

Local arrangement around OH groups in tourmaline studied by vibrational spectroscopy and structural refinement

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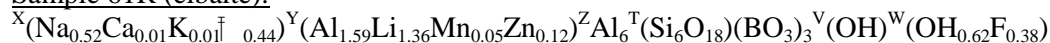
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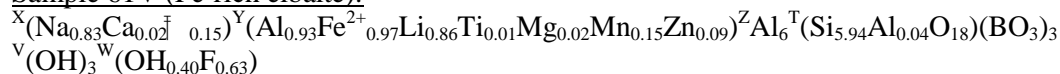
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Three tourmaline samples of different compositions, structurally and chemically characterized by single crystal X-ray diffraction and electron and ion microprobe, were studied by polarized Raman and Infrared spectroscopy in the OH-band spectral range in order to derive a model for OH band assignment. The obtained empirical formulae are:

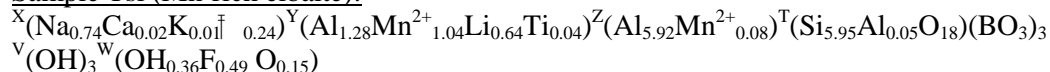
Sample 61R (elbaite):



Sample 61V (Fe-rich elbaite):



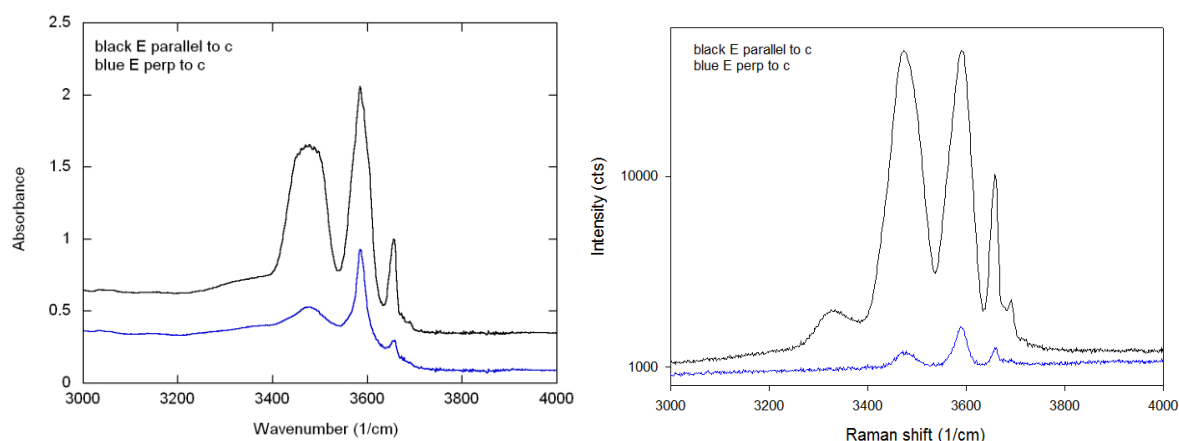
Sample Tsl (Mn-rich elbaite):



The Raman and IR spectra show strong similarities with 4 to 9 OH-bands observed for each sample. As noted in several previous studies, the IR spectra show very strong absorption bands when polarized along the c-axis direction (cf. Fig.), and it was not possible to thin down the absorbers sufficient to avoid truncation of the strongest bands. Raman spectra are not affected by this problem and are hence very useful to characterise the strong bands.

The OH-bands observed in the Raman and IR spectra of these tourmalines can be associated with two types of OH groups, which occupy the two crystallographic sites O1 (W) and O3 (V). The V site is surrounded by 3Y-cations, whereas the W site is surrounded by Y+2Z cations. In accordance with short-range bond-valence requirements (Bosi 2011), the following local arrangements around ^WOH can be considered stable in these tourmalines: ^Y(Al Li Li)⁵⁺; ^Y(R²⁺ R²⁺ R²⁺)⁶⁺; ^Y(Al R²⁺ Li)⁶⁺; ^Y(Al Al Li)⁷⁺; and ^Y(Al R²⁺ R²⁺)⁷⁺.

In a preliminary assignment model, bands at wavenumbers larger than 3600 cm⁻¹ are assigned to ^WOH, bands in the region 3600-3400 cm⁻¹ are assigned to ^VOH, and a band around 3335 cm⁻¹ is assigned to the hydrogen bond ^VO-H...O5.



Polarized IR and Raman spectra of sample 61R (elbaite).

References:

Bosi F. (2011), Canadian Mineralogist, 49, 17-27.