The influence of V^{3+} on the colour of rubies and emeralds, shown by spectral fitting of UV/Vis/NIR absorption spectra

Tom Stephan[1,2], Tobias Häger[2], Ulrich Henn[1] and Wolfgang Hofmeister[2]

[1]German Gemmological Association, Idar-Oberstein, Germany
[2]Center for Gemstone Research, Johannes Gutenberg-University, Mainz, Germany
t.stephan@dgemg.com

Born in Idar-Oberstein, Germany.
Study of geoscience at the Johannes Gutenberg University in Mainz, Germany. Master thesis (2016) with gemmological background. Ph.D. thesis (since 2016) with gemmological background in work. Since 2014 scientific assistant for research and education at the German Gemmological Association. Author of various articles in international journals.

Abstract

The red colour of rubies is due to the replacement of Al^{3+} by Cr^{3+}. If present during growth, however, they can incorporate trivalent vanadium (V^{3+}), too, which can also affect the colour of corundum (HARDER, 1969, GÜBELIN, 1975, SCHMETZER, 1978, 1982, FRITSCH & ROSSMAN, 1988 & STEPHAN et al., 2018). On the other hand, the influence of V^{3+} on the colour of emerald is stronger, which is why the colour cause for emeralds is given with Cr^{3+} and/or V^{3+} (WOOD & NASSAU, 1968, SCHMETZER, 1978, 1982 & FRITSCH & ROSSMANN, 1988).
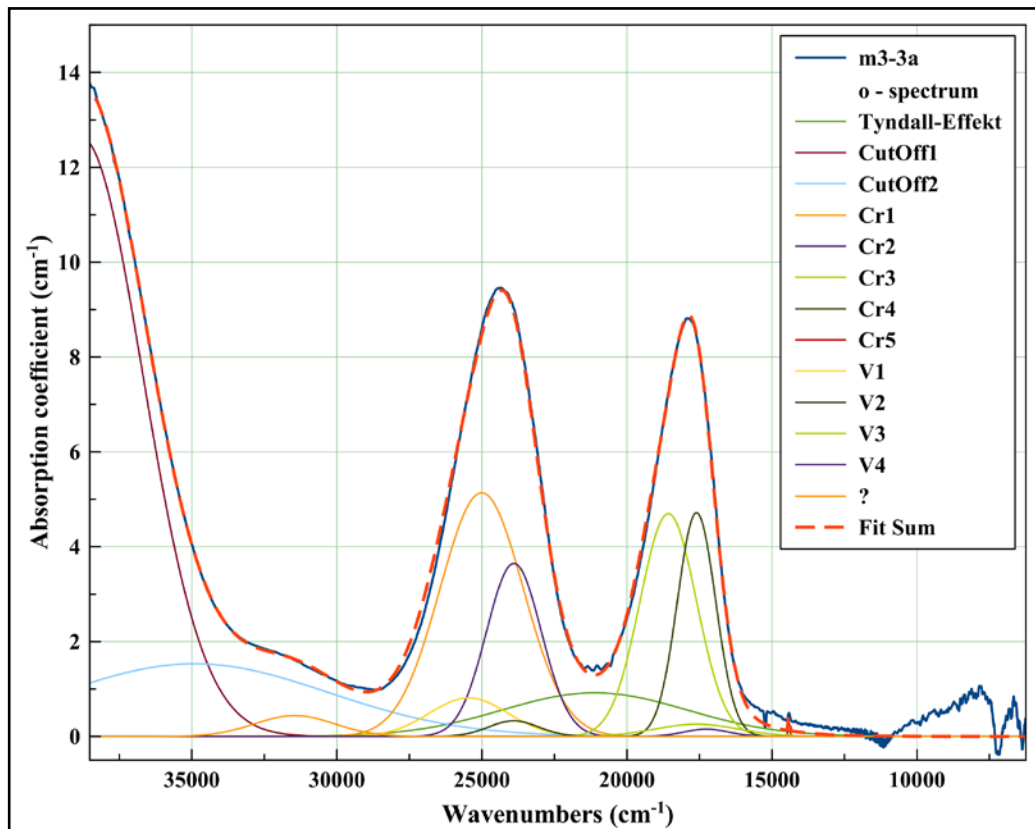
The spin-allowed absorption bands of the chromophores strongly overlap each other, so a just visual distinction between a Cr^{3+}- and V^{3+}-colouration from an absorption spectrum, especially if a mixture of both elements causes the colour, is difficult without a chemical analysis.

Two strong spin-allowed absorption bands dominate the visible range of the ultraviolet/visible/near-infrared (UV/Vis/NIR) absorption spectra of minerals coloured by Cr^{3+} and V^{3+} (in octahedral oxygen-coordination). A third spin-

Fig. 1 A ruby from Mogok, Myanmar (0.56 ct) and an emerald from Colombia (2.59 ct) - both stones are coloured mainly by Cr^{3+} with a weak influence of V^{3+}.

Fig. 2   The o-spectrum of a ruby from Mogok, Myanmar, decomposed mathematically by spectral fitting using the Cr^{3+}- and V^{3+}-models for ruby.

allowed absorption band is located in the UV-region. Because of oxygen-metal charge transfer, it is often not visible, but has no impact on the final colour. In addition, the spin-forbidden transitions for Cr^{3+} and V^{3+} and luminescence have just a little impact on the visible colour. Beside these absorption features, also other factors may influence the colour, e.g. scattering of light (Tyndall-effect), other colouring trace elements, as well as the absorption edge towards the UV-region (cut-off). In UV/Vis/NIR absorption spectra, all these factors overlap each other. With spectral fitting however, it is possible to investigate each of them individually.

For this study, the UV/Vis/NIR absorption spectra of various natural and synthetic chromium- and/or vanadium bearing rubies and emeralds were decomposed into Gaussian and Lorenz curves, to subdivide the overlapping Cr^{3+} and V^{3+} absorption bands. The curve fitting software MagicPlot Pro has been used. As an example figure 2 shows the absorption spectrum of a ruby from Mogok, Myanmar, which has been decomposed by spectral fitting. For both, ruby and emerald the spin-allowed absorption bands of Cr^{3+} and V^{3+} have been fitted

with four Gaussian curves each (Cr1-4 and V1-4) because of their asymmetry.

Based on (natural and synthetic) rubies and emeralds solely coloured by Cr^{3+} or V^{3+} and with known sample thickness, eight models were developed - two for each cause of colour (one for the e-, one for the o-spectrum) in each of the gemstones (cf. STEPHAN et al., 2018). Both, the applicability of the models and the transferability to the absorption spectra of natural rubies and emeralds from various occurrences as well as the correlation with chemical analyses were successfully tested.

These models were then used to calculate the theoretical absorption spectra of rubies and emeralds coloured solely by Cr^{3+} or V^{3+}, with varying concentrations of these elements - starting from 0 ppm in 800 ppm-steps up to 9600 ppm Cr^{3+} or V^{3+} (figure 3 and 4). Afterwards, the software ColorMaster viewer has been used to calculate the colour (as observable in D65 daylight) for each of the theoretical absorption spectra. This program calculates colour in the CIE L*a*b* system, a system which describes all perceptible colours, using a three-dimensional colour space in which the brightness value L* stands perpendicular to the colour space (a*,b*).

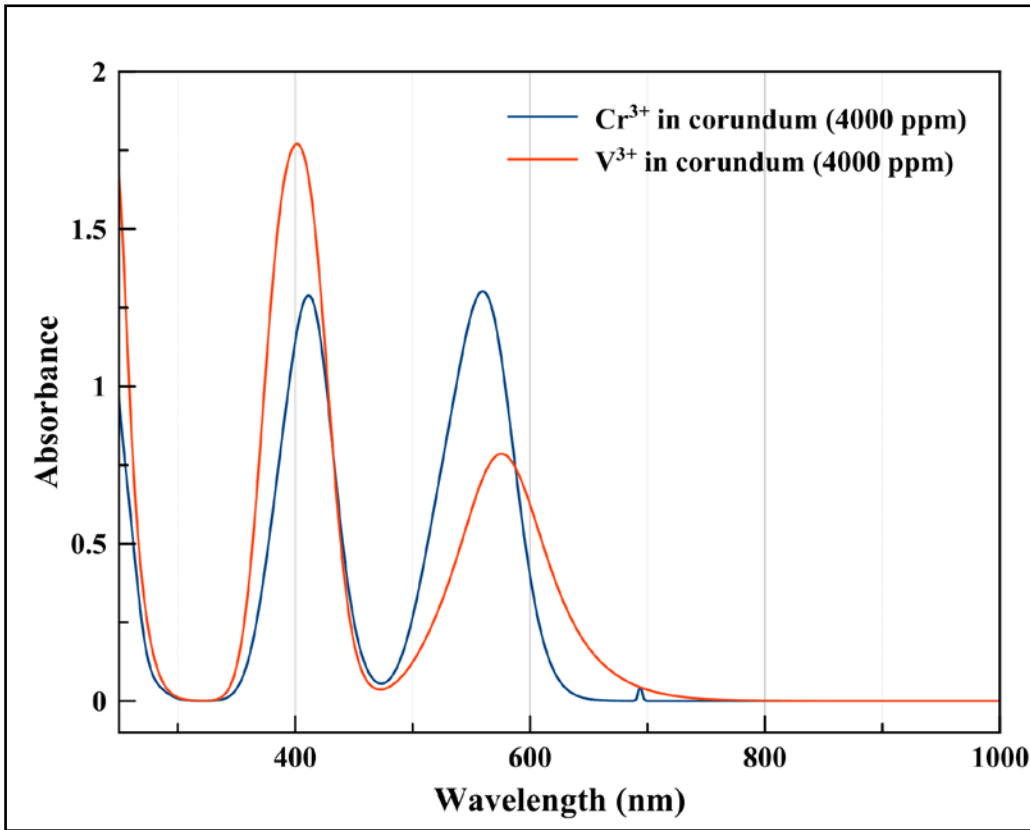Fig. 3 Comparison of the o-spectra of corundums coloured solely by 4000 ppm Cr^{3+} resp. V^{3+}.
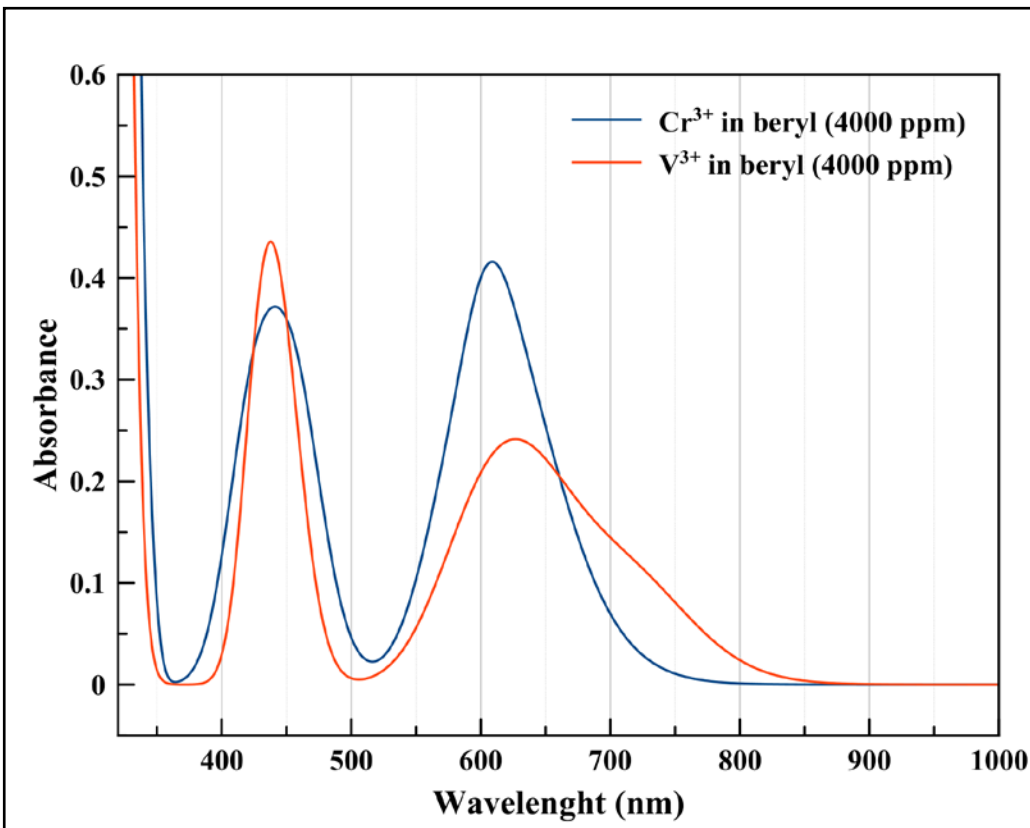

Fig. 4 Comparison of the o-spectra of beryls coloured solely by 4000 ppm Cr^{3+} resp. V^{3+}.

Figures 5 and 6 show the resulting colours for these theoretical absorption spectra; for clarity, the trends are shown as lines. The results show, that Cr^{3+} produces a red colour in corundum (ruby), ranging from a purplish-red (o-spectrum) to an orangey-red (e-spectrum). V^{3+} on the contrary produces the blueish-green colour (in daylight) of colour-change sapphires. Also shown in figure 5 is the colour of a ruby from Mogok, Myanmar (e-spectrum, red point). The blue point shows the

Fig. 5　The influence of V^{3+} on the colour of rubies shown at the example of a ruby from Mogok, Myanmar (the red point shows the stones colour (o-spectrum), the blue point the colour if the influence of V^{3+} is subtracted).
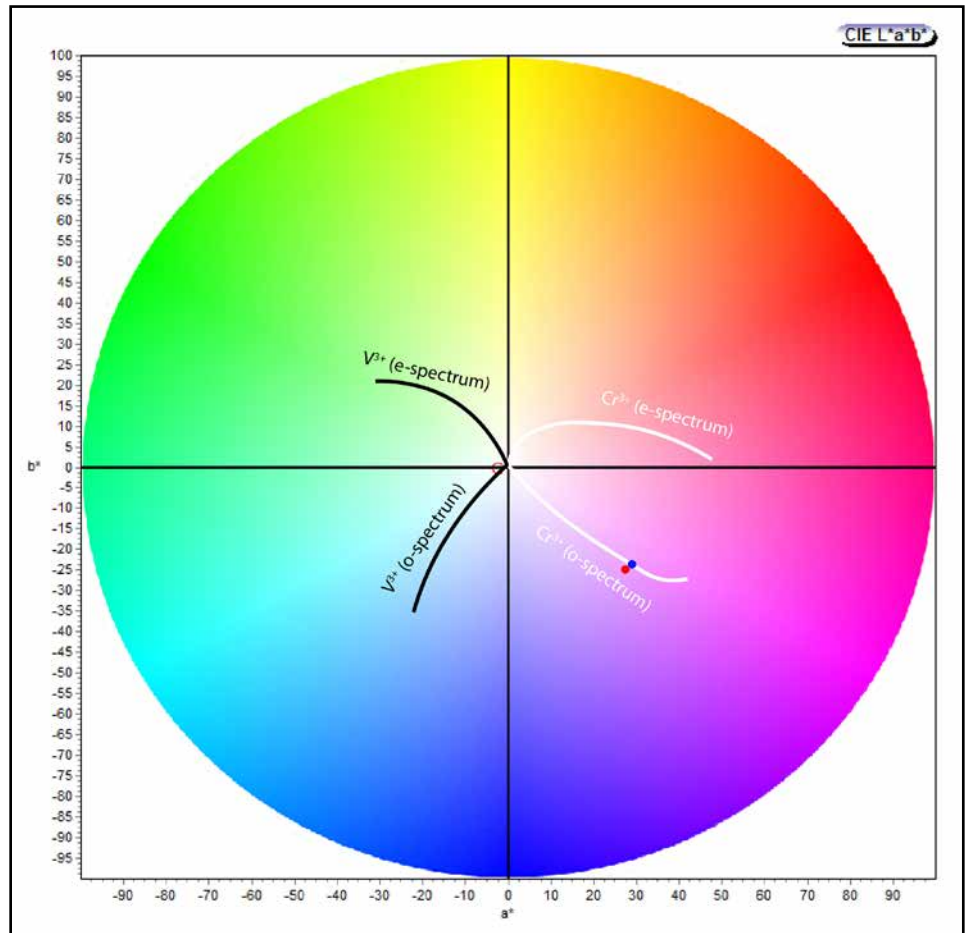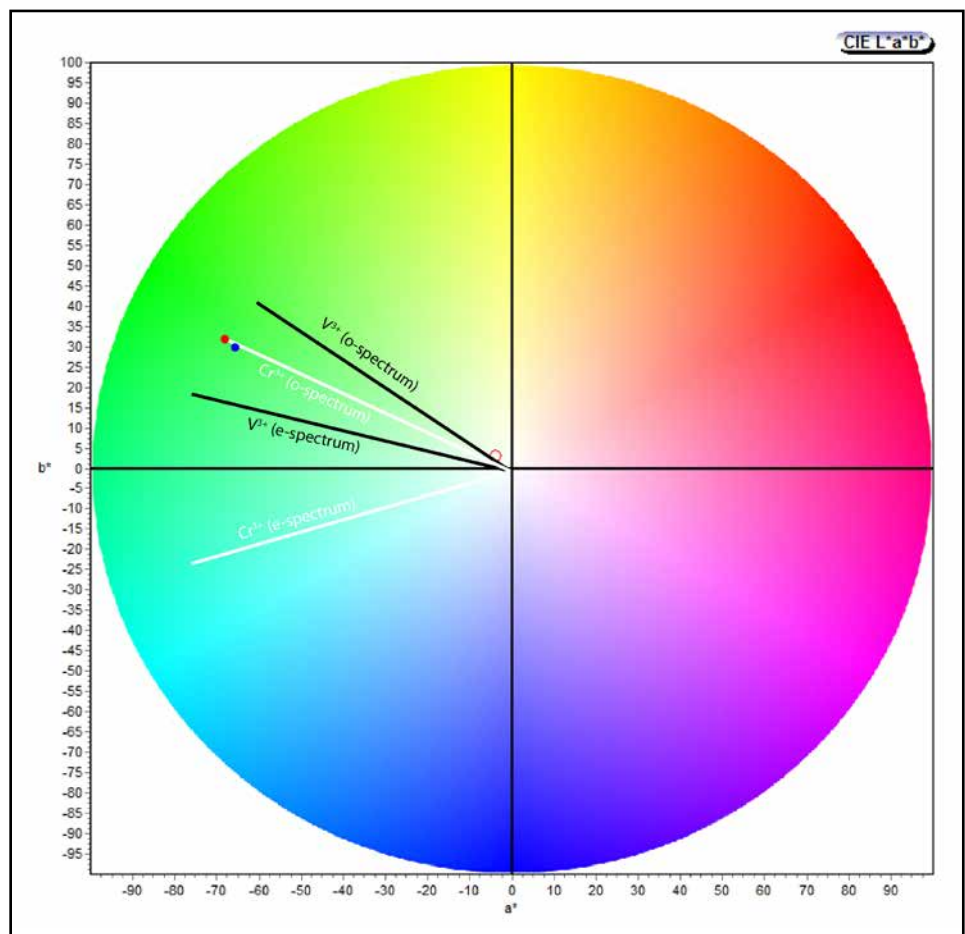

Fig. 6　The influence of V^{3+} on the colour of emeralds shown at the example of a Colombian emerald (the red point shows the stones colour (o-spectrum), the blue point the colour if the influence of V^{3+} is subtracted).

resulting colour of the stone when the influence of V³⁺ is subtracted.

For emerald (figure 6) both, Cr³⁺ and V³⁺ produce a green colour, whereby Cr³⁺ produces a blueish-green colour and V³⁺ a purer green with a lesser strong pleochroism. The red point in figure 6 shows the colour of a Colombian emerald (o-spectrum), the blue point the resulting colour when the influence of V³⁺ is subtracted.

Already SCHMETZER (1982) described that in general Cr- resp. V-impurities intensify the colour intensity of V- resp. Cr-bearing minerals. Spectral fitting used in the way described here, however, shows, that V^{3+} influences not only the intensity of a colour but also its hue. In rubies, it produces a more violetish hue, in emerald a purer (less blueish) green.

The results presented are part of the first author's ongoing PhD thesis, with one aim to formulate a model for each cause of colour in corundum. This would allow a simultaneous quantification of the involved concentration of the involved chromophores and their colour effect - also for mixed colours.

Furthermore, the applicability for faceted samples as well as the transferability of the method to other gemstones will be developed and tested.

References

FRITSCH, E. & ROSSMAN, G. R., 1988. An update on color in gems. Part III: Colors caused by band gaps and physical phenomena. Gems & Gemology, 24(2), 81-102.

GÜBELIN, E. J., 1975. The Color Treasury of Gemstones. Elsevier Phaidon, London.

HARDER, H., 1969. Farbgebende Spurenelemente in den natürlichen Korunden. Neues Jahrbuch für Mineralogie, Abhandlungen, 110, 128-141 (in German).

SCHMETZER, K., 1978. Vanadium III als Farbträger bei natürlichen Silikaten und Oxiden - ein Beitrag zur Kristallchemie des Vanadiums. Dissertation, Ruprecht-Karl-university, Heidelberg (in German).

SCHMETZER, K., 1982. Absorptionsspektroskopie und Farbe von V3+-haltigen natürlichen Oxiden und Silikaten - ein Beitrag zur Kristallchemie des Vanadiums. Neues Jahrbuch für Mineralogie, Abhandlungen, 144(1), 73-106 (in German).

STEPHAN, T., HÄGER, T., HENN, U. & HOFMEISTER, W., 2018. Quantitative Determination of Cr³⁺ and V³⁺ Contents in Rubies by Spectral Fitting of UV-Vis-NIR Spectra. Gems & Gemology, 54(3), 345-355.

WOOD, D. L. & NASSAU, K., 1968. The characterization of beryl and emerald by visible and infrared absorption spectroscopy. American Mineralogist, 53, 777-800.