Exploring the potential of Raman spectroscopy for crystallochemical analyses of complex hydrous silicates: II. Tourmalines

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ABSTRACT

A detailed Raman spectroscopic, electron microprobe, and laser ablation-induced coupled plasma-mass spectrometric study of 46 natural tourmalines \([XY_2Z_6(T_4O_{18})(BO_3)_3V_3W]\) from 10 subgroups was performed to evaluate the potential of the Raman scattering, in particular of the OH bond stretching vibrations, for the identification of tourmaline species and site-occupancy analysis. The widespread chemical variety of the studied samples is reflected in the different spectral shapes. The positions and intensities of the observed vibrational modes can be used for tourmaline species identification. Taking into account the charge of the Y- and Z-site cations as well as the X-site occupancy, the Raman peaks generated by the bond stretching mode of the \([OH]\) groups were attributed to different \(YZZ-YZZ-YZZ\) cationic configurations, while the peaks originating from \(WO\) stretching is due to chemically different \(YYY\) triplets next to an X-site vacancy, \(3Na\), or \(3Ca\). It is shown that the integrated intensities of the \(Y\)-OH-stretching peaks can be used to calculate the contents of the major Y-site elements Mg, (Fe\(^{2+}+\)Mn\(^{2+}\)), Li, and Al. The analysis of the \(Y\)-OH-peak positions information on the X-site occupancy. The fitted linear equations can be used to determine the content of \(3(Na+Ca)\) and X-site vacancy per formula unit. Guidelines for how to gain crystallochemical information from the Raman spectra of tourmaline are suggested. This study, along with Part 1 dedicated to amphiboles (Leissner et al. 2015), reveals that Raman spectroscopy is well suited as a non-destructive, preparation-free, and easy-to-handle method for species identification and site-occupancy analysis in complex hydrous silicates. Our results demonstrate that the chemistry on the non-tetrahedral positions substantially influences the Raman-active H-O bond stretching phonon modes, which allows for quantitative compositional analysis, including the content of lithium.

Keywords: Tourmaline, Raman spectroscopy, electron microprobe analysis, LA-ICP-MS

INTRODUCTION

Tourmalines are hydrous borosilicates with complex chemical composition that form a mineral supergroup. The majority of tourmalines exhibit rhombohedral symmetry with space group \(R3m\). The general formula is \(XY_2Z_6(T_4O_{18})(BO_3)_3V_3W\) with the common cations and anions at each site in order of their relative abundance (Henry et al. 2011):

- \(X = Na^+, Ca^{2+}, [\square], K^+\) (with \([\square]\) as symbol for a vacant site);
- \(Y = Fe^{2+}, Mg^{2+}, Mn^{2+}, Al^{3+}, Li^+, Fe^{3+}, Ti^{4+}, Zn^{2+}, Cu^{2+}, V^{3+}\);
- \(Z = Al^{3+}, Fe^{3+}, Mg^{2+}, Fe^{2+}, Cr^{3+}, V^{3+}\);
- \(T = Si^{4+}, Al^{3+}, B^{3+}\);
- \(B = B^{3+}\);
- \(V = (OH)^{2-}, O^{2-}\); and
- \(W = F^-, (OH)^-, O^{2-}\).

The crystal structure of tourmaline is composed of 6-membered rings of \(TO_4\) tetrahedra, whose apical oxygen atoms point toward the (\(-\)) c-pole, causing the acentric nature of the structure (Fig. 1). Triangular \(BO_3\) groups are sub-parallel to the (001) plane and they are placed above and below the tetrahedral rings. The ninefold-coordinated X site is located on the threefold axis of symmetry, out of plane of the tetrahedral rings. The two octahedrally coordinated sites Y and Z are just inside and outside with respect to the ring contour. The V site, labeled as O(3) in crystallographic data, is shared by one YO\(_6\) and two ZO\(_6\) octahedra. The W site, labeled as O(1) in crystallographic data, is located on the threefold axis central to the tetrahedral rings and linked to 3 YO\(_6\) octahedra.

The tourmaline supergroup currently consists of 32 species approved by the International Mineralogical Association’s Commission on New Minerals, Nomenclature and Classification. The classification is related to the dominant compositional variability that occurs at the X, Y, Z, and W site and, to lesser extent, also at the V site. The primary division is made according to the dominant X-site occupancy resulting in the three groups alkali, calcic, and X-vacant tourmaline. Secondary divisions distinguish between the dominant occupancies of the Y site considering also major variations in the Z- and T-site occupancy. Further divisions are made according to the dominant W-site occupancy resulting in hydroxy-, fluor-, and oxy-species. Details of the most recent tourmaline classification and nomenclature are given by