

BLUE COLOUR-CHANGING KYANITE FROM EAST AFRICA

By G. BOSSHART, *Dip.Min., G.G.*, * E. FRANK, *Ph.D.*, †
H. A. HÄNNI, *Ph.D.*, F.G.A., † and N. BAROT, *Ph.D.* ‡

*Swiss Foundation for the Research of Gemstones, Zurich, Switzerland.

†Mineralogical Institute, University of Basel, Switzerland.

‡Ruby Centre, Nairobi, Kenya.

ABSTRACT

The chromophore pairs Fe + (Ti) and Cr + Fe are shown to produce the various blue colorations of Kyanites rather than titanium traces, claimed in earlier reports to be the only cause for the blue hues. Vanadium and manganese have no apparent influence on the blue when present at trace levels.

As a novelty, Cr + Fe or Cr alone has been found to be responsible for an alexandrite effect displayed by a kyanite crystal from East Africa.

INTRODUCTION

Kyanite is rarely encountered as a faceted gem because it is difficult to cut. This is due to its perfect cleavage and marked anisotropy in hardness. The mineral commonly occurs in blue to bluish green hues. The intensely blue kyanites from Kenya and Tanzania are especially attractive, some resembling sapphire in colour and transparency. Three years ago, one of the authors was shown a crystal of this colour by a gemstone dealer in Nairobi. During a recent visit, the authors were presented with another unusual crystal specimen of kyanite. It exhibited a strong pleochroism and, in one direction, was definitely light green in daylight and changed to reddish in incandescent light. The term 'alexandrite-like' arose in the discussion with the dealer. It was decided to analyse this kyanite sample, together with three other collection stones from East Africa.

CHEMICAL COMPOSITION

Detailed analyses were performed on four kyanite samples (Table 1) using an ARL-SEMQ microprobe combined with an energy-dispersive detector system (Tracor-Northern). The microprobe was operated at an accelerating voltage of 15 kV and a sample current of 15 nanoamperes. To minimize drift effects,

TABLE 1. Microprobe analyses of East African Kyanites

sample	(1) colour-changing kyanite	(2) dark blue kyanite	(3) blue kyanite	(4) brown kyanite	blue kyanite (Kenya)	blue kyanite (India)
SiO ₂	37.08 ± 0.30	37.00 ± 0.29	37.44 ± 0.32	36.85 ± 0.31	—	—
Al ₂ O ₃	62.10 ± 0.18	62.20 ± 0.20	61.83 ± 0.17	61.30 ± 0.19	—	—
TiO ₂	≤ .04*	< .05	< .05	< .05	.07	.01
Fe ₂ O ₃	.35 ± 0.04	.87 ± 0.05	1.20 ± 0.10	1.15 ± 0.09	.04	.11
Mn ₂ O ₃	≤ .04*	< .05	< .05	.30 ± 0.06	—	—
Cr ₂ O ₃	.50 ± 0.07	< .05	< .05	.10 ± 0.05	.23	.01
V ₂ O ₃	≤ .04*	< .05	< .05	< .05	.60	.03
total	100.03	100.07	100.50	99.70		
cations on the basis of 20 oxygens						
Si	4.01	4.00	4.03	4.01	References Schmetzer (1978) White (1967)	
Al	7.92	7.92	7.86	7.86		
Fe ³⁺	.03	.07	.10	.09		
Mn ³⁺	—	—	—	.02		
Cr ³⁺	.04	—	—	.01		

no. 1 intense greenish blue kyanite crystal from Kenya/Tanzania, 10 × 5 × 3 mm

no. 2 dark blue kyanite, cut gem, 0.31 ct, from Kenya/Tanzania, 4.2 × 3.9 × 2.1 mm

no. 3 blue kyanite crystal, Machakos District, Kenya, 30 × 10 × 8 mm

no. 4 translucent brown kyanite crystal, Emali (?), Tanzania, 14 × 5 × 3 mm

*EDS-XRF data

counting time was controlled by means of beam current integration. For standardization, natural and synthetic compounds were used. Data reduction was accomplished with a ZAF-type correction program. Analytical details are described by Schwander & Gloor (1980).

Kyanite, the high pressure polymorph of Al_2SiO_5 , usually contains only minor amounts of impurities such as Ti, Fe, Mn, Cr, or V. White & White (1967) reported that the characteristic blue colour of kyanite is caused by the presence of very small Ti^{3+} contents. Smith & Strens (1976) and Schmetzer (1978) related it to the charge transfer pair $\text{Fe}^{2+}/\text{Ti}^{4+}$ and to the variable chromophore contents. Chromium-bearing kyanites are typically found in high-pressure rocks, as, e.g., eclogite or glaucophane schist, and show a blue or green colour. The presence of transition elements causes different colours. This has been summarized by Ribbe (1980):

substitution of Al^{3+} on octahedral sites in synthetic kyanites by	resulting colour
Fe^{3+}	yellow-green
Mn^{3+}	orange-yellow
V^{3+}	greyish-green
Cr^{3+}	green

The analyses of East African kyanites represented in Table 1 reveal considerable amounts of Fe, Cr and, in one case, Mn, whereas Ti as well as V are below the detection limit of the microprobe ($\leq 0.05\%$). It should be stressed that V is common in East African kyanites and often exceeds the Cr concentration (Schmetzer, 1978). Variable amounts of Fe can be observed in our four samples. They range up to 1.20 weight-% Fe_2O_3 in sample no.3. Specimen no.4 exhibits a brown colour which is due to the combination of Mn with Fe and Cr.

Of special interest is the composition of sample no.1. It shows a distinct colour-change effect. This sample contains a substantial amount of chromium which clearly exceeds the iron content. An additional XRF analysis of this specimen by an energy-dispersive detector system showed concentrations of Ti, Mn, and V, each of them being < 300 ppm. From this it may be concluded that the special colour effect observable in no.1 is mainly due to Cr, in the relative absence of V.

ABSORPTION SPECTRA OF BLUE KYANITES

White & White (1967) postulated that the characteristic blue colour of kyanites is generated by Ti^{3+} concentrations of as little as 50 ppm (0.005%), while considerably higher ferric iron contents could vary widely without affecting the colour. No clear correlation to minor contents of chromium, vanadium or manganese was detected either.

The first three samples of Table 1 seem to contradict the statement that Ti is the only cause for the blue coloration. The UV-VIS spectra of samples no. 2 and 3 are dominated by a very broad absorption band between approximately 540 and 800 nm. According to Schmetzer (1978) it has to be attributed to the charge transfer pair Fe^{2+}/Ti^{4+} and to eventual traces of Cr. Titanium, however, being supposed to produce a very strong and sharp peak at 600 nm in the gamma ray spectrum at trace level already, does not clearly show up in the absorption of the two iron-bearing samples. In contrast, Fe^{3+} underlines its presence by a triplet in the violet region (431 > 446 > 452 nm) and a slightly stronger one in the near ultraviolet (379 > 369 > 374 nm). The alpha and gamma ray spectra of no. 2 and 3 are strikingly similar to the extraordinary and ordinary ray absorption of blue sapphire, with a corresponding pleochroism of light bluish green and intense blue.

The alexandrite-like sample no. 1, strongly deviating in its chromophore content, is bound to exhibit a different optical spectrum and pleochroism but not necessarily another colour than blue. Bank (1980), though, described a kyanite from Tanzania with Cr, Fe, V, and Ti impurities to be 'emerald green' (but not colour-changing). The absorption of all three rays in Figure 1 essentially is characterized by the bands and absorption lines of chromium, the strongest of which appear in the red region as in many other chromic solids (e.g. in aluminates and aluminosilicates). The alpha ray of no. 1 displays the purest chromium spectrum while only the gamma vibration shows a clear but comparatively weak iron interference in the violet portion and around 620 nm as described above for samples no. 2 and 3. Gamma is almost the same greenish blue as beta but more saturated. Both are intense colours visible through the planes of the cleavage platelets. As is common in blue kyanites, the alpha ray is the weakest. It is seen in the direction parallel to the planes of the perfect cleavage (100) and perpendicular to the length of the crystal as a light green colour in daylight, changing to an obvious purple in incandescent light.

References to blue kyanites in recent mineralogical literature are numerous, but reference to specimens of kyanite with an elevated chromium content in gemmological journals is scarce. Liddicoat (1973) pictured a fine drawing of a spectroscope observation, however not giving any description or interpretation. As shown in Table 1, the chromium concentration of sample no. 1 is unusually high for cuttable material from East Africa, and exceeds the iron (and vanadium) contents. Line and band centre positions therefore are listed briefly, the relative intensities being left away for the sake of clarity:

Alpha 706, 688, 668, 657, 648, 578, 482, 475, 466, 461, 417 nm (± 1 nm)

Beta 704D, 688D, 663, 657, 651, 643, 582, 482, 475, 466, 461, 415 nm

Gamma 707, 688, 668, 660, 652, 616, 486, 476, 461, 443, 428, 415 nm

At liquid nitrogen temperature (LNT) the bands (underlined figures) shift to lower wavelengths and the lines sharpen up and become stronger. A number of new weak lines appear and the beta doublet at 704 nm (D) resolves into a triplet. The absorption edge moves from approximately 320 nm (RT) to 310 nm (LNT).

The chromium containing specimen no. 1 weakly fluoresces red under the stimulus of long-wave ultraviolet radiation as opposed to the iron-rich samples no. 2 and 3 which are inert.

THE ALEXANDRITE EFFECT IN BLUE KYANITE

Purity and depth of a colour depend on the steepness and strength of the absorption bands and on the degree of transparency between the bands. If the positions and depths of these transmitting areas (absorption minima) are appropriate, the alexandrite effect may become visible. It follows that the strength of this colour change phenomenon also depends on the position, steepness and intensity of the absorption minima, i.e. on the composition of the colouring transition metal impurities (substituting aluminium on the sites of certain distorted coordination octahedra). This phenomenon has been explained and the conditions for it to be observable have been derived by White *et al.* (1967) and Schmetzer *et al.* (1980). The prediction that a greater number of minerals could theoretically show the colour-change is supported by recent reports on alexandrite-like garnet, corundum, spinel, fluorite and, as a latest addition to the list, kyanite.

Abs. coeff.
(cm^{-1})

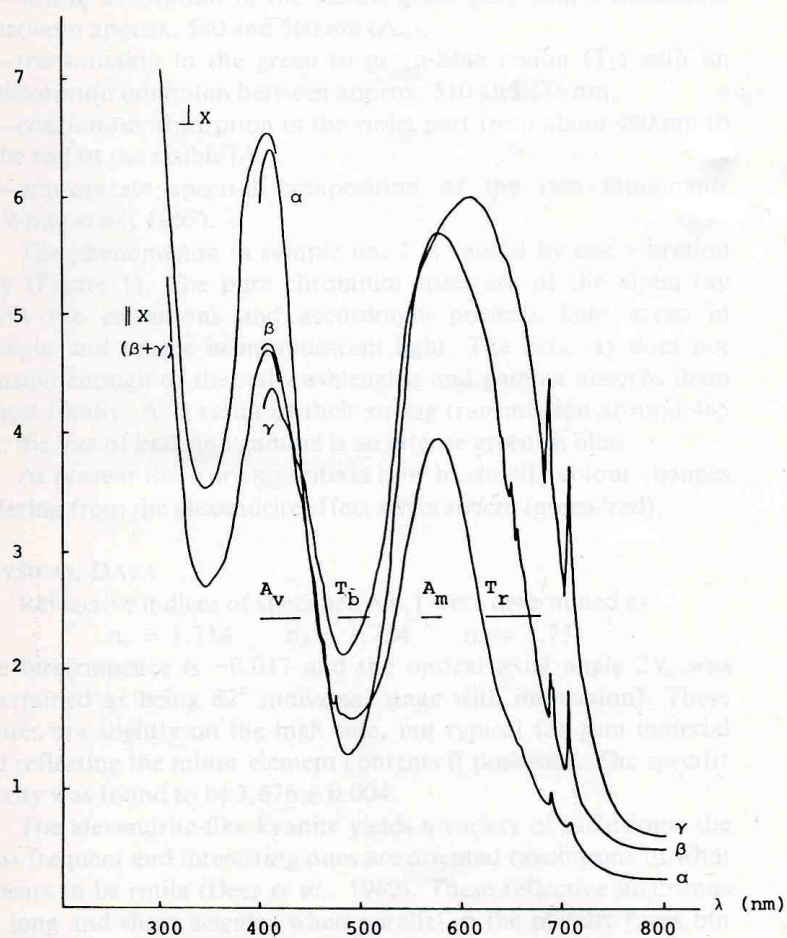


FIG. 1. Optical absorption spectra of chromium in a transparent blue colour-changing kyanite crystal from East Africa, polarized in the range of 400 to 800 nanometres and recorded at room temperature on a PYE Unicam SP8-100 UV-VIS spectrophotometer. Absorption coefficient is approximate.

The conditions for the alexandrite effect to become visible are (according to Schmetzer *et al.*, 1980):

- transmission in the red region above approximately 625 nm (T_r in Figure 1),
- strong absorption in the yellow-green part with a maximum between approx. 580 and 560 nm (A_m),
- transmission in the green to green-blue region (T_b) with an absorption minimum between approx. 510 and 475 nm,
- continuous absorption in the violet part from about 460 nm to the end of the visible (A_v),
- appropriate spectral composition of the two illuminants (White *et al.*, 1967).

The phenomenon in sample no. 1 is caused by one vibration only (Figure 1). The pure chromium spectrum of the alpha ray fulfils the conditions and accordingly presents light green in daylight and purple in incandescent light. The beta ray does not transmit enough of the red wavelengths and gamma absorbs them almost totally. As a result of their strong transmission around 485 nm, the hue of beta and gamma is an intense greenish blue.

At present there are no criteria how to classify colour changes differing from the alexandrite effect *sensu stricto* (green/red).

PHYSICAL DATA

Refractive indices of specimen no. 1 were determined as:

$$n_\alpha = 1.714 \quad n_\beta = 1.724 \quad n_\gamma = 1.731$$

The birefringence is -0.017 and the optical axial angle $2V_x$ was determined as being 82° (universal stage with immersion). These figures are slightly on the high side, but typical for gem material and reflecting the minor element contents it possesses. The specific gravity was found to be 3.676 ± 0.004 .

The alexandrite-like kyanite yields a variety of inclusions; the most frequent and interesting ones are oriented exsolutions of what appears to be rutile (Deer *et al.*, 1962). These reflective inclusions are long and short acicular when parallel to the platelet faces but more platy when perpendicular to them. Long growth tubes are parallel to the long direction of the crystal. In the same direction there are planar healing fissures consisting of mainly small negative crystals filled with a liquid and little gas. Other inclusions are fissures encrusted with goethite or haematite and colourless resorbed crystal prisms with tension haloes.

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