

Explanation on Yellow, Green and Brown Coloration Series of Basalt Related Bangkokja Sapphires

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The basalt related Bangkokja sapphires, excluding the black star ones, commonly occur in three coloration series, i.e., the yellow, the green and the brown. Two representative samples of each colour series, altogether six, were selected from our Bangkokja sapphire collection (43 stones); those six

samples, i.e., light yellow and yellow, greenish yellow and green, and brownish yellow and brown represent the yellow, the green and the brown colour series, respectively. They have been studied to explain the true causes of their colour variations by using band models. Trace element chemistry, UV-Vis-NIR (both absorption and excitation), and FTIR spectra of the samples were recorded. Besides, their L*a*b* colour notations were measured using UV-Vis reflectance spectroscopy (Table 1).







Sample	Colour	Name	L*	a*	b*
	Light yellow	Bkj-11	91.87	-0.08	27.53
	Yellow	Bkj-21	85.20	0.30	37.56
	Greenish yellow	Bkj-25	92.23	-9.17	32.77
	Green	Bkj-32	59.35	-9.68	0.20
	Brownish yellow	Bkj-36	75.33	9.90	28.64
	Brown	Bkj-41	67.82	12.48	12.70

Table 1: Six out of forty-three of Bangkokja sapphire samples representing the yellow (Bkj-11 and 21), the green (Bkj-25 and 32) and the brown (Bkj-36 and 41) coloration series; showing the L*a*b* colour notations together with their visual colours.

The results confirm the pure yellow component is caused by Fe^{3+} with increasing intensity to the bright brown coloration so called the Mekong whisky colour, the most preferable yellow sapphires from Bangkok, Chanthaburi, Thailand, which also commands high pricing in the market among Thai people. This colour series shows UV-Vis absorptions at 377 nm, 388 nm and 450 nm similar to their polychromatic UV-Vis excitation spectra confirming that the samples are natural without beryllium heat treatment (Monarumit et al., 2020 and 2023). The more intense brown stones also show pronounced absorption at 450 nm which is also designated for the $\text{Fe}^{3+}/\text{Fe}^{3+}$ forbidden state (Häger, 2001). The tinted green samples, i.e., greenish yellow gradually ranges to green stones tend to have an increasing of Ti content. The three series have proven that the green is caused by gradually adding the blue component to the yellow which finally turns to blue with elevated Ti together with Fe content. Though this is rather commonly understandable, however, when the blue component has been added to the yellow, and the green (also blue-green till blue) varieties visually appear, the 580 nm and 710 nm absorptions present with a remarkably additional broad absorption at around 890 nm. Besides, their FTIR absorptions display the structural Ti-OH peak at 3309 cm^{-1} (Phlayrahan et al., 2018a, 2018b and 2019) while the greenish tint increases, finally the whole 3309 cm^{-1} series (3309 cm^{-1} , 3232 cm^{-1} and 3184 cm^{-1}) appears in the blue Bangkok stones. It is thus

revealed that the 580 nm, 710 nm and 890 nm absorptions are related to Ti. The increasing 890 nm absorption also normally indicates green/blue sapphires of basalt hosted known by most gem scientists (e.g., Palke et al., 2019). Hence, it is time to explain and understand, why there is no 3309 cm^{-1} absorption and its series in yellow/brown sapphires whereas those with blue tint do; this is because the Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}^{3+}$ pairs provide balance substitution of Al^{3+} and 2Al^{3+} in the adjacent octahedral sites. Indeed, the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pairs proposed by our previous work using the XANES technique (e.g., Wongrawang et al., 2016; Mogmued, et al., 2017), are responsible for the blue component which is increasingly added to Bangkok yellow sapphires resulting in greenish yellow and green stones. Therefore, an OH^- is required to balance the one-more excess positive charge of octahedral structural units which contain the $\text{Fe}^{3+}/\text{Ti}^{4+}$ pair ($7+$) instead of $\text{Fe}^{2+}/\text{Ti}^{4+}$ ($6+$) as the IVCT concept previously claimed and widely followed (e.g., Townsend, 1968; Nassau, 1978; Burns, 1981; Fritsch and Rossman, 1988).

The band models of yellow, green, and brown colour series of Bangkok sapphires have been proposed; the yellow component gradually ranges to the intense-brownish yellow to brown colorations due to Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}^{3+}$ states in the yellow sapphire band gap (Figure 1a and c). Besides, the $\text{Fe}^{3+}/\text{Ti}^{4+}$ mixed acceptor states are additionally present in the green colour series (Figure 1b).

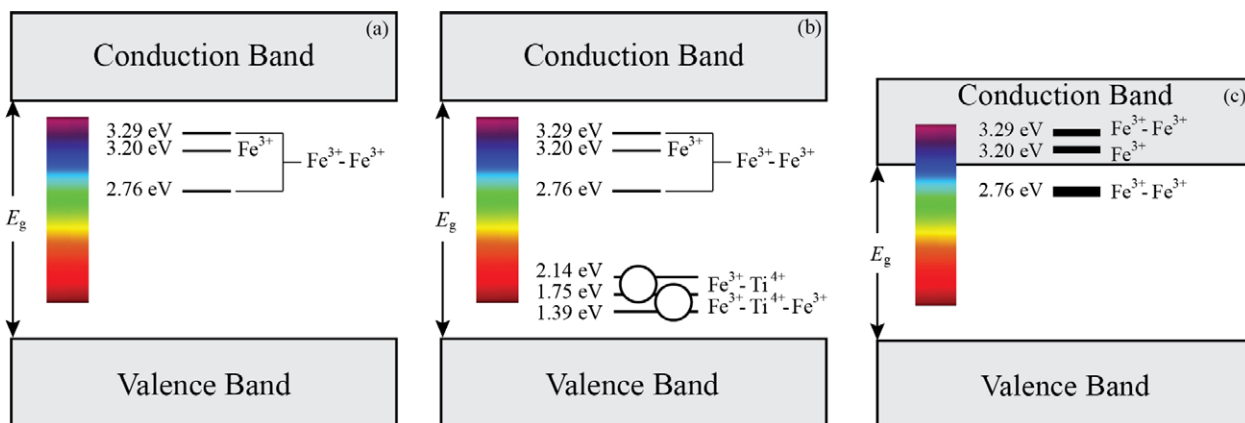


Figure 1: Band models showing (a) the stable defect centre of Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}^{3+}$ states in yellow sapphire coloration series; (b) the Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}^{3+}$ states and the $\text{Fe}^{3+}/\text{Ti}^{4+}$ mixed acceptor states in the energy gap of green sapphire series, and (c) the

Fe^{3+} and $\text{Fe}^{3+}/\text{Fe}^{3+}$ states with the very high density of states (thick bars) resulting in the intense brown colour series of Bangkok sapphires with the narrower energy band gap due to higher impurities in particular iron.

As the result of no-charge difference mentioned, the yellow as well as the brown sapphires never show the 3309 cm⁻¹ FTIR absorption (structural OH) unless the blue component which is caused by the Fe³⁺/Ti⁴⁺ mixed acceptor pair existing in the sapphire structure, resulting in the green coloration, and eventually the blue one. In the unheated stones, the molecular water would normally appear as a broad FTIR absorption at around 3400 cm⁻¹. The green coloration series of Bangkok sapphires is caused by addition of a blue component (Fe³⁺/Ti⁴⁺ pair) to the yellow. Hence, the OH⁻ is required only in greenish, green, and blue stones from Bangkok. This explanation can also be implied to yellow, green (till blue), and brown sapphires occurring elsewhere.

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