XAFS study on the location of Cu and Mn in a greenish blue elbaite from Alto dos Quntos mine, Brazil

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The local structure of Cu and Mn in a greenish-blue elbaite from Alto dos Quintos, Brazil, was studied by using X-ray absorption fine structure (XAFS) spectroscopy. The observed local structural features suggest the distribution of Cu$^{2+}$, Mn$^{2+}$, and Mn$^{3+}$ at the distorted $Y$-site.

Keywords: Greenish-blue elbaite, Tourmaline, XAFS, Single crystal X-ray diffraction

INTRODUCTION

Elbaite, Na(Li$_{1.5}$,Al$_{1.5}$)Al$_6$(Si$_6$O$_{18}$)(BO$_3$)$_3$(OH)$_4$, is a member of the alkali-tourmaline group and its remarkable colorization is of great interest with respect to the minor constituents. In particular, the concentration of Cu$^{2+}$ has been extensively discussed, after a new find of elbaite with unique green and blue color was made in 1988 from the state of Paraiba, northeastern Brazil (Koivula and Kammerling, 1989a, 1989b; Fritsch et al., 1990). The further mineralogical characterization on a blue tourmaline appeared in the literature by Carobbi and Pieruccini (1947). More recently, Rossman et al., (1991) described the optical absorption spectra for Cu$^{2+}$ and Mn$^{3+}$ and concluded that the yellowish green to blue green colors of elbaite are due to Cu$^{2+}$ and modified to show the violet colorization by the absorption of Mn$^{3+}$. The colorization from green to purple through general turquoise-blue was also discussed as a function of the coexisting Mn content (Wilson, 2002). On the other hand, the single distribution of Mn$^{3+}$ was reported as an agent for the pink to red color of elbaite (Manning, 1969, 1973; Reinitz and Rossman, 1988). The coloring agents of Cu and Mn were usually suggested to occupy the distorted octahedral site in the parent elbaite structure, because its coordination feature serves the structural flexibility for the various elements with different size and valence state (Rossman et al., 1991; MacDonald and Hawthorne, 1995; Vereshchagin et al., 2013).

Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy can be counted as one of the most powerful techniques for elucidating the local structure around an interesting element. And recent development allows us to simulate the theoretical EXAFS oscillation for an element by using the structure parameters of a host crystal (Rehr and Albers, 2000). This approach of XAFS technique is applicable in order to specify the crystallographic site for the coloring agents. This paper reports the distribution of Cu and Mn in a greenish blue elbaite from Alto dos Quintos mine, Rio Grande do Norte, Brazil, inferred by the combinatorial analysis of single crystal X-ray diffraction and XAFS measurement.

EXPERIMENTAL

After the discovery of blue-green elbaite from the Batalha, the state of Paraiba, similar copper-bearing elbaites were found in granitic pegmatites at the nearby localitie of Mulungu and Alto dos Quintos in the state of Rio Grande del Norte (Karfunkel and Wegner, 1996; Shigley et al. 2001; Milisenda, 2005). The chemical composition of blue or blue-green elbaites from Mulungu and Alto dos Quintos mines indicates a lower CuO content than of elbaite from Batalha (up to 0.8 wt% CuO versus up to 2.4 wt% CuO, respectively).

Our tourmaline sample from Alto dos Quintos mine shows a deep pink core surrounded by a greenish blue zone, and the latter greenish blue part was subsequently studied in order to discuss the distribution of Cu and Mn.
Quantitative analysis of the chemical composition was carried out using a JEOL JXA-8900L electron microprobe analyzer in wavelength-dispersion mode with the following operating conditions: accelerating voltage of 15 kV and beam current of 6 nA. The greenish blue part was crushed into powders and dissolved in an aqueous solution by using a Na2CO3 flux, and the concentrations of Li2O and B2O3 were analyzed by inductively coupled plasma optical emission spectrometry (ICP–IRIS Advantage DUO). The weight fraction of H2O component was analyzed by the Pregl–Dumas method (Thermo Fischer Flash EA1112). The chemical composition obtained by the chemical analysis is listed in Table 1.

**Table 1.** Chemical composition of blue-green elbaite from Alto dos Quntos mine, Brazil

| Chemical composition (wt%) | SiO2 | Al2O3 | FeO  | MnO  | CuO  | CaO  | B2O3 | Na2O | K2O  | Li2O | F    | H2O  | O=Fe |
|---------------------------|------|-------|------|------|------|------|------|------|------|------|------|------|------|
| SiO2                      | 37.18|       |      |      |      |      |      |      |      |      |      |      |      |
| Al2O3                     | 40.56|       |      |      |      |      |      |      |      |      |      |      |      |
| FeO                       | 0.04 |       |      |      |      |      |      |      |      |      |      |      |      |
| MnO                       | 1.58 |       |      |      |      |      |      |      |      |      |      |      |      |
| CuO                       | 1.08 |       |      |      |      |      |      |      |      |      |      |      |      |
| CaO                       | 0.35 |       |      |      |      |      |      |      |      |      |      |      |      |
| B2O3                      | 9.99 |       |      |      |      |      |      |      |      |      |      |      |      |
| Na2O                      | 1.99 |       |      |      |      |      |      |      |      |      |      |      |      |
| K2O                       | 0.02 |       |      |      |      |      |      |      |      |      |      |      |      |
| Li2O                      | 1.93 |       |      |      |      |      |      |      |      |      |      |      |      |
| F                         | 1.01 |       |      |      |      |      |      |      |      |      |      |      |      |
| H2O                       | 3.36 |       |      |      |      |      |      |      |      |      |      |      |      |
| O=Fe                      | -0.42|       |      |      |      |      |      |      |      |      |      |      |      |

* Calculated based on stoichiometry.

A single crystal sample with dimensions of 0.110 × 0.092 × 0.072 mm was selected for single crystal X-ray diffraction. Intensity measurement was carried out by using an X-ray diffractometer equipped with an imaging plate and a rotating anode X-ray tube (Rigaku Vario-MAX–RAPID). The focused MoKα radiation was utilized and the ordinary oscillation technique was applied. After Lorentz and polarization corrections, an absorption correction was performed by using the integration method on the basis of the shape of the specimen (Higashi, 1995). The maximum and minimum transmission factors were 0.954 and 0.946, respectively. Data reduction yielded 1045 independent reflections, among which 1038 reflections met the condition of $I_{obs} > 2.0 \sigma(I_{obs})$. Scattering factors for neutral atoms and anomalous dispersion coefficients were taken from International Tables for Crystallography Volume C (1992). The structural parameters for Cu-bearing elbaite (Donald and Hawthorne, 1995) were used as initial parameters and the least-squares refinement was carried out by using the software program SHELXL (Sheldrick, 2008).

Tourmaline has a generalized structural formula $X_T Z_T (B O_3)_2 Z_O_1 X_F W$ (Henry et al., 2011), and $X = Na, Ca$ and vacant, $Y = Li, Al, Mn, Fe$, and $Cu$, $Z = Al$, $B = B, Y = OH, W = OH, F$ and $O$. In this study, the $X$-site was modeled using the scattering factor of Na and the $Y$-site was constrained to be fully occupied by Li and Al. The $Z$-site and $T$-site were considered to be fully occupied by Al and Si, respectively. Although the chemical analysis suggested that the $W$-site is occupied either by OH and F, the scattering factor for the $W$-site was approximated by that of F. H3 associated with O3 ($V^3$-site) was located in the difference Fourier maps. The atomic coordinates for the H3 site was subsequently treated as a riding model in the present analysis and its isotropic displacement parameter was restricted by using the equation of $U_{iso}(H3) = 1.5 U_{eq}(O3)$. Finally, an anisotropic thermal model was introduced for all non-hydrogen atoms, and the least-squares refinement of all variables converged to $R$ indices of 1.89% for the observed reflections. Cell parameters and other detailed information on the structural refinement are listed in Table 2. Final positional and displacement parameters are given in Tables 3 and 4. The calculated interatomic distances are listed in Table 5. Figure 1 shows the structure of tourmaline and the coordination environment around the Y and Z-sites.

**XAFS measurement**

Extended X-ray absorption fine structure (EXAFS) spectra at the Cu and Mn K-absorption edges were measured at Photon Factory (PF) BL–9A and BL–12C, respectively, Institute of Material Structure Science (IMSS), High Energy Accelerator Research Organization, Tsukuba, Japan. The X-rays were monochromatized with a Si (111) double-crystal monochromator. An ionization chamber was used to monitor the X-ray incidence irradiating the specimen, and a Ge solid state detector (SSD) was mounted at about 90 degrees against the incident beam within the photon polarization plane. The X-ray Absorption Near Edge Structure (XANES) spectra near the Mn K absorption edge was measured at the BL11 of the SAGA light source. The XANES spectra were measured in fluorescent mode by using a Lytle-type detector. The pre-edge centroid position obtained for the greenish blue elbaite was compared with the standard MnO and Mn$_2$O$_3$ samples. The XANES spectra and EXAFS interference functions were extracted from the measured absorption spectra using the Athena and Artemis software program (Ravel and Newville, 2005), an interface to the IFEFFIT.
library (Newville, 2001). EXAFS simulation was performed based on the structural parameters obtained by single crystal X-ray diffraction. It should be noted that the present simulation includes single and multiple scattering paths within the coordination shell up to 3.5 Å around Cu and Mn. Phase shifts and oscillation amplitudes were calculated with FEFF6 code (Rehr and Albers, 2000). Although Cu and Mn in the elbaite structure have three types of anion ligands such as O, OH and F, the present least-squares fitting and FEFF calculation were carried out by using O for the anion sites. The energy shift parameters were fixed to 0 eV for all calculations. The values of the amplitude reduction factor and the EXAFS Debye–Waller factor for the longer paths were held constant at 0.8 and 0.005, respectively.

**RESULTS AND DISCUSSION**

**Crystal structure**

The obtained chemical composition was normalized to 31 anions. The calculated unit formula indicates an apparent

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**Table 2. Structural analysis of greenish blue elbaite from Alto dos Quntos mine, Brazil**

| Site | Site occupancy | x   | y   | z   | Ueq.  |
|------|----------------|-----|-----|-----|-------|
| X    | Na=0.75(1)     | 0   | 0   | 0.8386(4) | 0.0203(10) |
| Y    | Al/Li = 0.798(8)/0.202 | 0.0618(2) | 0.2970(4) | 0.4617(8) | 0.0062(1) |
| Z    | Al = 1         | 0.1899(4) | 0.1919(4) | 0.0751(2) | 0.0052(1) |
| B    | B = 1          | 0.8909(11) | 0.5836(3) | 0.0154(5) |
| F(6) | 3a 1           | 0   | 0   | 0.2906(6) | 0.0437(12) |
| O2   | 0.9366(8)      | 0.5638(3) | 0.0133(4) |
| O3(I) | 0.9138(10) | 0.5836(3) | 0.0154(5) |
| O4   | 0.9063(8)      | 0.9063(8) | -0.009(3) | 0.0095(4) |
| O5   | 0.9357(8)      | -0.0237(3) | 0.0101(4) |
| O6   | 0.18518(10)    | 0.19584(10) | 0.2970(2) | 0.0079(3) |
| O7   | 0.28618(10)    | 0.28651(10) | -0.0071(2) | 0.0070(3) |
| O8   | 0.26993(11)    | 0.20936(11) | 0.6321(2) | 0.0079(3) |
| H3   | 0.1261         | -0.6921 | 0.020* |

* See text.
shortage of B$_3$+ (B$_3$+ < 3.0 apfu) in the present case. Since the result of single crystal X-ray diffraction shows the structural features of the B-site common to the ordinary BO$_3$ triangle, B$_2$O$_3$ content was estimated so as to indicate the full occupation of the B-site. The further normalization together with the estimation of Mn$_3$/Mn$_2$ by XANES measurement lead to the unit formula of Na$_{0.61}$Ca$_{0.06}$□$_{0.33}$(Li$_{1.23}$Al$_{1.47}$Mn$_{2+0.17}$Mn$_{3+0.04}$Cu$_{0.13}$)Al$_{6}$B$_3$(Si$_{5.89}$Al$_{0.11}$)O$_{26.96}$(OH)$_{0.04}$(OH)$_3$[(OH)$_{0.49}$F$_{0.51}$]. It is interesting to compare this chemical formula with the structural formula Na$_{0.75}$(Li$_{0.61}$Al$_{2.39}$)Al$_3$(BO$_3$)$_3$(Si$_6$O$_{18}$)(OH)$_3$F obtained by the present refinement.

The result of single crystal X-ray diffraction found an occupation of 0.75 Na at the X-site, which corresponded well with the occupation of 0.61 Na and 0.06 Ca calculated from the results of the chemical analysis.

As shown in Figure1, the Y-site is composed of four oxygens, the W-site and the hydroxyl V-site. The Y-O3 (V-site) = 2.142 Å and Y-F (W-site) = 2.004 Å for the present sample is the first and second longest neighboring atomic pairs among the six ligands around the Y-site, such a feature is common to the structures of Cu-bearing elbaite (Vereshchagin et al., 2013). The distribution of Al inferred by the structural refinement shows the significant discrepancy from that of the chemical analysis. This inconvenience, however, appears to be resolved by introducing the distribution of Cu, Mn and Li at the expense of that of Al, since the numbers of electron at the Y-site assigned from the unit formulae (31.9 electrons) were in reasonable accord with the refined site-scattering values (32.9 electrons). The averaged interatomic distance of Y-O2 and Y-O6 = 1.975 Å is greater than the 1.94 Å calculated for the refined population and the ionic radii provided by Bosi and Lucchesi (2007). This may also support the residence of Cu, Mn, and Li for small Al.

The Z-site is coordinated by five oxygens and the hydroxyl V-site and is assigned as being completely occupied by Al in the structural refinement and the converged equivalent displacement parameter readily suggests no significant occupation by other elements. Six Z-O distances are between 1.860 and 1.964 Å, with an averaged value of 1.909 Å. This average value is in accord with those for Z sites realized in the Cu-bearing elbaite (MacDonald and Hawthorne, 1995; Ertl et al., 2013; Vereshchagin et al., 2013). In particular, the distance of Z-O3 (V-site) is the longest among six and this feature corresponds well to the hydroxyl at this V-site.

A substantial amount of B and Al at the T-site ([4]B and [4]Al, respectively) was sometimes suggested to exist in the structure of elbaite tourmaline through the structur-
refinement, chemical analysis, and $^{11}\text{B}$ and $^{27}\text{Al}$ magic-angle-spinning nuclear magnetic resonance spectroscopy (Ertl et al., 2007; Lussier et al., 2008, 2009). Therefore, it may be interesting to discuss the site population of the $T$-site by using the information on the unit formulae calculated from chemical analysis, and mean bond length obtained from the structure analysis. The averaged $<T$-$O>$ = 1.622 Å of the present sample provides no indication for the existence of $^{18}\text{B}$ in its structure. Additionally, the value agrees well with the calculated one of $<T$-$O>$ = 1.622 Å for the occupation of $T$ = Si$_{5.89}$Al$_{0.11}$ when the relation between $<T$-$O>$ distance and chemical composition by Ertl et al. (2007) is applied.

The $B$-$O$ distances vary from 1.361 to 1.383 Å, with a mean distance of 1.376 Å. These results suggest full occupation of B at the $B$-site ($^{11}\text{B}$).

The distribution of anions such as $\text{F}^-$, $\text{OH}^-$, and $\text{O}_2^-$ at the $V$- and $W$-sites in the tourmaline structure is quite interesting. The position of H atom bonded to O3 was taken from the difference Fourier maps, and the calculated distance of O3-H3 = 0.93 Å showed a quite reasonable value. For the $W$-site, the chemical analysis clearly indicated the distribution of OH and F and this also confirmed the very long Y-$F$ ($W$-site) distance mentioned above.

**Distribution of Cu and Mn**

Figure 2 shows the Mn K-edge XANES spectra of tourmaline together with those of MnO and Mn$_2$O$_3$. Each vertical line on the spectra is the position of the absorption edge, which is defined by the half maximum of an edge jump in the normalized XANES spectra. The edge position for greenish blue elbaite is just between those of the standard oxides, suggesting a mixed valence state of Mn. Although the fine structure of each XANES spectra is different from the others, a population of Mn$^{2+}$/(Mn$^{2+}$ + Mn$^{3+}$) = 0.6 could be obtained by its edge energy relative to those of

**Figure 1.** The structure of elbaite and coordination environment of $Y$ and $Z$-sites (Dowty, 2005).

**Figure 2.** Mn K-edge XANES spectra of blue elbaite from Dos Quintos, MnO, and Mn$_2$O$_3$. Vertical lines on the spectra are the positions of the absorption edges, defined as half the normalized edge jump.
the standard oxides. Figure 3 shows the results of the fitting for the first neighbor coordination obtained by the least-squares calculation starting from the structural parameters obtained by single crystal X-ray diffraction. The present EXAFS analysis allowed us to obtain the averaged Mn–O distance of 2.11 Å. The obtained distance is longer than the distances of Mn$^{3+}$–F = 1.91 Å, Mn$^{3+}$–O = 1.99 Å and Mn$^{3+}$–OH = 2.09 Å appeared in the crystal structures. These results conclude the mixed valence state of Mn$^{2+}$ and Mn$^{3+}$. The observed EXAFS oscillation for any element in crystals can be simulated readily by using the structure parameters determined by ordinary single crystal X-ray diffraction (Rehr and Albers, 2000). Figures 4a and 4b indicate the experimental EXAFS profile of greenish blue elbaite together with those of simulated ones for the two models in which Mn resides at either the Y-site or Z-site, respectively. The oscillation profiles in Figure 4a readily indicate that the model in which Mn prefers the Y-site is superior to another model.

Figure 5 indicates the results of Cu EXAFS for greenish blue elbaite. The obtained local structure around Cu appears to indicate typical two shell structure of Cu$^{2+}$ with four shorter and two longer ligands. This may suggest Jahn–Teller splitting of Cu$^{2+}$ in a distorted octahedral structure.
site (Taran and Lebedev, 1990; Rossman et al., 1991). Figures 6a and 6b show the experimental Cu EXAFS profile for greenish blue elbaite together with those of simulated ones for the two models in which Cu resides at either the Y–site or Z–site, respectively. The oscillation profiles in Figure 6a show the superior fit and the location of Cu at the Y–site was confirmed.

CONCLUSION

The structure and chemical composition of greenish–blue elbaite from Alto dos Qintos, Brazil were studied by a combined analysis of single crystal X-ray diffraction and XAFS analysis. The measured EXAFS oscillation could be well reproduced only when Cu and Mn are distributed at the distorted Y–site. The absorption edge position of Mn and the obtained Mn–O distance, supports the mixed valence state of Mn with about the ratio of Mn$^{2+}$/Mn = 0.6. The structural features obtained by single crystal X-ray diffraction also confirm the location of Cu and Mn at the Y–site. These results clearly indicate that the distribution of Cu together with the mixed-valence Mn at the Y–site is responsible for the greenish–blue color of present elbaite.
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K. Sugiyama, H. Arima, H. Konno and T. Mikouchi

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