Zoisite and its many colors

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The mineral zoisite is a calcium alumosilicate belonging to the class of silicates, more exactly sorosilicate minerals. Its chemical formula is $Ca_2Al_3(SiO_4)(Si_2O_7)O(OH)$ and it crystallizes in the orthorhombic crystal system. It was first found at the Saualpe in Carinthia, Austria at the end of the 18th century. After the initial finds in Austria, zoisite has been found in many other localities such as in Norway, USA, Pakistan, Afghanistan, Kenya and Tanzania. While the pink thulite from Norway and the ruby bearing green zoisite (also known as anyolite) from Longido, Tanzania are used for carving or decorative purposes, the only occurrences of gem quality material so far are Alchuri in Pakistan where small amounts of grey, brownish green and sometimes multi-colored crystals have been found, and Merelani in Tanzania. The latter one became famous mostly for the blue-to-violet V-bearing variety of zoisite which was first documented in the 1970ies by Manuel de Souza and made its way into the hands of Tiffany's who suggested to market this new gem material under the name tanzanite (reportedly as zoisite sounds too close to suicide) (Cairncross, 2020; Liddicoat, 1968; Wilson *et al.*, 2009).

Of course, the most famous color of zoisite from Merelani is blue or violet. In the strict sense it is also only those colors that are allowed to be called tanzanite according to the CIBJO rules. All other colors must be called zoisite with the appropriate color descriptor, such as pink zoisite, however, the terms pink tanzanite or fancy tanzanite are frequently found, especially in the mineral trade where CIBJO does not apply. While in the early years much of the material found had a natural blue-to-violet color, most material mined later on was of yellow-brownish, purplish, or greyish color (Smith, 2011). Luckily, a simple heat treatment to temperatures of around 500-550 °C can turn such material into blue or violet (Schmetzer, 1978). The reason for the blue-to-violet coloration has soon been identified to be related to vanadium, however, there is still lots of discussion on its oxidation state – especially its fate during the heat treatment.

Figure 1. The various colors of zoisite in its rough and cut form.

We have collected samples mainly from the Merelani mines in Tanzania covering almost all known colors, including colorless, yellow, blue, green, pink and orange (Figure 1). Analysis of the material was carried out with UV-Vis-NIR spectroscopy as well as LA-ICP-MS to determine minor and trace elements (Table 1).

Colorless zoisite is much rarer than tanzanite and unsurprisingly the level of trace elements in such stones is very low. Despite the low abundancy of bands in the visible range, indicative bands in the NIR region can be found which allow identification of the crystallographic axes, as can be seen in Figure 2 (Smith, 2024). The α-ray has a band at 2470 nm, the β-ray one at 2300 nm and the γ-ray is indicated by a broad band at 1600 nm as well as strong absorption above 2400 nm.

Whereas the reason for the blue coloration of tanzanite is long known to be vanadium, the reason for the yellow to brown color, which often dominates in unheated tanzanite, is less well known. According to our findings, a correlation of titanium and a band at 445 nm in the γ-ray is given. Comparison of the band position and the bandwidth at half maximum of 5300 cm^{-1} leads us to the conclusion, that the reason for the yellow color is an Fe^{2+}-Ti^{4+} intervalence charge transfer (IVCT). This interpretation is in good agreement with data reported by Rondeau *et al*. (2018) and Taran and Koch-Müller (2011).

Green zoisites owe their color either a combination of the aforementioned chromophores vanadium and Fe-Ti-IVCT, where the contribution of yellow and blue have to be balanced, or there is a dominance of chromium, having absorption bands at 455, 488, 580, 650, 658 and 695 nm (Figure 3).

Pink zoisites, as well as thulite, owe their color trace amounts of manganese in its trivalent state. The oxidation state is very important, as only Mn^{3+} is a strong chromophore, whereas Mn^{2+} is almost colorless. Thus, conventional heating always results in destruction of the pink chromophore while heating under oxygen atmosphere can prevent discoloration along the α-ray (Schwarzinger, 2022).

A special unicorn amongst the zoisite colors is orange. While an easy explanation can again be given in the mixture of pink and yellow, some samples show an extremely high concentration of rare earth elements, of which Nd^{3+} can also be seen in the UV-Vis spectra. A summary of the coloring elements can be found in Table 1.

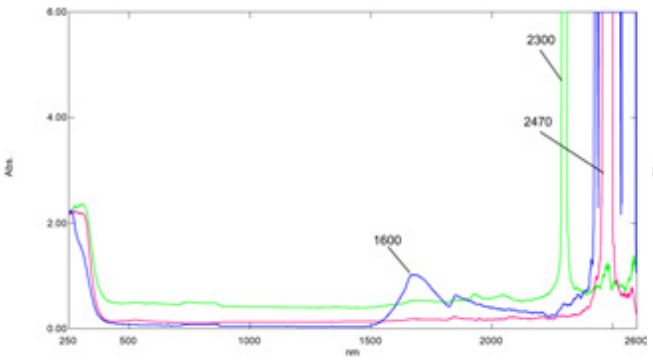

Figure 2. Polarized UV-Vis-NIR spectrum of a colorless zoisite (α-ray: red; β-ray: green; γ-ray: blue), optical pathlength 3.0 mm.

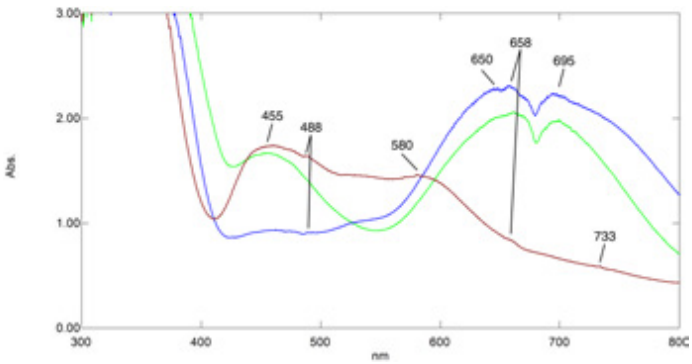

Figure 3. Polarized UV-Vis spectra of a 32.7 ct green zoisite dominated by chromium showing a green (γ-ray), bluish green (β-ray), and yellow-brown (α-ray) axis. Optical pathlengths are 16 and 17 mm.

Color	^{47}Ti	^{51}V	^{52}Cr	^{55}Mn	^{56}Fe	^{146}Nd
Colorless	190 (55-332)	172 (146-198)	9 (3-13)	40 (33-59)	0 (0-6)	0.6 (0.3-1.1)
Yellow	191 (26-927)	579 (78-1375)	34 (5-90)	46 (1-110)	30 (0-92)	54 (0.5-285)
Blue	225 (33-746)	1780 (392-3568)	150 (16-964)	69 (3-162)	121 (0-614)	54 (3-267)
Violet	144 (29-416)	922 (640-1476)	20 (8-48)	174 (64-428)	523 (38-1956)	70 (1-370)
Green	423 (45-1132)	1146 (675-2166)	144 (37-470)	20 (2-76)	9 (0-80)	15 (2-100)
Pink	156 (2-366)	318 (52-709)	14 (0-77)	298 (20-1067)	580 (16-2442)	387 (0.1-1666)
Orange	207 (118-422)	463 (456-1184)	50 (23-106)	132 (52-244)	171 (40-453)	998 (122-1882)
Greenish Brown	205 (132-345)	1234 (620-1899)	89 (31-147)	115 (64-212)	100 (26-238)	156 (30-599)

Table 1. Color contributing trace elements sorted by color.
Average values in ppmw with ranges in parentheses.

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