006).

X-ray single crystal analysis data

The results of X-ray studies (Tables 5-7) confirmed that the X-site cation of the investigated tourmalines was Na^{+},which reached 0.86 apfu (Sample 1). The content of Ca^{2+}ions in the natural samples 2 and 3 was ≤0.1 apfu. The X site was partly vacant in all the investigated samples.

In the synthetic tourmaline (Sample 1) the experimental value <Y-O> =1.978(6) Å within the standard deviation matched the calculated value of <Y-O> = 1.972 Å for the content of the Y site ($Al_{0.62}Cu^{2+}_{0.38}$), obtained as a result of site scattering. The size of that octahedron is smaller in comparison to the size of the octahedron (1.992 Å) in the structure of Fe-bearing olenite $(Na_{0.54}Ca_{0.14}K_{0.01}\square_{0.31})(Al_{2.15}Fe^{2+}_{0.78}Mn^{2+}_{0.06}Ti^{4+}_{0.01})(Al_{5.90}Mg_{0.10})(Si_{5.60}Al_{0.40})B_3O_{27}(OH)_{2.49}O_{0.51}]$ $(O_{0.99}F_{0.01})$ (Cempirek et al., 2006). This fact is associated with the presence of large Fe^{2+} cations in the Y-octahedron. The mean bond distance of Z octahedron <*Z*–O> is 1.907(5) Å. Taking into account the site scattering of Z site we suggest the Cu-cation share less than ~0.1 apfu. It should be mentioned that such a concentration of copper in the Z position is close to the within the possible definition of this method. The length of the bond (Y-O3) was 2.123 Å, which is significantly longer than (Y-W1(O1)) = 1.958 Å, and confirmed that the O3 site is occupied by $(OH)^{-}$ and the W1(O1) site by oxygen. This is in good agreement with the assumption of Hawthorne (2002): "about occupancies O3 and O1 sites in olenite as $^{O3}[O_2(OH)]^{O1}(O)$, because the strength of the hydrogen bond involving OH at O3 is stronger than the strength of the hydrogen bond involving OH at the O1 site".

In the natural elbaites studied (Samples 2 and 3), in addition to Cu cations (atomic number 29), Mn cations (atomic number 25) were also found (Table 3). In Sample 3 cations of Zn (atomic number 30) and Fe (atomic number 26) were also present. These 3d-elements (Cu, Zn, Mn, Fe) are similar not

only in their scattering power, but also in size: $r_{Cu+2} \cong r_{Zn+2}$ (0.73, 0.74 Å, respectively), $r_{Fe+2} \cong r_{Mn+3}$ (0.78, 0.81 Å, respectively) (Bosi et al., 2007). The results of defining the scattering sites and analyzing the bond lengths (Tables 5 and 6) showed an admixture of heavy elements (compared to Al and Li) in both octahedral sites (in proportions similar to those for the synthetic olenit). Taking into account that Mn^{2+} cations normally occupy the Y site (according to structural studies of Mn-containing tourmaline (Burns et al., 1994; Ertl et al., 2003)), we can assume these cations also occupy only the Y site in studied natural tourmalines (Table 5). The experimental value of <Y-O> = 2.024(6) Å for the crystal structure of Sample 2 is in good agreement with the calculated value of <Y-O> = 2.022 Å for the composition of the Y site ($Al_{0.50}Li_{0.25}[Cu,Zn]_{0.18}Mn_{0.06}Fe_{0.01}$) obtained from the scattering power of the site. The composition of that site, which is occupied by the large cations Cu^{2+}, Zn^{2+}, and Li^{+}, as well as even larger Mn^{2+} cations, significantly increases the size of this octahedron, compared to the size of the Y-octahedron (1.978 Å) in the structure of the synthetic Cu-containing tourmaline (Sample 1). It is comparable in size to the Y-octahedron (2.022 Å) in the structure of elbaite with Y site composition ($Li_{0.52}Al_{0.48}$) (Rozhdestvenskaya et al., 2005). In Sample 3 the experimental value for the Y-octahedron (<Y-O> = 1.999(4) Å) within one esd is also in good agreement with the calculated value of <Y-O> = 2.000 Å for the composition of the Y site ($Al_{0.54}Li_{0.36}Mn_{0.10}$), obtained from the scattering power. A significant portion of this site (0.54 atoms) is occupied by trivalent Al^{3+} cations. Another 0.46 atoms per site are occupied by the cations Li^{+} or Mn^{2+}, which result to a decrease in the size of this octahedron compared to the Y-octahedron in the structure of elbaite (2.022 Å) (Rozhdestvenskaya et al., 2005). In both elbaites the real bond length <Z-O> = 1.906(2) Å, taking into account the site scattering of Z site, which corresponds to the following composition$Al_{0.95}[Cu,Zn]_{0.05}$ and $Al_{0.97}Cu_{0.03}$ for Samples 2 and 3, respectively. Such a slight increase of the <Z-O>-distance (by 1.907(5) Å) which has already been found earlier in copper-free elbaite (Rozhdestvenskaya et al., 2005) can be explained by a positive correlation between <X-O> and <Z-O> distances due to inductive effects in the structure (Ertl & Tillmanns, 2012). Overall, analysis of the cations distribution in natural copper-containing tourmalines (Samples 2 and 3) showed that aluminum is a major element in the *Y*- and *Z*-octahedra.

In two case, sizes of tetrahedra (<T-O> = 1.625, 1.621 Å for samples 1 and 2) exceed the distance characteristic of a tetrahedron, which is fully occupied by Si (~1.620 Å, MacDonald and Hawthorne 1995; Hawthorne 1996; Ertl et al. 2010), which points to entry of a larger cation. It should be Al^{3+} cations based on the data of chemical analysis. The site scattering data shows that this site is occupied by lighter cation (Al or B).If we assume the absence of boron cations, the percentage of aluminum in the T-position will be 0.60, 0.32, 0.30 apfu for sample 1, 2, 3 respectively. The total assigned Al content is consistent with the chemical data (Table 3). Thus we assume that the amount of $^{[4]}B$ in the investigated tourmalines is

relatively small, if present. Accurate data would have been necessary to estimate the T-site occupation in detail.

The average bond length in the boron triangle of all the investigated samples is almost the same (<B-O> = 1.375, 1.373 Å), suggesting that the *B*-site is occupied by boron (<B-O> = 1.376, Bosi et al., 2004.)

As is known, the tendency for orderly distribution of OH^- and F^- ions leads the W1(O1) site to split in the elbaite structure (Rozhdestvenskaya et al., 2005). In the crystal structures of the natural elbaites investigated (Samples 2 and 3), the W1(O1) site is also split into two partially occupied sites, namely, the W1 threefold site and the W2 ninefold site (Table 5). Each atom (vacancy) at the W1 site (on the threefold axis) is surrounded by three corresponding structural units at the W2 sites. The total occupancy of this grouping is 0.94 and 1.00 for Samples 2 and 3, respectively. As a consequence, the following are the shortest forbidden distances appearing in the structures: W1–W2 = 0.50(3) and 0.44(3) Å and W2–W2 =0.85(5) and 0.72(4) Å (for Samples 2 and 3, respectively). In both structures, the Y–W2 bond lengths are approximately equal to 1.70–1.74 Å (Table 6). This suggests that the W2 sites are statistically occupied by fluorine anions. The above assumption is confirmed by the fact that the fluorine contents determined by chemical analysis of Samples 2 and 3 (0.24 and 0.28 apfu) are close to those calculated from the occupancies of the W2 site (0.16 and 0.18 apfu).

The final crystal-chemical formulas of the tourmalines examined (Table 7) are in good agreement with those calculated from the chemical analysis data (Table 3).

Crystal chemistry peculiarities of copper bearing tourmalines

The copper content of the Cu-bearing tourmalines studied and described in the literature (Table 7) ranges from 0.38 to 8.39 wt.% CuO (0.05 to 1.26 apfu). All natural Cu-bearing elbaites (No 1–6) also contain cations of other 3d elements (Zn, Mn and Fe). Copper and other 3d elements cations almost only occupy Y octahedron. Their content in it varies from 0.13 to 1.14 apfu. Such ordering distribution of copper cations is well explained by the Goldschmidt rule, characterizing the closeness of the ionic radii of elements that replace each other (Goldschmidt, 1933). In the case of ideal elbaite, the differences between the ionic radii of copper cations, and cations occupying Y- octahedra ($Al_{0.5}Li_{0.5}$) and Z-octahedra ($Al_{1.0}$), is 11 and 25 %, respectively. The content of 3d elements in the Z site, as estimated by crystal structure refinement, is very small (0.12 – 0.19 apfu), and is independent of the overall copper content.

In a synthetic olenite (No 1, Table 7), compensation for charge imbalances arising while exchanging a portion of the Al^{3+} for Cu^{2+} cations is provided by the appearance of vacancies in the X-site, and the replacement of oxygen atoms in the V-site for $(OH)^-$ anions according to the equation:

$^{X}Na^{+}+^{Y,Z}Al^{3+}+2^{V}O^{2-} \leftarrow {}^{X}\square+^{Y,Z}Cu^{2+}+2^{V}OH^{-}$. In the structures of the elbaites analyzed, as the copper content rises, then the Al and Li content in the Y site, and the number of vacancies in the X-site, both decrease. Al^{3+} cations partly redistribute from octahedral to tetrahedral sites. The charge balance is retained according to the equation: $^{X}\square+^{T}Si^{4+}+^{Y}Li^{+}+^{Y,Z}Al^{3+} \leftarrow {}^{X}Na^{+}+^{T}Al^{3+}+2^{Y,Z}Cu^{2+}$. As the content of Cu^{2+} cations increases, the fluorine content also decreases insignificantly. There is an inverse correlation between the content of 3d elements and Al^{3+} cations in the Y-octahedron (r = -0.94, P (probability) =0.98, Fig. 1a). The existence of this inverse correlation between copper content and Al^{3+} cations in the Y site (r = -0.95, P =0.99, Fig. 1b) is well explained by preferential localization of Cu^{2+} cations in this site.

The size of the Y-octahedron is the most variable parameter in the structure of copper-bearing tourmalines: the range of <Y-O> varied from 1.987 to 2.024 Å (Table 8). This is the result of significant variations in their compositions (Table 6). For elbaites (No 2–6, Tables 7, 8), there is a direct correlation between the average size of the Y-octahedron <Y-O> and overall content of Cu^{2+} cations (r = 0.99, P = 0.99; Fig 2a,) as well as the content of 3d elements in the Y site (r = 0.98, P = 0.99). There is an inverse correlation (r = -0.98, P = 0.99; Fig. 2b) between the value of <Y-O> and the content of Al^{3+} cations in the Y site. This is well explained by the earlier mentioned correlation between the content of Y site occupying elements for all the investigated tourmalines. Values for the size of <Y-O> in the structures mentioned (2.022, 1.978 Å, respectively) are well explained by the ratio between Al^{3+} / another large cation (Li^{+} or Cu^{2+}) (Table 7).

The variations in the average size of the Z-octahedron (<Z-O> = 1.903-1.907 Å) are insignificant and this is due to the fact that they are characterized by almost unchangeable content (mostly occupied by Al).

There is a direct correlation between values of <Y-O>-distance in the structures of Cu-bearing elbaites (No 2-7, Table 7, 8) and the parameters of the unit cell (Fig. 3). Such a dependency has already been mentioned for elbaite (Bosi et al., 2005).

Values of the <T-O> -distance in copper-bearing tourmalines (No 1– 6, Tables 7, 8) vary from 1.616 to 1.625Å. As was shown before the increasing <T-O> -distance in some cases (No 1-3, Table 8) can be explained by the entry of Al^{3+} cations (by 0.60 apfu). Ertl et al. (2002) suggested that the T sites of a Cu-bearing elbaite (No 4, Table 8) partially occupied by B cations, (0.26 apfu), which should lead to reduction in the size of the tetrahedron.

The values of the bond-angle polyhedra distortions in Cu-bearing tourmalines increase according to: T site < Z site < Y site < X site. This is typical for the entire tourmaline group, and well explained by the polyhedral coordination number and its mixed occupation by cations of different sizes (Ertl et al., 2002). The distortions ΔX and $\Delta_{oct} Y$ in structures of F-bearing elbaites (No 2-7, Table 7, 8) are close to each other, and significantly higher than in the structure of the Cu-bearing synthetic olenite (No 1, Tables

7, 8). These are also well matched with earlier published data (Ertl et al., 2002, Frank-Kamenetskaya & Rozhdestvenskaya, 2004). Values of $\Delta_{oct}Z$ distortion for all the investigated tourmalines are almost the same, which is well explained by the similarity in chemical composition of the Z-octahedra. The value of T-site distortion is almost insignificant, and reaches its maximum in copper-bearing olenite, where it can be explained by the maximum Al cation content in the T-site.

Conclusion

The crystal-chemical regularities of tourmalines with copper admixture ranging from 0.38 to 8.39 wt.% CuO were analyzed. The maximum value of copper content in natural Cu-bearing elbaites (Paraiba occurrence) was 3.59 wt. % CuO, which can be related to the specific conditions of mineral formation.

Copper and other 3d element cations (Mn, Zn, Fe) almost only occupy the Y octahedron. Such ordering distribution of copper cations is well explained by the Goldschmidt rule.

The entry of copper and other 3d elements increases the parameters of the tourmaline unit cell and the sizes of Y-octahedra As the site scattering and size of Z octahedron is almost similar, the difference between the size of the Y and Z octahedra is increasing with increasing Cu content. Our results indicate that very small amounts of Cu also occupy the Z site (<4%). However, for a final proof of these refinement results spectroscopic investigations would be necessary.

Values of polyhedron distortion in structures of copper-bearing elbaite are close to each other, but significantly higher than in the structure of copper-bearing olenite.

Additional studies of synthetic Cu-rich tourmaline, especially focusing on the tetrahedral positions are now in progress.

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Table 1. Characteristics of examined tourmalines

Smp.	*Origin/Occurrence*	*Crystal description*
1	Synthetic	Fragments of the crystal, size up to 0.6 mm, colored blue.
2	Paraiba, Brasil	Elongated, up to 1 cm zone-colored crystals, the internal parts colored blue, border – purple.
3		

Table 2. Parameters of X-ray data collection and unit cell parameters of the examined tourmalines

Characteristic	*Samples*		
	1	*2*	*3*
Size smp. (mm)	0.10*0.10*0.10	0.10*0.05*0.10	0.10*0.15*0.10
Diffractometer	Nicolett R3	Bruker APEX2	Nicolett R3
Scan mode, detector	ω- scan mode, V = 2-30 degree /min, scintillation detector	CCD camera	ω- scan mode, V = 2-30 degree /min, scintillation detector
$2\theta_{max}$	80.00°	71.80°	80.00°
Measured reflections $I>2\sigma_I$	2289	9289	3201
$F^{un.}_{obs} > 4.0\sigma_F$	1153	890	1152
R_{sig}/ R_{eq}	0.039/0.045	0.005/ 0.038	0.029/ 0.034
R/ R_w	0.041/0.045	0.022/ 0.025	0.031/ 0.033
GOF	0.91	0.96	1.03
a, Å	15.840(4)	15.881(1)	15.840(3)
c, Å	7.091(1)	7.112(1)	7.1028(9)

Note. Here and in Tables 3–5 the sample numbers are those of Table 1

Table 3. Chemical compositions of examined tourmalines (wt. %) and coefficients in the formula $X_{0-1}Y_3Z_6\ (T_6O_{18})(BO_3)_3V_3W$

Component	Sample		
	1	*2*	*3*
SiO_2	30.84	36.65	37.68
Al_2O_3	43.10	37.27	41.32
CuO	8.39	3.59	1.46
FeO	0.00	0.26	0.00
ZnO	0.00	2.30	0.00
Mn_2O_3	0.00	1.38	1.11
Li_2O*	0.00	1.62	1.97
CaO	0.00	0.16	0.52
Na_2O	3.22	2.79	1.99
F	0.00	0.43	0.49
B_2O_3 (calc)	12.71	10.75	11.15
H_2O (calc)	0.47	3.50	3.61
Sum	98.73	100.69	101.29

Site	Component	Sample		
		1	*2*	*3*
T	Si	5.26	5.93	5.87
	Al	0.74	0.07	0.13
Sum		6.00	6.00	6.00
Y + Z	Al	7.92	7.03	7.46
	Cu	1.08	0.44	0.17
	Fe	0.00	0.03	0.00
	Zn	0.00	0.27	0.00
	Mn	0.00	0.17	0.13
	Li*	0.00	1.05	1.24
Sum		9.00	9.00	9.00
X	Ca	0.00	0.03	0.09
	Na	1.06	0.87	0.60
Sum		1.06	0.90	0.69
V+W	O	1.00	0.00	0.00
	OH	3.00	3.78	3.76
	F	0.00	0.22	0.24
Sum		4.00	4.00	4.00

Note: * Li_2O content was calculated from the charge balance. In Sample 2 the lithium content was obtained by calculation, and is close to that obtained by the flame photometry method at the Institute of Geochemistry SB RAS, Irkutsk, Russia, by L.G. Kuznetsova.

Table 4. Typical chemical compositions of Paraiba tourmalines (wt. %)

	Peretti, A et al., 2009		Beurlen, H. et al., 2011
	ICP MS	EMPA	EMPA
	Blue zone	Average	05-3a
SiO_2	37.86	37.74	38.48
Al_2O_3	39.69	41.77	41.08
CuO	1.23	0.55	1.80
FeO	0.00	0.08	0.03
ZnO	0.04	0.07	0.00
Mn_2O_3	1.06	0.45	0.46
Li_2O	2.15	-	2.01
CaO	0.30	0.13	0.67
Na_2O	2.00	1.83	1.98
Bi_2O_3	0.11	0.13	0.09
K_2O	0.01	0.02	0.02
Ga_2O_3	0.01	-	-
F	-	0.72	1.46
H_2O	-	-	3.18
B_2O_3	12.07	11	11.21
Sum	96.53	94.49	101.85

Table 5. The site scattering, atom coordinates and isotropic displacement parameters in the crystal structures of the tourmalines investigated

Site	Smp.	Site scattering, e per site	*x*/*a*	*y*/*b*	*z*/*c*	$U^*_{is/eq}\cdot 100$, Å^{-2}
X 3*a*	1	9.57(2)	0	0	0.2186(9)	2.3(1)
	2	10.50(1)	0	0	0.2350(4)	2.42(6)
	3	8.95(2)	0	0	0.2348(6)	1.90(10)
Y 9*b*	1	19.08(1)	0.12342(7)	1/2x	0.6347(2)	0.73(2)
	2	14.32(1)	0.12456(5)	1/2x	0.6305(1)	0.81(2)
	3	10.60(1)	0.1234(1)	1/2x	0.6332(2)	0.65(3)
Z 18*c*	1	13.32(1)	0.29747(7)	0.26001(7)	0.6055(2)	0.53(3)
	2	13.83(1)	0.29773(4)	0.26045(4)	0.6109(1)	0.67(2)
	3	13.48(1)	0.29688(5)	0.26004(5)	0.6095(1)	0.57(2)
T 18*c*	1	13.90(1)	0.19206(6)	0.18989(6)	0.00000	0.44(2)
	2	13.95(1)	0.19208(3)	0.19001(3)	0.00000	0.40(1)
	3	13.95(1)	0.19197(4)	0.18979(4)	0.00000	0.33(2)
B 9*b*	1	5.00	0.1092(2)	2x	0.4525(6)	0.41(10)
	2	5.00	0.10899(8)	2x	0.4564(3)	0.57(6)
	3	5.00	0.1091(1)	2x	0.4545(5)	0.45(2)
W1(O1)3a	1	8.00	0	0	0.772(2)	3.3(3)
	2	6.56(3)	0	0	0.7873(8)	4.7(3)
	3	6.64(2)	0	0	0.7773(13)	2.7(2)
W2(F) 9b	1	-	-	-	-	-
	2	1.62(3)	0.0357(9)	1/2x	0.796(2)	2.38(2)
	3	1.71(2)	0.030(1)	1/2x	0.799(3)	3.6(5)
O2 9*b*	1	8.00	0.0599(1)	2x	0.4922(5)	0.68(8)
	2	8.00	0.06050(7)	2x	0.4893(3)	1.47(6)
	3	8.00	0.06033(9)	2x	0.4887(4)	1.33(7)
O3(V) 9*b*	1	8.00	0.2627(4)	1/2x	0.5059(6)	1.7(2)
	2	8.00	0.2692(2)	1/2x	0.5079(3)	1.11(5)
	3	8.00	0.2653(2)	1/2x	0.5078(3)	1.10(8)
O4 9*b*	1	8.00	0.0942(2)	2x	0.0738(6)	1.09(10)
	2	8.00	0.09309(7)	2x	0.0723(3)	0.79(4)
	3	8.00	0.0937(1)	2x	0.0733(4)	0.73(6)
O5 9*b*	1	8.00	0.1869(3)	1/2x	0.0975(5)	1.05(10)
	2	8.00	0.1861(1)	1/2x	0.0952(3)	0.84(5)
	3	8.00	0.1871(2)	1/2x	0.0956(3)	0.71(6)
O6 18*c*	1	8.00	0.1954(2)	0.1836(2)	0.7719(4)	0.64(7)
	2	8.00	0.19719(8)	0.18614(9)	0.7750(2)	0.67(3)
	3	8.00	0.1955(1)	0.1848(1)	0.7743(2)	0.60(5)
O7 18*c*	1	8.00	0.2877(2)	0.2867(2)	0.0746(4)	0.65(7)
	2	8.00	0.28616(8)	0.28592(8)	0.0796(2)	0.60(3)
	3	8.00	0.2865(1)	0.2860(1)	0.0785(2)	0.51(4)
O8 18*c*	1	8.00	0.2087(2)	0.2687(2)	0.4352(4)	0.59(6)
	2	8.00	0.20945(9)	0.26984(9)	0.4407(2)	0.68(4)
	3	8.00	0.2094(1)	0.2697(1)	0.4386(3)	0.59(4)
H	1	1.00	0.2760(12)	1/2x	0.428(2)	5.2(5)
	2	1.00	0.305(4)	1/2x	0.397(8)	5.1(5)
	3	1.00	0.2629(9)	1/2x	0.3996(7)	9.1(8)

Note: * $U_{eq} = 1/3[U_{11}\, a^{*2}a^2 + ... + 2U_{23}\, b^*c^*bc\, \cos\alpha]$

Table 6. Bond lengths (Å) in the crystal structures of the tourmalines investigated

Atoms	Samples		
	1	2	3
X - O2 [3]	2.542(7)	2.457(3)	2.448(4)
- O4 [3]	2.782(5)	2.810(2)	2.815(3)
- O5 [3]	2.703(7)	2.746(3)	2.751(5)
average	2.676	2.671	2.671
Y - W1 [1]	1.954(7)	2.044(4)	1.979(6)
- O2 [2]	1.951(5)	1.965(2)	1.964(4)
- O3v [1]	2.118(8)	2.172(3)	2.140(5)
- O6 [2]	1.943(4)	1.997(2)	1.971(4)
average	1.977	2.024	1.998
Y– W2	-	1.70(4)	1.74(2)
Z - O3v [1]	1.958(7)	1.957(3)	1.958(4)
- O6 [1]	1.874(5)	1.849(2)	1.859(3)
- O7 [1]	1.935(4)	1.951(2)	1.946(3)
- O7 [1]	1.875(4)	1.881(2)	1.883(3)
- O8 [1]	1.910(5)	1.914(2)	1.905(3)
- O8 [1]	1.892(5)	1.884(2)	1.887(4)
average	1.907	1.906	1.906
T - O4 [1]	1.625(5)	1.626(3)	1.624(3)
- O5 [1]	1.641(4)	1.641(3)	1.635(4)
- O6 [1]	1.623(4)	1.605(2)	1.607(3)
- O7 [1]	1.614(5)	1.612(2)	1.611(4)
average	1.625	1.621	1.619
B - O2 [1]	1.383(5)	1.354(2)	1.360(3)
- O8 [2]	1.370(6)	1.386(3)	1.380(4)
average	1.375	1.375	1.373
H – O3v	0.58(1)	0.93(6)	0.77(1)
H – O5	2.64(1)	2.70(6)	2.40(1)
W1-W2	-	0.50(2)	0.44(2)
W2-W2	-	0.85(3)	0.72(3)

Table 7. Chemical characteristics of Cu-bearing tourmalines

No	CuO, wt. %	*Crystal chemical formula*	*Reference*
1	8.39	$(Na_{0.86}\square_{0.14})(Al_{1.86}Cu_{1.14})(Al_{5.88}Cu_{0.12})(Si_{5.40}Al_{0.60})O_{18}\times (BO_3)_3((OH)_{3.00}O)$	*Our date (Smp.1)*
2	3.59	$(Na_{0.90}Ca_{0.03}\square_{0.07})(Al_{1.50}Li_{0.75}[Cu,Zn]_{0.54}Mn_{0.18}Fe_{0.03})\times (Al_{5.85}[Cu,Zn]_{0.15})(Si_{5.65}Al_{0.32})O_{18}(BO_3)_3((OH)_{3.82}F_{0.18})$	*Our date (Smp.2)*
3	1.46	$(Na_{0.65}Ca_{0.09}\square_{0.26})(Al_{1.63}Li_{1.07}Mn_{0.30})(Al_{5.81}Cu_{0.19})(Si_{5.70}Al_{0.30})O_{18}\times (BO_3)_3((OH)_{3.83}F_{0.17})$	*Our date (Smp.3)*
4	0.94	$(Na_{0.54}Ca_{0.11}\square_{0.35})(Al_{1.62}Li_{1.13}Cu_{0.11}Mn_{0.08})(Al_{5.91}\square_{0.09})\times (Si_{5.74}B_{0.26})O_{18})(BO_3)_3((OH)_{3.61}F_{0.39})$	Ertl et al., 2002
5	0.81	$(Na_{0.54}Ca_{0.05}\square_{0.41})(Al_{1.66}Li_{1.21}Cu_{0.10}Mn_{0.04})Al_{6.00}((Si_{5.92}Al_{0.08})O_{18})\times (BO_3)_3((OH)_{3.56}F_{0.44})$	MacDonald & Hawthorne, 1995
6	0.38	$(Na_{0.55}Ca_{0.11}\square_{0.34})(Al_{1.71}Li_{1.16}Cu_{0.05}Mn_{0.08})Al_{6.00}((Si_{5.88}Al_{0.12})O_{18})\times (BO_3)_3((OH)_{3.70}F_{0.30})$	
7	0	$(Na_{0.68}Ca_{0.22}\square_{0.10})(Li_{1.56}Al_{1.44})(Al_{5.82}Mn_{0.18})(Si_6O_{18})(BO_3)_3\times ((OH)_{3.64}F_{0.36})$	Rozhdestvenskaya *et al*., 2005

Table 8. Geometric characteristics of Cu-bearing tourmalines

No	*a*, Å	*c*, Å	<Y-O>, Å	<Z-O>, Å	<T-O>, Å	ΔX^*10^3	$\Delta_{oct}Y^*10^3$	$\Delta_{oct}Z^*10^3$	ΔT^*10^3
1	15.840(4)	7.091(1)	1.978	1.907	1.625	2.07	0.37	0.43	0.15
2	15.881(1)	7.112(1)	2.024	1.906	1.621	3.31	1.25	0.42	0.07
3	15.840(3)	7.1028(9)	1.999	1.906	1.619	3.59	1.05	0.34	0.05
4	15.8308(32)	7.0957(8)	1.998	1.905	1.619	3.50	1.06	0.35	0.05
5	15.818(2)	7.087(1)	1.992	1.904	1.617	3.18	0.98	0.36	0.06
6	15.805(2)	7.084(1)	1.987	1.903	1.616	3.21	1.05	0.36	0.05
7	15.826(3)	7.098(1)	1.996	1.907	1.618	3.71	1.35	0.34	0.08

Note: a, c – unit cell parameters; <Y-O>, <Z-O>, <T-O> - average polyhedron sizes; ΔX, $\Delta_{oct}Y$, $\Delta_{oct}Z$, ΔT – bond-length distortion

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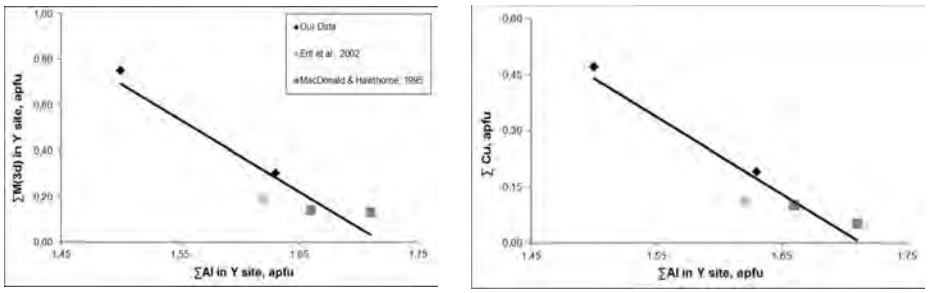
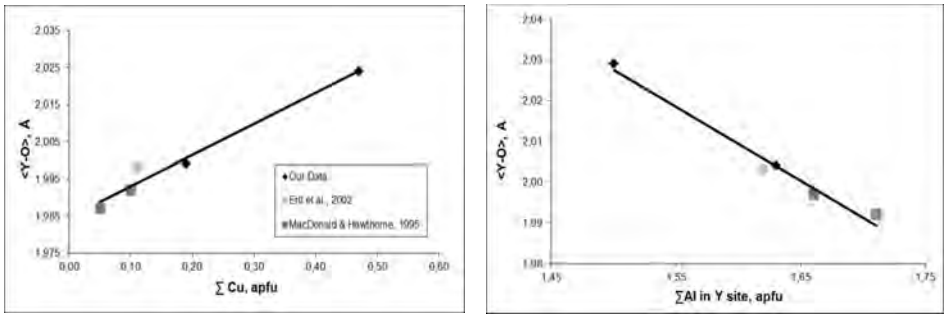


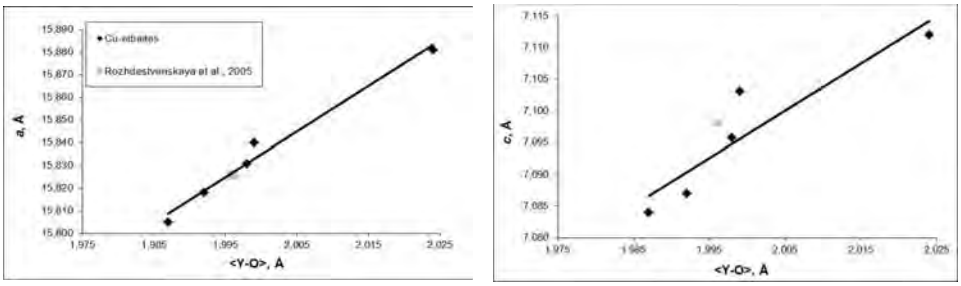
a b

Fig. 1. Content of Al^{3+} cations in Y-octahedron of copper-bearing elbaites vs their content of 3d elements (a) and their overall copper content (b).



a b

Fig. 2. The value of <Y-O> in copper-bearing elbaites vs their total contents of Cu^{2+} (a) and Al^{3+} in the Y-octahedron (b).



a b

Fig. 3. The value of <Y-O> in copper-bearing elbaites vs unit cell parameters: *a* (a) and *c* (b).