

The position of vanadium in the crystal structure of zoisite, a variety tanzanite

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Tanzanite is the most valued gemmological variety of zoisite in which V is the dominant trace element and chromophore. However, the exact position and state of V in the zoisite structure are quite enigmatic and subject to many hypotheses based mainly on spectroscopic evidence but lacking any definite structural proof. Therefore, we combined a structure refinement with optical absorption spectroscopy and used two separate theoretical approaches to shed some light on this enigma.

Structure refinement of the zoisite–tanzanite structure did not provide sufficient evidence of the V location in the zoisite structure due to the small V content in tanzanite as evidenced by Electron-Probe Micro-Analysis and Laser-Ablation Inductively Coupled Plasma Mass Spectrometry. Structure refinement of the studied sample revealed an average bond length of the less distorted $M1,2O_6$ octahedron lower than 1.90 Å. At the same time, $M3O_6$ has slightly longer bonds with an average of ca. 1.96 Å. The $M1,2$ site has a slightly higher bond valence sum (BVS) of 3.03 vu, whereas BVS of $M3$ is significantly lower (2.78 vu).

Optical absorption spectra of the studied sample with measured bands at 13 160, ~15 500, 16 350, 16 700, 18 800, 26 120, 26 650, and 34 000 (?) cm^{-1} revealed that most V is trivalent with only a small portion likely in a four-valent state. Therefore, a crystal-field superposition-model and bond-valence model calculations were applied here with two necessary basic assumptions: (1) V is at octahedral sites; (2) it can be present in two oxidation states, V^{3+} or V^{4+} . Crystal field superposition model calculations made to interpret the optical spectra indicated that V^{3+} prefers occupying the $M1,2$ site; the preference of V^{4+} was impossible to determine from the present data.

Bond-valence model calculations showed no unambiguous preference for V^{3+} , although based on the simple bond-length calculation, the preference of the $M3$ -site could be suggested. In contrast, it is quite straightforward to assume that the $M1,2$ site has a more natural environment for V^{4+} . However, if the calculated octahedral distortions are taken into account, the $M1,2O_6$ octahedron shows a smaller change in distortion if occupied by V^{3+} than the $M3O_6$ octahedron.

Consequently, based on both the crystal field superposition model and bond-valence model calculations, it can be concluded that both V^{3+} and V^{4+} prefer the $M1,2$ site.