

Crystal structure and Raman spectroscopic studies of OH stretching vibrations in Zn-rich fluor-elbaite

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ABSTRACT

Zinc-rich fluor-elbaite from Piława Górna, Poland, was studied by electron microprobe (EPMA), single-crystal X-ray diffraction (SREF), and Raman spectroscopy (RS) to check the possibility of the application of RS to draw crystal-chemical conclusions for Al-rich and Li-bearing tourmalines on basis of the O–H stretching vibrations in the spectral range 3400–3800 cm⁻¹. This tourmaline, forming a thin metasomatic zone around gahnite, features varying compositions with a ZnO content reaching in the studied fragment of 5.70(12) wt%. The crystal structure of this Zn-rich fluor-elbaite [$a = 15.921(1)$, $c = 7.127(1)$ Å] was refined with a $R1$ value of 1.67%. Its formula was determined on the basis of electron-microprobe and structure refinement as $X(\text{Na}_{0.84}\square_{0.14}\text{Ca}_{0.01})_{\Sigma 1.00}Y(\text{Al}_{1.06}\text{Li}_{0.84}\text{Zn}_{0.69}\text{Fe}_{0.32}^{2+}\text{Mn}_{0.09})_{\Sigma 3.00}Z\text{Al}_6(\text{BO}_3)_3(\text{T}^{\text{Si}_6\text{O}_{18}})^V(\text{OH})_3^W(\text{F}_{0.65}\text{OH}_{0.26}\text{O}_{0.09})$. The deconvolution of the O–H stretching vibration bands, performed by fitting of an input model of component bands with Gaussian function shapes for the empirical spectrum, indicates that each of the three maxima assigned for ^VOH bonded to ^YAl³⁺, Y²⁺, and ^YLi⁺ and with the total integral intensity of at least 75% of the total OH content could be resolved into 1 to 3 bands, depending on the X-site occupation (vacancies, Na⁺, and Ca²⁺). The deconvolution indicates further that several low intense bands of ^WO–H modes above a Raman shift of 3600 cm⁻¹, totally reaching $\leq 25\%$, are dependent on the occupation of triplets of YYY cations bonded to the hydroxyl. These ^WO–H modes are also influenced by the X-site occupation. Due to ordering of all octahedral cations (except Al) at the Y site and a complete occupation of the Z site by Al and the V site by OH, it seems possible to evaluate the Li and OH contents in a Al-rich and Li-bearing tourmaline directly from the Raman spectrum. By using the ratio ${}^{\text{VOH}}I_{\text{YAlZAlZAl}}/({}^{\text{VOH}}I_{\text{YZZ}} + {}^{\text{WOH}}I_{\text{YYY}})$ as evaluated from RS, corresponding to the ratio ^YAl^{V+}/^WOH in the crystal, the formula of the Zn-rich fluor-elbaite can be calculated as $X(\text{Na}_{0.85}\square_{0.14}\text{Ca}_{0.01})_{\Sigma 1.00}Y(\text{Al}_{1.11}\text{Y}_{1.11}^{2+}\text{Li}_{0.78})_{\Sigma 3.00}Z\text{Al}_6(\text{BO}_3)_3(\text{Si}_6\text{O}_{18})(\text{OH})_3(\text{F}_{0.65}\text{OH}_{0.13}\text{O}_{0.22})$, where $Y^{2+} = \text{Zn} + \text{Fe} + \text{Mn}$. The formula, determined only on basis of EPMA and deconvolution of RS in the O–H stretching bands, corresponds very well (≤ 1 SD range of EPMA) to the formula determined on basis of EPMA and SREF. This result implicates that the O–H stretching vibrations, measured by Raman spectroscopy, could be applied for Al-rich and Li-bearing tourmalines as a useful tool for providing additional information for determining the crystal-chemical formula. It is also very helpful when crystal structural data are not available.

Keywords: Zn-rich fluor-elbaite, structure refinement, Raman spectroscopy, OH stretching vibrations, lithium content, hydroxyl content; Lithium, Beryllium, and Boron: Quintessentially Crustal