Supporting Information

For

The Nature of the Mn(III) Color Centers in Elbaite Tourmalines

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Determination of Mn concentration in sample

From EMP data, empirical formula is
$Na_{0.70}(Li_{0.96}Al_{1.5}Mn_{0.47}Fe_{0.006}Ti_{0.001}Ga_{0.007})Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)_{0.68}F_{0.32}$

$$Mn\%\ in\ Y\ site = \frac{0.47}{2.945} * 100\% = 16.0\%\ Mn\ ions \tag{1}$$

There are 7.5 Y site ions in a single unit cell, therefore:

$$\#Mn\ in\ unit\ cell = 7.5\ ions * 16.0\%\ Mn\ ions = 1.20\ Mn\ ions/unit\ cell \tag{2}$$

$$1.31\ Mn\ ions/unit\ cell * \frac{1\ mol}{6.02\times10^{23}\ ions} = 1.99\times10^{-24}\ mol\ Mn\ ions/unit\ cell \tag{3}$$

According to crystal structure data from reference 1, unit cell volume is 1,530 Å^3, or 1.53×10^{-24} L.

$$Conc\ of\ Mn\ ions = \frac{2.18\times10^{-24} mol\ Mn\ ion}{1.53\times10^{-24} L} = 1.30\ M\ Mn\ ions \tag{4}$$

Determination of the extinction coefficient of the transition $^5E(a_1)^1(e)^2(e)^1 \rightarrow {}^5E(a_1)^1(e_2)^1(e_2)^2$ at 530 nm (1.81 AU, E⊥c)

Assuming that all Mn is converted to Mn^{3+} upon irradiation with a dose of 240 Mrad, then:

$$\varepsilon = \frac{Abs}{l*conc} = \frac{1.81}{(0.565\ cm)*(1.30\ M)} = 2.47\ M^{-1}cm^{-1} \tag{5}$$

Determination of Fe concentration in sample

From XRF data, empirical formula is
$Na_{0.70}(Li_{0.96}Al_{1.5}Mn_{0.47}Fe_{0.006}Ti_{0.001}Ga_{0.007})Al_6(Si_6O_{18})(BO_3)_3(OH)_3(OH)_{0.68}F_{0.32}$

$$Fe\%\ in\ Y\ site = \frac{0.006}{2.954} * 100\% = 0.20\%\ Fe\ ions \tag{6}$$

There are 7.5 Y site ions in a single unit cell, therefore:

$$\#Fe\ in\ unit\ cell = 7.5\ ions * 0.33\%\ Fe\ ions = 0.015\ Fe\ ions/unit\ cell \tag{7}$$

$$0.025\ Fe\ ions/unit\ cell * \frac{1\ mol}{6.02\times10^{23}\ ions} = 2.5\times10^{-26}\ mol\ Fe\ ions/unit\ cell \tag{8}$$

According to crystal structure data from reference 1, unit cell volume is 1,530 Å^3, or 1.53×10^{-24} L.

$$Conc\ of\ Fe\ ions = \frac{2.5\times10^{-26} mol\ Fe\ ion}{1.53\times10^{-24} L} = 0.017\ M\ Fe\ ions \tag{9}$$

Determination of the extinction coefficient of transition at 700 nm (0.079 AU, Fe(II) *d-d*, 0.079 AU, E∥c)

$$\varepsilon = \frac{Abs}{l*conc} = \frac{0.048}{(0.565\ cm)*(0.017\ M)} = 5.1\ M^{-1}cm^{-1} \tag{10}$$

Determination of the extinction coefficient of transition at 1,030 nm (0.079 AU, Fe(II) *d-d* and Fe(II)/Fe(III) IVCT, 0.33 AU, E⊥c)

$$\varepsilon = \frac{Abs}{l*conc} = \frac{0.33}{(0.565\ cm)*(0.017\ M)} = 35\ M^{-1}cm^{-1} \tag{11}$$

References

(1) Ertl, A.; Rossman, G. R.; Hughes, J. M.; Prowatke, S.; Ludwig, T. Mn-Bearing “Oxy-Rossmanite” with Tetrahedrally Coordinated Al and B from Austria: Structure, Chemistry, and Infrared and Optical Spectroscopic Study. *Am. Mineral.* **2005**, *90* (2–3), 481–487.