Zoisite – More than just Tanzanite

By Thomas Hainschwang and Franck Notari, GGTL Laboratories

Figure 1. An exceptional unheated purple pink zoisite of 2.06 carats. GGTL Collection. (Photo: T. Hainschwang)

Practically everybody knows tanzanite, the blue to violet gemstone from Tanzania, but by far not everybody knows that it is a variety of zoisite. It is even less known that zoisite is a species of the epidote group and that it occurs in a wide range of colors. Besides the well-known blue to purple color, this attractive gem material occurs in pink, orange, yellow, green and brown. While the vast majority of tanzanites are produced by heating greenish blue to brownish zoisite, the other color varieties are generally unheated, since most react unfavorably to such a treatment. As a gemstone, only tanzanite has found a large market, while the differently colored varieties remain largely unnoticed. In recent years, such zoisites have become objects of desire for more and more collectors and prices for attractive pieces have risen sharply. Today, certain colors of zoisite have largely surpassed the price of tanzanite, especially greens and pinks to purples. Even if some of these attractively colored zoisites are rare and supply can be difficult, they are worthy of recognition just like their big brother, tanzanite.

Background Information

Zoisite is a sorosilicate (hydrated calcium aluminum silicate) with the chemical formula $Ca_2Al_3 (Si_2O_7) (SiO_4) O(OH)$ with traces of Fe, Mn, Mg, Cr, Ti, Ca, Na, V, Sr, Ga and H_2O. It belongs to the orthorhombic crystal system and belongs to the minerals of the epidote group. It has a hardness of 6.5 to 7 and perfect {010} and imperfect {100} cleavage. It was named by Abraham Gottlob Werner in honor of the Austrian (today Slovenian) natural scientist, Baron Sigmund Zois Freiherr von Edelstein (1747-1819), who first identified the mineral that was discovered by Simon Prešern in 1805 on the Saualpe in Carinthia, Austria.

Today, the main source for zoisite is Tanzania, and here particularly the Merelani region with its major mines that produce mainly tanzanite, the blue to purple variety of zoisite, but also all other color varieties of zoisite and other minerals such as tsavorite garnet and diopside. The first samples of zoisites from Merelani were reported between 1959 and 1962; the first claim at the Merelani deposit, situated in the center of the Western part of the Lelatema Mountains, was registered by Manuel de Souza (1913-1969) in July 1967.

Today, the Merelani deposit consists of four major blocks called A, B, C and D; of these, the very large block C is operated by an important well-known company, while block B and D are operated by small-scale miners. Details on the history and development of the Merelani mines can be found in a paper by Wilson et al. (2009) in "The Mineralogical Record."

Figure 2. A heat-treated tanzanite of 8.84 carats. *(Photo: T. Hainschwang)*

The Different Color Varieties

Tanzanite: The blue to purple zoisites

The best known variety of zoisite is the blue- to purple-colored tanzanite (Figure 2). Tanzanite occurs almost exclusively in Tanzania, although some minor finds were reported from Kenya. The stones can be very large, the largest known but heavily included specimen weighs 6.5 kilograms and was found by TanzaniteOne in 2008; gemmy crystals of weights up to 2,500 carats and more have been reported.

The color of tanzanite that has been marketed extensively by Tiffany's and Co. in the United States and by Gebrüder Leyser in Europe at the end of the 1960s is tentatively related to its vanadium content. The precise mechanisms involved are much discussed but still not known with certainty. In most deeply colored samples, the vanadium content strongly dominates other chromophores, but chromium, manganese, titanium and iron are generally present in variable concentrations. The main problem is the behavior upon heat treatment which indicates that more complicated mechanisms such as simple charge transfers (as claimed by some) and/or color centers seem to play a role in the color of these zoisites. The pleochroic colors of unheated tanzanite are purple (alpha ray), blue (beta ray) and brownish to greenish yellow (gamma ray) (Figure 3); in heat-treated tanzanite, the gamma ray is transformed from brown yellow to greenish blue to blue, and in consequence the beta and the gamma ray look very alike.

By far, most tanzanites are obtained by heating brownish zoisites at 400°C to 700°C for a short time; the color modification starts at about 400°C but the process can be strongly accelerated at temperatures above 550°C. The color was found to remain unchanged up to 1000°C, when zoisite dehydrates and forms an opaque white crazed material that is chemically close to a feldspar (Figure 4). Figure 5 shows the polarized UV-Vis-NIR absorption spectra that correlate to the stone shown in Figure 4; it can be seen that the gamma ray spectrum is strongly modified by the heat treatment.

In very rare cases, tanzanite can occur in a chatoyant form (Figure 6, left); such cat's eye tanzanites exhibit a chatoyant band in intense reflected light, which is caused by abundant parallel empty and/or liquid-filled

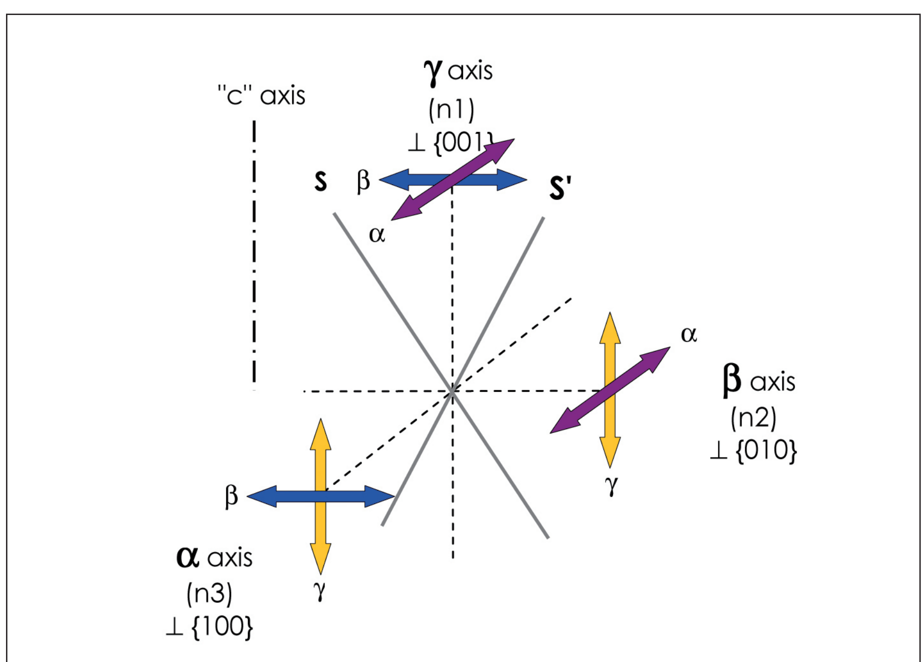

Figure 3. The correlation diagram that explains the axes, rays and associated pleochroic colors: S, S' optical axis, α, β, γ axis and α, β, γ rays.

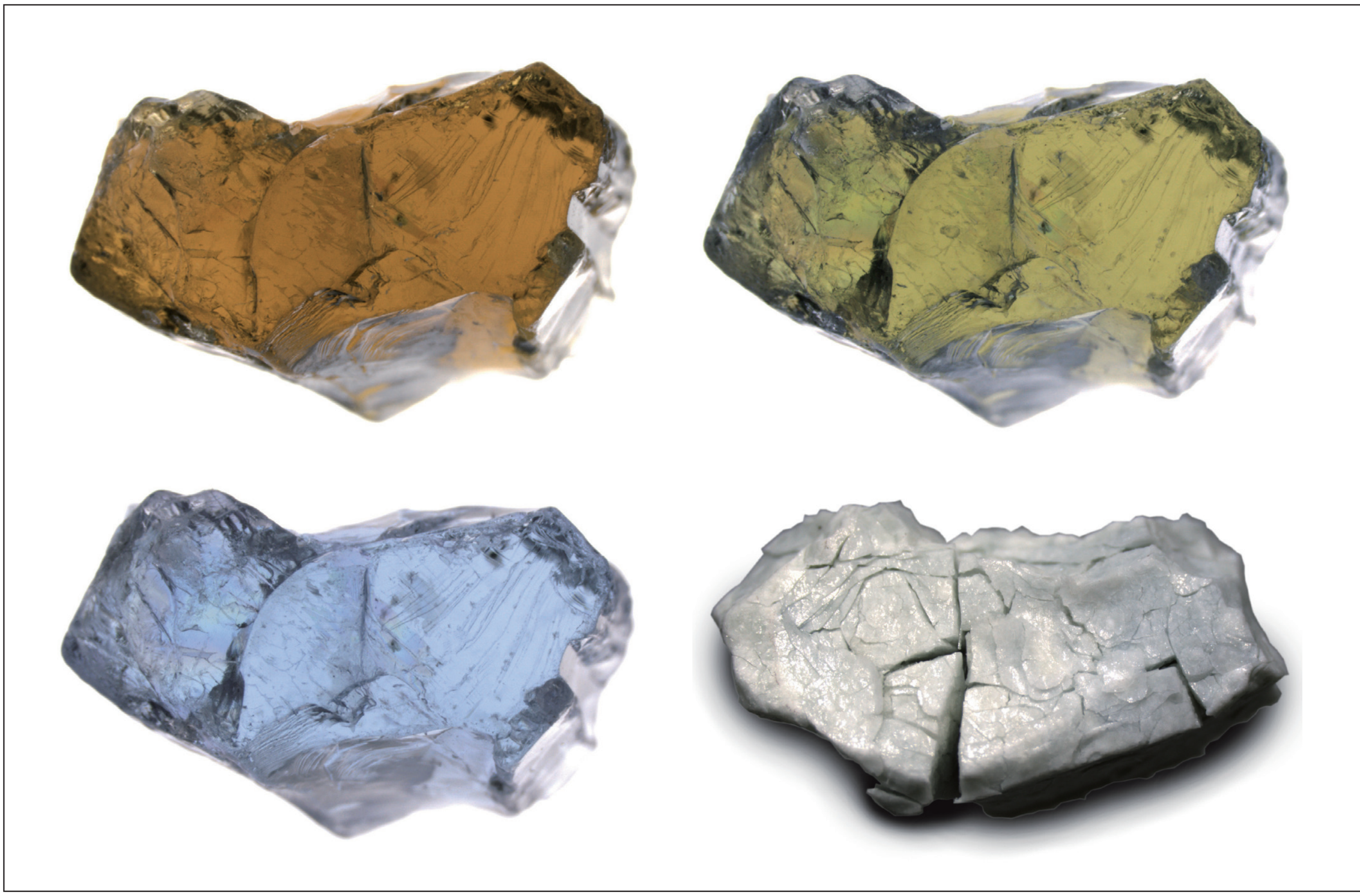

Figure 4. The behavior of brownish zoisite upon heat treatment; shown is the brown yellow gamma ray of the alpha axis before heating (top left) and after different heat treatment steps of 410°C (top right), 500°C (bottom left) and 1000°C (bottom right). GGTL Collection. (Photos: T. Hainschwang)

hollow growth channels (Figure 6, right). Cat's eye tanzanite is so rare that the authors have seen only very few specimens so far, the one in Figure 5 being in their collection.

Pink zoisite

The rare and much sought-after transparent pink variety of zoisite can come in shades of pale pink up to very saturated purple pink (Figure 1). They are found in Tanzania but as much as is known, not in block C; they occur as sporadic finds in pockets and good stones of an appreciable size are not frequently available. In consequence even pink zoisites larger than 1 carat are uncommon.

The pleochroic colors of this variety are strong pink (alpha ray), blue (beta ray)

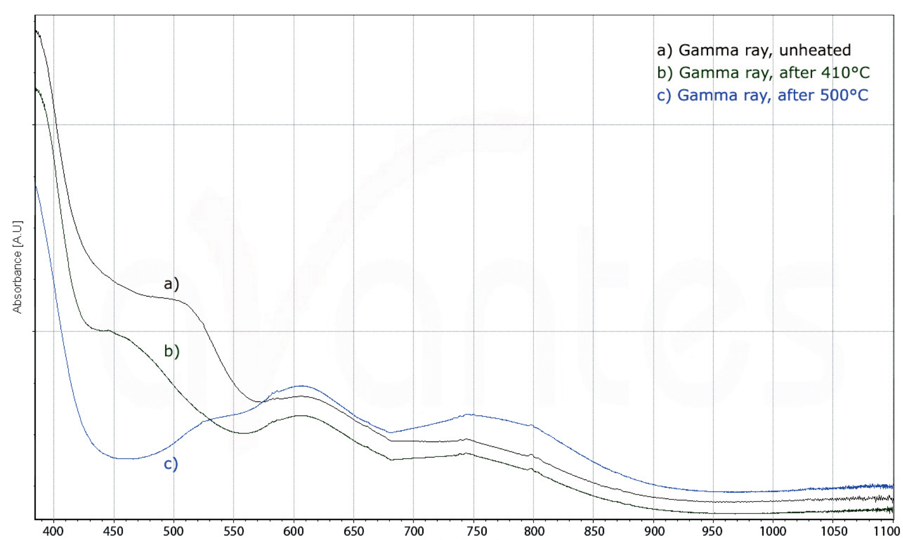

Figure 5. The polarized UV-Vis-NIR spectra of the sample shown in Figure 3. Trace (a) corresponds to the brown yellow gamma ray of the alpha axis before heating, trace (b) to the "olive" gamma ray after 410°C and trace (c) to the blue gamma ray after 500°C.

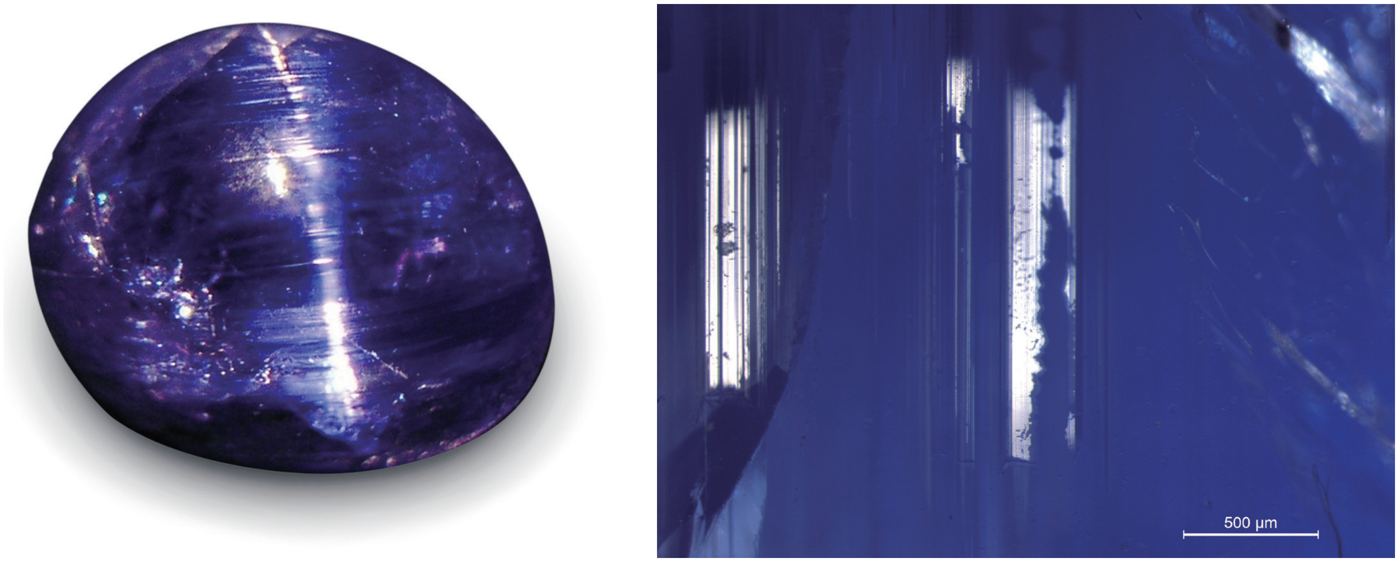

Figure 6. A heat-treated tanzanite cat's eye of 8.89 carats. The image on the right shows hollow empty and filled growth channels responsible for the chatoyancy. GGTL Collection. (Photos: T. Hainschwang.)

and strong yellow (gamma ray), just like they are for unheated tanzanite. The intensity of the individual colors is very different though, since the pink ray dominates strongly in the pink variety, while the blue ray dominates in the tanzanites.

The color of such pink-colored zoisite is caused by a mechanism that is at the moment not quite understood, just like tanzanite. In the pink zoisites analyzed at the GGTL Laboratories the chromophore trace elements were often distributed the following ratios: Fe>>V>Mn>>Cr>Ti. The manganese content was distinctly higher than in zoisites of other colors. Likely the interaction of the various chromophores with dominant Mn related absorption is responsible for the pink coloration.

Blue-green to yellowish green zoisite

Green zoisites are also desired by collectors and connoisseurs. These stones can vary in color from blue-green to yellowish green and are very rare (Figure 7). While most of the green zoisites seem to originate from Tanzania, some have been reported from Pakistan (Barot and Boehm, 1992). The pleochroic colors of such rare zoisites are green, blue and brown; upon heat treatment, the green ray is modified to greenish blue while the brown ray stays brown; in consequence, such heat-treated stones look greenish blue. Since the value of the greenish blue color is significantly lower than the original green color, it is very unlikely that somebody intentionally heat treats these uncommon zoisites.

Figure 7. Two unheated green zoisites; on the left, a blue-green stone of 2.12 carats and on the right, a yellowish green zoisite of 44 points. GGTL Collection. (Photos: T. Hainschwang)

Figure 8. An unheated orange zoisite of 1.86 carats. GGTL Collection. (Photo: T. Hainschwang)

The curious pleochroism can be understood when the green ray is understood as a yellow gamma ray on top of a greenish blue color, and when the brown ray is interpreted as a pink alpha ray on top of the same greenish blue hue; the beta ray is practically equal to the greenish blue "background color" and is thus not discernible as an individual color.

The color origin of green zoisites is again the complex interaction of a mix of chromophores, with dominance of chromium which is responsible for the greenish blue "background color". The blue-green zoisite in Figure 7 contains approximately equal concentrations of vanadium and chromium, while the chromium strongly dominates the vanadium in the yellowish green zoisite shown in Figure 7.

Orange zoisite

Another exotic color of zoisite is orange. Such stones are often of relatively light tone and low saturation and stones like the one shown in Figure 8 are very uncommon. These stones originate from Tanzania; more details are not known. The pleochroic colors of orange zoisites are also yellow, pink and blue, with yellow and pink strongly dominating the blue ray.

Chemically, the orange zoisites are rather unique since they are very low in vanadium, chromium and manganese, but they are rich in the rare earths Cerium and Neodymium which play a direct role in the color of these stones. Other mechanisms are likely involved since the broad bands and the continuum cannot be explained by elevated rare earth element content.

Yellow zoisite

Yellow zoisites are generally of brownish yellow to brown yellow coloration (Figure 9) and the samples analyzed by the authors represented the same material that is heat treated to produce tanzanite. In these dominantly yellow stones, the vanadium dominated all other chromophores but the vanadium content was very low compared to samples that are used for heat treatment. The pleochroic colors are yellow, pink and blue; as expected, the yellow ray strongly dominates the other ones. Now the origin of this strong yellow color is unknown. No chromophores in the sample seemed to correlate with the yellow coloration so a more complex color mechanism must be the reason for the deep yellow coloration.

Discussion and Concluding Remarks

The different main color varieties of zoisite have been presented.

These often rare colors represent superb specimens for collectors and connoisseurs and they would certainly attract many more clients if they knew about their existence. In contrast to tanzanite, the vast majority of differently colored zoisite is untreated; most of them react in an unfavorable way to heat treatment since in contrast to the tanzanites their attractive color needs the yellow gamma ray.

Figure 9. An unheated yellow zoisite of 1.21 carats. GGTL Collection. (Photo: T. Hainschwang)

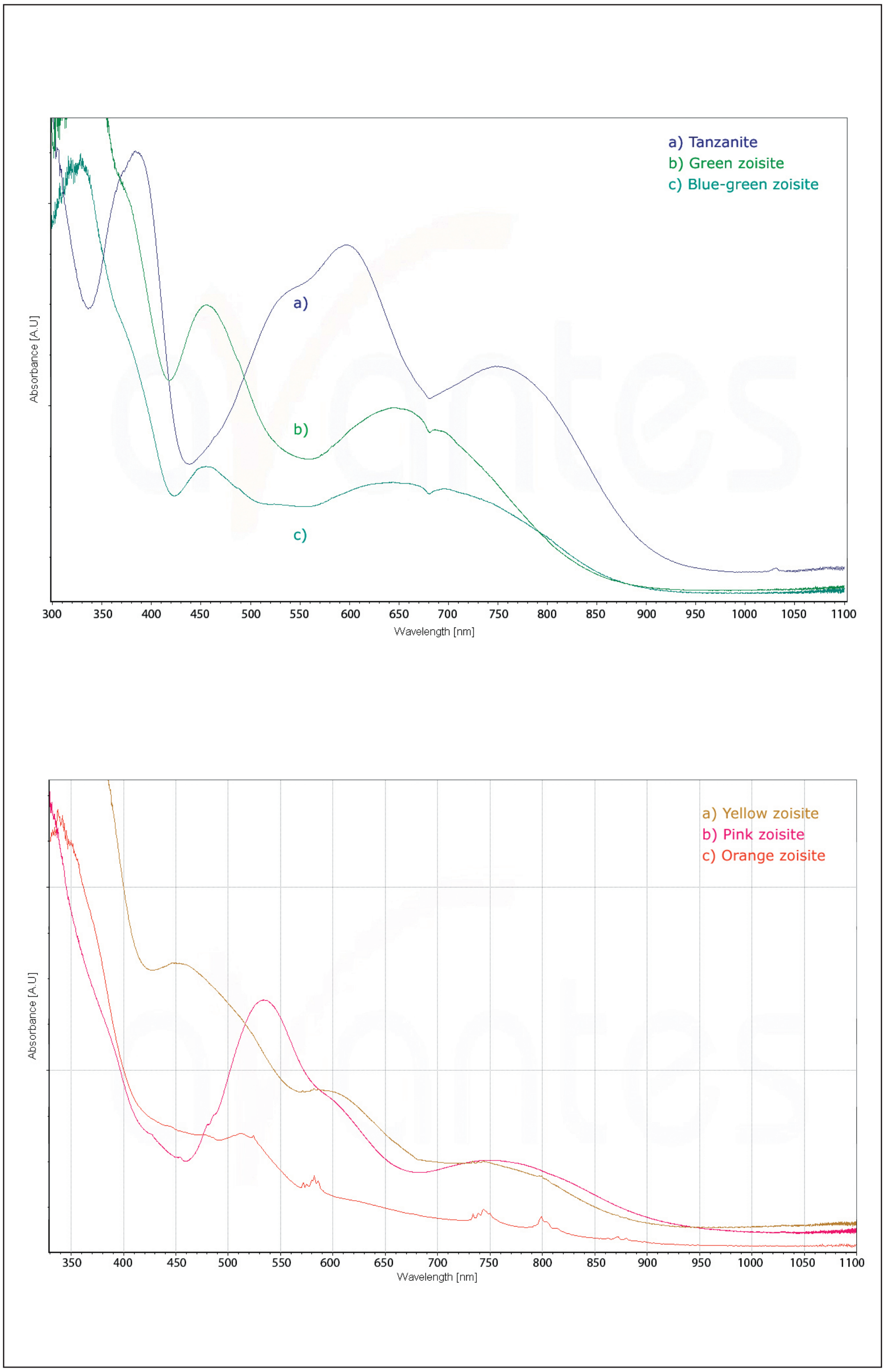

Figure 10. The non-polarized UV-Vis-NIR spectra of the differently colored zoisites shown in figures 1, 5, 6, 7 and 8.

Besides the presentation of the range of attractive colors of zoisite, this study is scientifically interesting; all colors except truly red zoisite have been analyzed by the authors and the results from this raise many questions on the origin of the different colors of zoisite. It can be seen that all colors of zoisite exhibit the same pleochroic colors with exception of green samples that appear to have a greenish blue "background" color. Now the question must be answered why the intensity of the individual rays can vary so strongly in order to cause the large range of colors presented in this paper.

Figure 10 shows the range of UV-Vis-NIR absorption spectra of the zoisites included in this article; the large variation from spectrum to spectrum shows that the balance of the same chromophores present in differently colored zoisites cause all these colors. Only green and orange zoisites have differences in color origin, since additionally they contain more significant concentrations of chromium and rare earths respectively.

Even though chemically the samples are similar the balance of the different chromophoric elements induces very different absorption spectra.

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