

The role of vanadium and titanium in natural and synthetic chrysoberyl and alexandrite – coloration, chatoyancy and asterism

Karl Schmetzer¹, Michael S. Krzemnicki², Thomas Hainschwang³, Heinz-Jürgen Bernhardt⁴

¹ 85238 Petershausen, Germany, SchmetzerKarl@hotmail.com

² SSEF Swiss Gemmological Institute, CH-4001 Basel, Switzerland, gemlab@ssef.ch

³ GGTL Laboratories, Gemlab (Liechtenstein)/GemTechLab, FL 9496 Balzers, Liechtenstein/CH 1227 Geneva, Switzerland, thomas.hainschwang@ggtl-lab.org

⁴ ZEM, Institut für Geologie, Mineralogie und Geophysik, Ruhr-University, 44780 Bochum, Germany, Heinz-Juergen.Bernhardt@rub.de

Vanadium-bearing natural chrysoberyl is known from Tunduru, Tanzania (Johnson and Koivula, 1996; Bank et al., 1997; McClure, 1998), and vanadium-bearing synthetic chrysoberyl was also described (Krzemnicki & Kiefert, 1999; Schmetzer & Bosshart, 2010). Vanadium-bearing chrysoberyl crystals show weak pleochroism, but no colour change between daylight and incandescent light. Chrysoberyl with almost equal amounts of vanadium and chromium, e.g. from Orissa or Andrah Pradesh, India, are also bright green in daylight, but change their colour in incandescent light only to a pale grayish green, almost colourless (see again Schmetzer & Bosshart, 2010).

Titanium-bearing synthetic chrysoberyl crystals are known for technical use as laser materials, and faceted gemstones were briefly mentioned by Krzemnicki & Kiefert (1999). It is assumed that the pink coloration of these samples is caused by trivalent titanium. Furthermore, synthetic titanium-bearing alexandrite cat's-eyes as well as synthetic asteriated alexandrite is also known (Kane, 1987; Scarratt, 1988; Koivula et al., 1988; Schmetzer & Hodgkinson, 2011). Minute needle-like particles are found in three orientations with the alexandrite crystals, causing three different light bands which are inclined to each other at 60°.

Vanadium-bearing synthetic chrysoberyl (Figure 1) has been grown by Kyocera in Japan. Vanadium contents were found in the range of 0.11 to 0.13 wt% V_2O_3 . Vanadium-bearing natural chrysoberyl in which the vanadium contents exceed the chromium contents of the samples were examined from four different sources, from Tunduru in Tanzania, from Ilakaka in Madagascar, from Sri Lanka and from Mogok, Myanmar (Figure 2). The samples from Ilakaka, Madagascar, revealed vanadium contents in the range of 0.02 to 0.15 wt% V_2O_3 with chromium being always below 0.01 wt% Cr_2O_3 . Vanadium-bearing chrysoberyl from Tunduru, Tanzania, can be subdivided into two varieties. Some lighter bluish green samples are almost chromium-free (with Cr_2O_3 at or below 0.01 wt%) and vanadium contents in the range of 0.04 to 0.10 wt% V_2O_3 . Some more intense bluish green chrysoberyls from Tunduru with vanadium contents of 0.16 and 0.18 wt% V_2O_3 showed chromium contents of 0.03 to 0.04 wt% Cr_2O_3 . The somewhat more yellowish green vanadium-bearing chrysoberyls from Sri Lanka, in general, showed chromium contents in the range of or only slightly below the vanadium contents of the samples. One crystal, for example, showed vanadium contents of 0.08 wt% V_2O_3 with chromium contents of 0.05 wt% Cr_2O_3 . The extremely intense bluish green gem chrysoberyls from Mogok, Myanmar, showed distinctly higher vanadium and chromium contents. For one faceted gemstone, the amounts of colour causing trace elements were determined as 0.38 wt% V_2O_3 and 0.24 wt% Cr_2O_3 . A similar chrysoberyl from Mogok was already described by Payne (1956).

Absorption spectra of the synthetic vanadium-bearing chrysoberyls and the chromium-free or almost chromium-free natural samples show the known absorption maxima of trivalent vanadium in chrysoberyl (Bukin et al., 1980). Additional iron bands were recorded in natural samples from Tanzania, Madagascar, and Sri Lanka, the bright green samples from Myanmar were iron-free. According to the overlap of the absorption bands of trivalent vanadium and chromium in chrysoberyl (Figure 3), no separated absorption maxima for vanadium and chromium were recorded. There is, however, a shift observed for the main absorption maximum in the visible range. This maximum was recorded

for chromium-free, vanadium-bearing samples in the range of 608 nm, and shifts towards lower wavelengths with increasing chromium contents. For the chrysoberyl from Myanmar mentioned above, the maximum of this strong absorption band was observed at 589 nm.



Figure 1. Rough and faceted vanadium-bearing synthetic chrysoberyls produced by Kyocera in Japan in daylight; size of the rough crystal above right 15.5 x 14.5 x 15.5 mm, weight 52.50 ct, the faceted sample below left weighs 0.49 ct and measures 6.0 x 4.0 mm. Photo by K. Schmetzer.



Figure 2. Natural and synthetic vanadium-bearing chrysoberyls; from left to right (a) three chrysoberyls from Sri Lanka, (b) chrysoberyl from Mogok, Myanmar, (c) three chrysoberyls from Tunduru, Tanzania, (d) two synthetic chrysoberyls produced by Kyocera in Japan; daylight, the triangular chrysoberyl from Tunduru weighs 0.38 ct and measures 4.3 x 4.2 mm. Photo by K. Schmetzer.

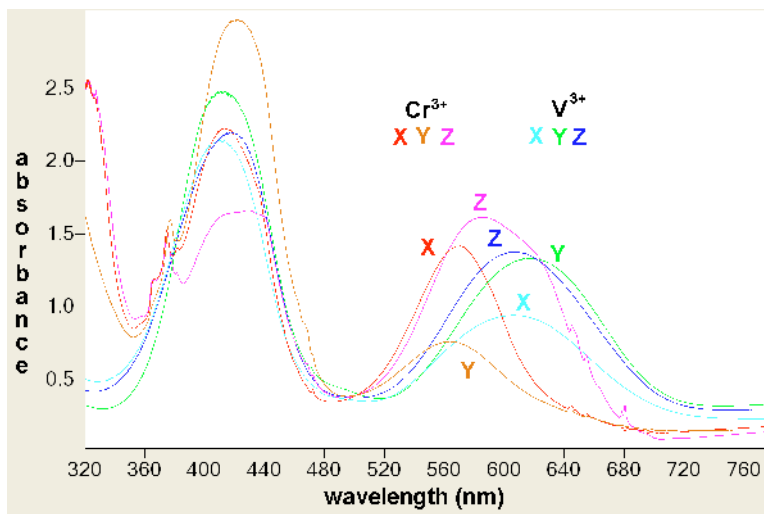


Figure 3. Plot of the polarized absorption spectra of chromium (Cr^{3+}) and vanadium (V^{3+}) in chrysoberyl; both transition metal ions show two strong absorption bands, a first absorption band at higher wavelength, and a second absorption band at lower wavelength. For all three directions (X, Y and Z) the absorption maxima for the first absorption band of vanadium are located at higher wavelengths than the maxima of the first chromium absorption band; for the second absorption band of vanadium the maxima are in the range of the maxima representing the second chromium band. Spectra were recorded from a synthetic alexandrite grown by Creative Crystals (for chromium) and from a synthetic chrysoberyl grown by Kyocera (for vanadium).

Titanium-bearing synthetic chrysoberyl (Figure 4) has been grown by Kyocera in Japan. Titanium contents were found in the range of 0.21 to 0.37 wt% TiO_2 . Synthetic alexandrites showing asterism or chatoyancy, on the other hand, revealed higher titanium-contents of 0.46 to 0.56 wt% TiO_2 , with chromium and vanadium contents of the range of 0.23 to 0.26 wt% Cr_2O_3 and 0.11 to 0.12 wt% V_2O_3 , respectively. This material (Figure 5) was also produced by Kyocera

in Japan. Chatoyancy and asterism are due to three series of minute needle-like inclusions, which are located in planes parallel to the a (100) pinacoid. These elongated particles (Figure 6) are oriented parallel to the c-axis of the chrysoberyl crystals and at angles of about $+60^\circ$ and -60° to this direction.

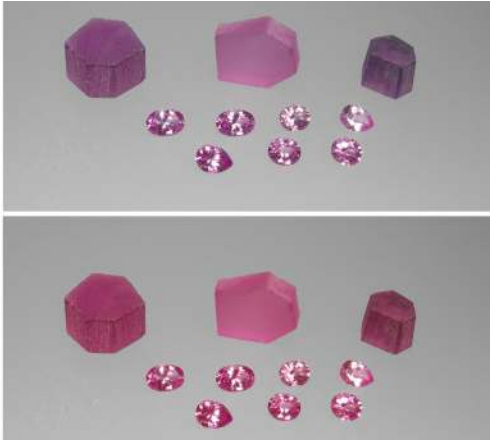


Figure 4. Rough and faceted titanium-bearing synthetic chrysoberyls produced by Kyocera in Japan in daylight (above) and incandescent light; size of the rough crystal above left 16.0 x 15.5 x 10.0 mm, weight 34.12 ct, the faceted sample below left weighs 1.08 ct and measures 7.8 x 5.7 mm. Photo by K. Schmetzer.

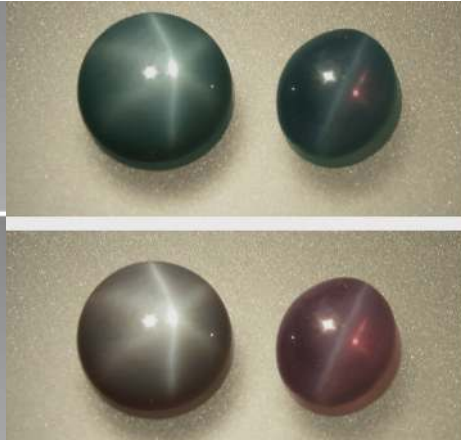


Figure 5. Synthetic asteriated alexandrite (left, 2.62 ct, diameter 8.0 mm) and synthetic alexandrite cat's-eye (1.55 ct, 7.0 x 6.0 mm) produced by Kyocera in Japan in daylight (above) and incandescent light. Photo by K. Schmetzer.

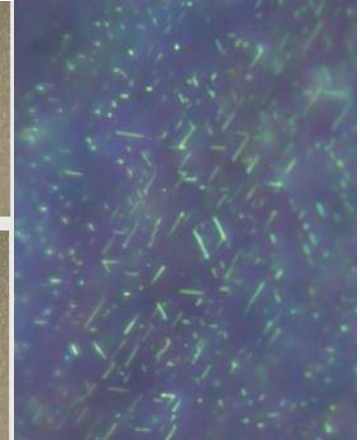


Figure 6. A thin section of an asteriated synthetic alexandrite from Kyocera oriented almost parallel to the a pinacoid shows three series of needles which form angles near 60° to each other. Reflected light, crossed polarizers, field of view 56 x 42 μm . Photo by H.-J. Bernhardt.

The production of synthetic chrysoberyl and alexandrite cat's-eyes is described in numerous Japanese and international patent applications, most of them published in the 1980s.

The production of alexandrite cat's-eyes involves a two-step growth and annealing process. The first step includes the production of homogeneous single crystals containing titanium oxide as dopant. Crystal growth is performed under neutral (e.g. argon or nitrogen) or reducing atmospheres and titanium is present in its trivalent state. In the second step annealing of the crystal at elevated temperatures in an oxidizing atmosphere is performed. During this second part of the process titanium is oxidized and elongated particles, most probably rutile needles, are precipitated. These exsolved particles are responsible for chatoyancy or asterism of the material when cut as a cabochon. The observation of one or three light bands in the center of the cabochon is only dependant of the orientation of the cut.

Absorption spectra of the synthetic titanium-bearing chrysoberyls and the chromium-free or almost chromium-free natural samples show the known absorption maxima of trivalent titanium in chrysoberyl (Segawa et al., 1987). Absorption spectra of the alexandrite cabochons showed a chromium spectrum with somewhat less transparency around 500 nm, i.e. in the area between the two strong chromium absorption bands. In this area, the known absorption maxima of trivalent titanium in chrysoberyl are located (Figure 7). Thus, the colour and pleochroism of the Kyocera synthetic chatoyant or asteriated alexandrites is understood if we assume the presence of various amounts of titanium in its trivalent state (in addition to chromium and vanadium as main colour causing trace elements). Most probably, not all titanium is exsolved by the heating step of production to form the minute rutile needles.

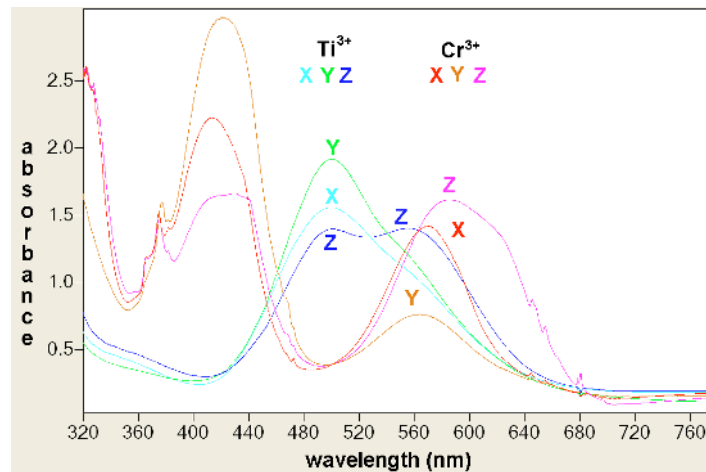


Figure 7. Plot of the polarized absorption spectra of chromium (Cr^{3+}) and titanium (Ti^{3+}) in chrysoberyl; for all three directions (X, Y and Z) the absorption maxima for the strong titanium band are located between the two strong chromium absorption bands; for samples which contain distinct amounts of chromium together with titanium in its trivalent state, only X is intense red orange, and Y and Z become very dark, almost non-transparent. Spectra were recorded from a synthetic alexandrite grown by Creative Crystals (for chromium) and from a synthetic chrysoberyl grown by Kyocera (for titanium).

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