

Color measurement of yellow sapphire by UV-Vis reflectance spectroscopy

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Abstract. Yellow sapphire is a gemstone variety of corundum (Al_2O_3). The yellow color is commonly caused by Fe^{3+} impurity substituting for Al^{3+} in the Al_2O_3 structure. The depth of yellow color is linked to Fe^{3+} concentration. The higher content of Fe^{3+} produces a deeper yellow color. However, there is low content of the impurity such as Be^{2+} in cooperating with the low content of Fe^{3+} to produce the yellow color in yellow sapphires. It is difficult to differentiate between the natural yellow sapphire caused by high Fe^{3+} content and the beryllium-treated yellow sapphire by naked eyes. Some advanced techniques to identify the Be heat-treated yellow sapphire have been practiced such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and laser-induced breakdown spectroscopy (LIBS). We measured the colors of naturals and beryllium-treated yellow sapphires by UV-Vis reflectance spectroscopy. The concentration of impurities in the sapphire samples was measured by the LA-ICP-MS technique. To compare the yellow colors of CIE $L^*a^*b^*$ and CIE L^*C^*h , we found that the lightness and hue values of the Be-treated yellow sapphires were higher than the natural yellow sapphires with high Fe^{3+} content.

1. Introduction

Ruby and sapphire are gems variety of corundum (Al_2O_3). The colors in corundum relate to impurities in the crystal structure, such as Cr^{3+} for ruby [1] and Fe^{3+} - Ti^{4+} for blue sapphire [2]. The yellow sapphire is caused by either Fe^{3+} replacing Al^{3+} or by color centers [3]. The intensity of the yellow color caused by Fe^{3+} depends on Fe^{3+} concentration. The quantitative relationship between color and impurities of natural corundum has been comprehensively studied [4]. However, there is a beryllium heat treatment technology to enhance the yellow color of yellow sapphire. The technique requires low content of Be^{2+} in cooperating with low content of Fe^{3+} [5].

It is difficult to differentiate between natural yellow sapphires with high Fe^{3+} content and beryllium-treated yellow sapphires by naked eyes. Hence, some advanced techniques have been developed to characterize the beryllium-treated sapphire, such as laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), secondary ion mass spectrometry (SIMS) and laser-induced breakdown spectroscopy (LIBS) [6].

The spectra of the UV-Vis spectrophotometer could be converted to color scales such as ADMI (American Dye Manufacturers' Institute) for color measurement of wastewater [7] and CIE L^*c^*h for

color measurement of pigmented rice grain [8]. In this work, we carried out UV-Vis reflectance spectroscopy to compare the CIE $L^*a^*b^*$ and CIE L^*C^*h values between natural yellow sapphires and Be-treated yellow sapphires.

2. Experiment

Two non-polished natural yellow sapphires with high Fe^{3+} content labeled as NY 3 and NY 5, and two polished Be-treated yellow sapphires labeled as BeY 8 and BeY 9, were collected as shown in figure 1. The trace elements of the samples have been measured by the LA-ICP-MS technique. The UV laser ablation system, a New Wave Research 266 nm Nd: YAG, is coupled to an Agilent 7500 ICP-MS. The LA-ICP-MS analyses for all samples were done under a pulse rate of 5 Hz and beam energy of approximately 0.5 mJ per pulse, producing a spatial resolution of 30 μm to 50 μm in diameter on the samples.



Figure 1. Natural yellow (NY) and Be-treated yellow (BeY) sapphires.

To measure the color of yellow sapphires, we carried out the UV-Vis reflectance spectroscopy using a portable spectrophotometer with an integrating sphere. The spectrometer was AvaSpecTM fiber optic type based on the Czerny-Turner design with a 2048 pixel CCD detector array. The spectrum range was about 275 nm to 1100 nm. The spectra were exported from raw data to 360 nm to 830 nm with the wavelength steps of 5 nm for color calculation. The CIE XYZ values can be calculated by [9]

$$X = k \sum_{\lambda} S(\lambda)R(\lambda)\bar{x}(\lambda)\Delta\lambda \quad (1)$$

$$Y = k \sum_{\lambda} S(\lambda)R(\lambda)\bar{y}(\lambda)\Delta\lambda \quad (2)$$

$$Z = k \sum_{\lambda} S(\lambda)R(\lambda)\bar{z}(\lambda)\Delta\lambda \quad (3)$$

where $S(\lambda)$ is the relative spectral power, $\bar{x}(\lambda)$, $\bar{y}(\lambda)$, $\bar{z}(\lambda)$ are the color matching function, $R(\lambda)$ is the spectral reflectance of an object surface and k is a normalizing factor,

$$k = \frac{100}{\sum_{\lambda} S(\lambda)\bar{y}(\lambda)\Delta\lambda} \quad (4)$$

The CIE 1931 standard observer matching function (2°) and the spectral power distribution illuminant source of D65 were selected. In practice, the CIE XYZ is transformed to a more uniform color space CIE $L^*a^*b^*$ in rectangular coordinate. L^* is represented as lightness with values from 0 (black) to 100 (white). The a^* value indicates red and green components of a color, where $+a^*$ and $-a^*$ indicate red and green values, respectively. The yellow and blue components are represented on the b^* axis as $+b^*$ and $-b^*$ values respectively.

The color space is defined by

$$L^* = 116f(Y/Y_n)-16 \quad (5)$$

$$a^* = 500[f(X/X_n)-f(Y/Y_n)] \quad (6)$$

$$b^* = 200[f(Y/Y_n)-f(Z/Z_n)] \quad (7)$$

where being $t = \frac{X}{X_n}$, $\frac{Y}{Y_n}$ or $\frac{Z}{Z_n}$:

$$f(t) = t^{1/3} \quad \text{if } t > (24/116)^3 \quad (8)$$

$$f(t) = (841/108)t + 16/116 \quad \text{if } t \leq (24/116)^3 \quad (9)$$

where X_n , Y_n , Z_n are the tristimulus values of a reference white object color stimulus.

However, a more natural representation of the quantities is CIE L^*C^*h color in cylindrical coordinate that is

$$C^* = \left((a^*)^2 + (b^*)^2 \right)^{1/2} \quad (10)$$

$$h = \tan^{-1} \left(\frac{b^*}{a^*} \right) \quad (11)$$

where C^* (chromaticity) gives vividness and h (hue) gives shades of color.

3. Results and discussion

Table 1 shows the quantitative chemical elements of the yellow sapphires analyzed by LA-ICP-MS to measure some trace elements (Be, Fe, Ti and Cr) involving in the causes of sapphire coloration. The Fe content of NY 3 and NY 5 were 12 478.5 mg kg⁻¹ and 16 797.9 mg kg⁻¹ respectively which is more than twice the Fe content of BeY 8 and BeY 9 that were 7 444.3 mg kg⁻¹ and 6 182.5 mg kg⁻¹ respectively. On the other hand, the Be content of NY 3 and NY 5 were 2.1 mg kg⁻¹ and 2.2 mg kg⁻¹ respectively which is less than half of the Be content of BeY 8 and BeY 9 that were 5.0 mg kg⁻¹ and 10.5 mg kg⁻¹ respectively. The higher content of Be in Be-treated yellow sapphire indicated the undergone Be heat treatment of the Be-treated yellow sapphires [10]. Ti and Cr content of all samples were less than about 50 mg kg⁻¹ that was insufficient to affect the coloration of yellow sapphires.

Table 1. Trace element (Be, Fe, Ti, Cr) content in yellow sapphires measured by LA- ICP-MS.

Sample	Concentration / (mg kg ⁻¹)			
	Be	Fe	Ti	Cr
NY 3	2.1	12 478.5	15.2	6.3
NY 5	2.2	16 797.9	45.2	6.9
BeY 8	5.0	7 444.3	48.8	23.4
BeY 9	10.5	6 182.5	54.8	27.0

Figure 2 shows the UV-Vis reflectance spectra of natural yellow sapphires (NY 3 and NY 5) and Be-treated yellow sapphires (BeY 8 and BeY 9). The spectra of BeY 8 and BeY 9 are higher reflectance compared to NY 3 and NY 5. The fluorescence peak at 694 nm is the typical Cr³⁺ R line [11]. The peak was low intensity due to the low content of Cr. The fluorescence peaks at 630 nm and 840 nm are caused by Fe³⁺-Be²⁺ mixed donor states [5]. The fluorescence peaks at 630 nm, 694 nm and 840 nm were observed due to the CCD type of the spectrophotometer. However, the surface polishing qualities of these two groups of samples might also influence the reflectance. The non-polished natural sapphire surface would result in more scattering and extinction of light.

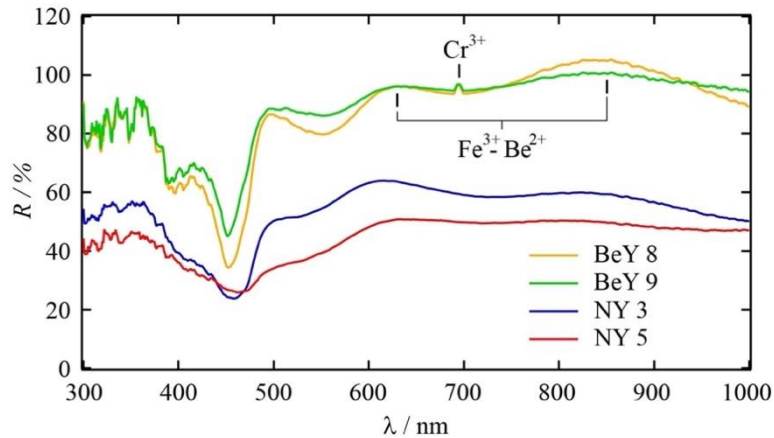


Figure 2. UV-Vis reflectance spectra of natural yellow sapphires and Be-treated yellow sapphires.

For quantitative analyses, we calculated CIE XYZ , CIE $L^*a^*b^*$ and CIE L^*C^*h as shown in table 2 to compare the natural yellow sapphires and Be-treated yellow sapphires.

Table 2. The CIE XYZ , CIE $L^*a^*b^*$ and CIE L^*C^*h of natural and Be-treated yellow sapphires.

	X	Y	Z	L^*	a^*	b^*	C^*	h
NY 3	51.78	55.33	33.45	79.23	-2.11	29.24	29.32	94.13
NY 5	40.62	40.86	31.42	70.08	5.59	16.25	17.18	71.02
BeY 8	77.24	83.67	57.29	93.31	-4.54	27.00	27.37	99.54
BeY 9	81.23	88.08	67.65	95.19	-4.78	21.05	21.58	102.80

The CIE XYZ values of Be-treated yellow sapphire (BeY 8 and BeY 9) were higher than natural yellow sapphire (NY 3 and NY 5). The values correspond to the higher reflectance of UV-Vis spectra shown in figure 2. For CIE $L^*a^*b^*$ values, L^* of BeY 8 and BeY 9 were higher than NY 3 and NY 5 indicated more lightness of Be-treated yellow sapphires than natural yellow sapphires while a^* values of BeY 8 and BeY 9 were lower than NY 3 and NY 5 indicated more greenness of Be-treated yellow sapphires than natural yellow sapphires and b^* values could not differentiate between Be-treated yellow sapphires and natural yellow sapphires. For CIE L^*C^*h values, C^* values could not differentiate between Be-treated yellow sapphires and natural yellow sapphires while h values of BeY 8 and BeY 9 were higher than NY 3 and NY 5 indicated difference shades of yellow color between Be-treated yellow sapphires and natural yellow sapphires.

4. Conclusion

The natural yellow sapphires and Be-treated yellow sapphires have been prepared for color measurement by UV-Vis reflectance spectroscopy. Some trace elements (Be, Fe, Ti and Cr) involving in the causes of sapphire coloration have been measured by the LA-ICP-MS technique. CIE XYZ , CIE $L^*a^*b^*$ and CIE L^*C^*h were calculated to compare the color of yellow sapphires. The L^* and h values of Be-treated yellow sapphires were higher than natural yellow sapphires. Hence, the color measurement by UV-Vis reflectance spectroscopy could be a promising technique to differentiate the natural yellow sapphires with high Fe^{3+} content and Be-treated yellow sapphires.

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References

- [1] Monarumit N, Lhuaamporn T, Satitkune S and Wongkokua W 2019 *J. Appl. Spectrosc.* **86** 486–92
- [2] Wongrawang P, Monarumit N, Thammajak N, Wathanakul P and Wongkokua W 2016 *Mater. Res. Express* **3** 026201
- [3] Nassau K and Valente G K 1987 *Gems Gemol.* **23** 222–31
- [4] Dubinsky E V, Stone-Sundberg J and Emmett J L 2020 *Gems Gemol.* **56** 2–28
- [5] Monarumit N, Lhuaamporn T, Sakkaravej S, Wathanakul P and Wongkokua W 2020 *J. Phys. Commun.* **4** 105018
- [6] Abduriyim A and Kitawaki H 2006 *Gems Gemol.* **42** 98–118
- [7] Suwanboriboon J, Meesiri W and Wongkokua W 2018 *J. Phys. Conf. Ser.* **1144** 012064
- [8] Kaisaat K, Keawdonree N, Chomkokard S, Jinuntuya N and Pattanasiri B 2017 *J. Phys. Conf. Ser.* **901** 012069
- [9] Schanda J 2007 *Colorimetry Understanding the CIE System* (New Jersey: John Wiley & Sons)
- [10] Pisutha-Arnond V, Häger T, Wathanakul P and Atichat W 2004 *J. Gemm.* **29** 77–103
- [11] Wongkokua W, Pongkrapan S, Dararutana P, T-Thienprasert J and Wathanakul P 2009 *J. Phys. Conf. Ser.* **185** 012054