

Color Enhancement of Natural Sapphires by High Pressure High Temperature Process

Jeongho Song, Yunyoung Noh, and Ohsung Song[†]

Department of Materials Science and Engineering, University of Seoul, Seoul 130-743, Korea

(Received December 2, 2014; Revised January 26, 2015; Accepted February 2, 2015)

ABSTRACT

We employed the high-pressure high temperature (HPHT) process to enhance the colors of natural sapphires to obtain a vivid blue. First, we analyze the content of the coloring agent Fe_2O_3 using the wavelength dispersive X-ray fluorescence (WD-XRF) method. The HPHT procedure operates under 1 GPa at various temperatures of 1700, 1750, and 1800°C for 5 minutes using a cubic press. We determine the color changes using the optical microscopic images, UV-VIS near-infrared (NIR) spectra, micro-Raman spectra, and Fourier transform-infrared (FT-IR) spectra for all sapphire samples before and after the treatment. The optical microscopic results indicate that the HPHT process can enhance the sapphire color to a vivid blue at temperatures above 1750°C. The UV-VIS-NIR spectra identify the color changes explicitly and quantitatively through providing the Lab color scales and color differences. Both results demonstrate that the colors of natural sapphires can be enhanced to a vivid blue using the HPHT process above 1750°C under 1 GPa for 5 minutes.

Key words : Sapphire, Color enhancement, HPHT, WD-XRF, FT-IR

1. Introduction

Sapphire, a precious gem stone, belongs to the corundum structure as a natural mineral that consists of an Al_2O_3 single crystal. Sapphires are named after their color such as blue sapphire, pink sapphire, green sapphire, etc. Used alone, however, the word 'sapphire' refers only to blue-colored one that normally has good clarity and color and, thus, is traded in high prices.¹⁾

The colorless or light-blue sapphires from Sri Lanka and other places are currently less than 100 USD per carat which is much lower than the prices of high-quality blue sapphires (> 1,500 USD per carat). Researches on its color enhancement, thus, have been quite active to increase the value for the low-quality blue sapphires.²⁾

A typical procedure of the color enhancement consists of heat treatment under an oxidation atmosphere in an electric resistant furnace mostly made of Super Kanthal heating elements which is able to maintain temperatures up to 1700°C. The process, however, has suffered low yield by failing to have the reproducible color enhancement that strongly depends on furnace atmosphere, treatment time and temperature, and cooling rate.³⁾

Other methods include the diffusion treatment with Be, the chemical dyeing, and etc. It all involves in introducing other foreign elements into the sapphire system for the color

enhancement. Therefore, the added values of treated stones are far from satisfactory and customers have tendency to lose their interests on them.⁴⁻⁶⁾

Recently, Song *et al.*⁷⁾ reported that the color enhancement of a low-grade light-blue sapphire to a blue one by thermal treatment was successful in a vacuum furnace at 1800°C for 1 h overcoming the low-yield problem. The process, however, decreased clarity of stone owing to the growth of TiO_2 inclusions which eventually led to a trivial added value.

The process of high pressure high temperature (HPHT) normally utilizes an equipment that is capable of pressures up to 10 GPa and temperatures of over 2000°C. Recently, this HPHT equipment has been developed up to the stable status and adopted for the diamond synthesis or its color enhancement.^{8,9)} By embedding the sample within sintered body of MgO, pressure and heat readily transferred to the sample and the set-up, thus, can create super-high pressures under an oxidation atmosphere. Furthermore, carbon heating elements can provide very fast ways of heating and cooling; for example, heating in 30 seconds up to 1800°C, holding steadily at the intended temperature, and cooling down to room temperature in 3 minutes.

It is well established that the blue color in sapphire comes from Fe^{2+} and Ti^{4+} impurities in Al_2O_3 when they substitute Al^{3+} and become Fe^{3+} and Ti^{3+} ions by electron transfer. The coloring mechanism involves absorption of the complementary blue color out of incident white light by the generated ions.^{10,11)}

HPHT apparatus is designed to achieve the formation of these coloring ions of Fe^{3+} and Ti^{3+} according to the mechanism. In addition, the application of high pressure acceler-

[†]Corresponding author : Ohsung Song

E-mail : songos@uos.ac.kr

Tel : +82-2-6490-2410 Fax : +82-2-6490-2404

ates the diffusion of these ions, especially for the natural sapphire, into the proper positions so that the coloring can take place.

In this study, we selected the low-quality light-blue sapphires as our samples that already contain coloring elements but its blue color is not satisfactory. We adopted the HPHT process to confirm whether the process is favorable for color enhancement. We aimed to have blue sapphire at temperature of 1800°C at most in such a short time period of 5 minutes.

2. Experimental Procedure

Table 1 shows the prepared samples of light-blue sapphires that appear to have almost no genuine blue. The #1 ~ #3 samples are all from Sri Lanka. The #2 sample was gem-cut in oval shape, while the #1 and #3 samples into flat shape with polished surfaces to investigate the presence of inclusions.

We analysed these samples quantitatively for the main constituent Al_2O_3 , the coloring ingredients such as Fe_2O_3 , TiO_2 , and other impurities such as Cr_2O_3 , MgO , etc. by wavelength-dispersive X-ray spectroscopy (WD-XRF, Shimadzu Co., XRF-1700). We used Rh target with 40 kV and 90 mA for the spectroscopy.

We treated the prepared samples in an high pressure high temperature (HPHT) apparatus (Guilin Co., $\phi 420$) for color enhancement. We fixed the pressure at 1 GPa, varied the temperature at 1700, 1750, and 1800°C for 5 minutes, and cooled for 3 minutes.

We analyzed the samples before and after the treatments by visual inspection and optical microscope (GIA Instruments Co., 815000) under the overhead illumination to verify changes in color and to inspect any presence of inclusions. We also obtained the images of optical micros-

copy taken by the digital camera (Nikon Co., Coolpix4500) attached on eyepiece lens.

We utilized UV-VIS-NIR spectrophotometer (Shimadzu Co., UV-3105) for a quantitative analysis of color differences appeared on the samples before and after the treatments. We obtained the spectra by setting in the reflective mode considering the sample's translucency and by using wavelength range of 200 ~ 800 nm with slit value of 20 and under medium scan rate. The resulted spectra in visible-light range were used to quantitatively determine the CIE Lab color scales by a color analysis program.

Micro-Raman analysis (Unithink Co., UniRaman) was used to confirm the changes in Raman characteristics of sapphires by the HPHT treatment. Samples were illuminated by 531 nm source from DPSS laser with exposure of 5 seconds and Raman spectra were recorded in the range of 250 ~ 2000 cm^{-1} .

We also employed FT-IR analysis (Thermo Scientific Co., Nicloet 5700) to quantitatively evaluate the adsorption properties of samples in the range of 400 ~ 4000 cm^{-1} (resolution of 8 cm^{-1}) and scan value of 32. We first set the analyzer in reflective mode considering the sample's translucency and switched to absorption mode to obtain the needed spectra.

3. Results and Discussion

Table 2 shows the results of WD-XRF analysis before the high pressure high temperature (HPHT) treatment for the prepared sapphire samples. Included are those of synthetic blue sapphire (#4) and synthetic colorless sapphire (#5) for comparison. Note that, to have blue coloring, it is necessary to have Fe and Ti elements according to the known mechanism mentioned above.

We found that the #1 sample before the HPHT treatment

Table 1. Sample Description



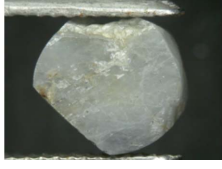
No.	Shape	Polishing	Source and HPHT condition
#1		two-sides polished	natural light blue geuda sapphire from Sri Lanka 1700°C/1 GPa/5 minutes
#2		oval brilliant	natural light blue sapphire from Sri Lanka 1750°C/1 GPa/5 minutes
#3		two-sides polished	natural light blue geuda sapphire from Sri Lanka 1800°C/1 GPa/5 minutes

Table 2. Chemical Compositions of Sapphires by WD-XRF

Sample	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	SiO ₂	CaO	MgO	CuO
#1	99.784	0.111	0.012	0.044	0.005	0.015	0.002
#2	99.322	0.103	0.019	-	0.186	0.305	-
#3	98.226	0.060	0.016	0.927	0.198	0.431	-
#4	99.805	0.020	0.022	0.044	-	-	0.015
#5	99.903	-	-	0.024	-	-	-

contains Fe₂O₃ and TiO₂ in the amounts of 0.111 wt% and 0.012 wt%, respectively. It also contains other impurities such as SiO₂, CaO, MgO, etc. In the case of the #2 sample, the contents of Fe₂O₃ and TiO₂ were 0.103 wt% and 0.019 wt%, respectively. In the #3 sample, the contents were 0.060 wt% and 0.016 wt%, respectively. We, thus, confirmed that all three samples have their own coloring elements.

However, the #4 sample, a synthetic blue sapphire, the contents of Fe₂O₃ and TiO₂ were 0.020 wt% and 0.022 wt%, indicating that the contents of Fe₂O₃ is lesser than the #1 ~ #3 samples by 0.040 ~ 0.091 wt%. We thus concluded that if the contents of Fe₂O₃ is higher than 0.020 wt%, blue coloring of sapphire could be possible.

The #5 sample, a synthetic colorless sapphire, has only a very small amount of SiO₂ as impurity and has no trace of Fe₂O₃ or TiO₂. This implies that the presence of some proper amounts of coloring ingredients are critical to accomplish color enhancement. We further concluded that the #1 ~ #3 samples have enough Fe₂O₃ for blue coloring but the coloring ions are either not in the right sites in the hexagonal corundum structure or are not in the Fe³⁺ state. Hence, they are unable to create the needed color centers for blue.

Figure 1 shows the images of optical microscopy after the HPHT treatment at 1700 ~ 1800°C under 1 GPa for 5 minutes for each sapphire samples. Also shown in the upper right corners of each images are the images before the treatment for comparison.

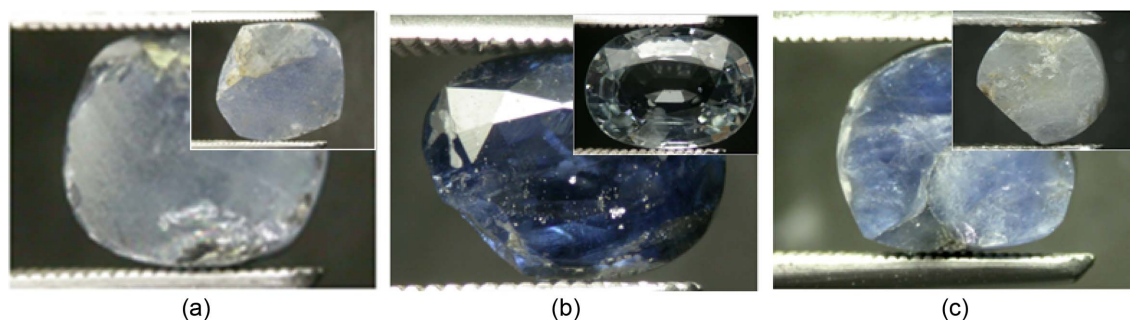
Figure 1(a) shows the #1 sample after the HPHT treatment at 1700°C, revealing grey color mixed with blue. Compared to the sample before the treatment, there is no noticeable difference. We concluded that the relatively low treatment temperature of 1700°C was not high enough to activate the mechanism of color change.

Figure 1(b) shows the #2 sample after the HPHT treatment at 1750°C, revealing definite color change to blue compared to the sample before the HPHT treatment that was originally in light greenish color. We, thus, confirmed that color enhancement can take place above 1750°C in 5 minutes. We also observed many cracks around the circumference of oval sample and concluded that the high pressure of 1 GPa caused them to originate from the relatively thinner part of gem-cut edges due to stress concentration. They could also be originated from the pre-existing cracks such as the so-called 'feather.' To prevent these cracks, we propose the gem-cutting after the HPHT treatment and color enhancement.

Figure 1(c) shows the #3 sample after the HPHT treatment at 1800°C, revealing color change to blue compared to the sample before the HPHT treatment that was originally translucent with light greenish color. We, however, observed that the color change is rather nonuniform. The central part around a crack was pale-blue with lesser degree of color change. We speculated that it is due to the low-grade 'geuda' sample which already had the preexisting crack.

Figure 2 shows the UV-VIS-NIR spectra of the light-colored sapphires before and after the treatments. Fig. 2(a) is for the #1 sample that indicates no noticeable peak change of reflectance in the visible light range leading to no color change. This result is in agreement with the optical microscope analysis.

Figure 2(b) is for the #2 sample, before the treatment that indicates the reflectance related with blue color decreases (450 ~ 550 nm). After the treatment, however, blue color regime did not decrease which indicating blue color enhancement. Fig. 2(c) is for the #3 sample that shows simi-

**Fig. 1.** Optical-microscopic images of sapphires before (insets) and after the HPHT treatment: (a) #1, (b) #2, and (c) #3 sample.

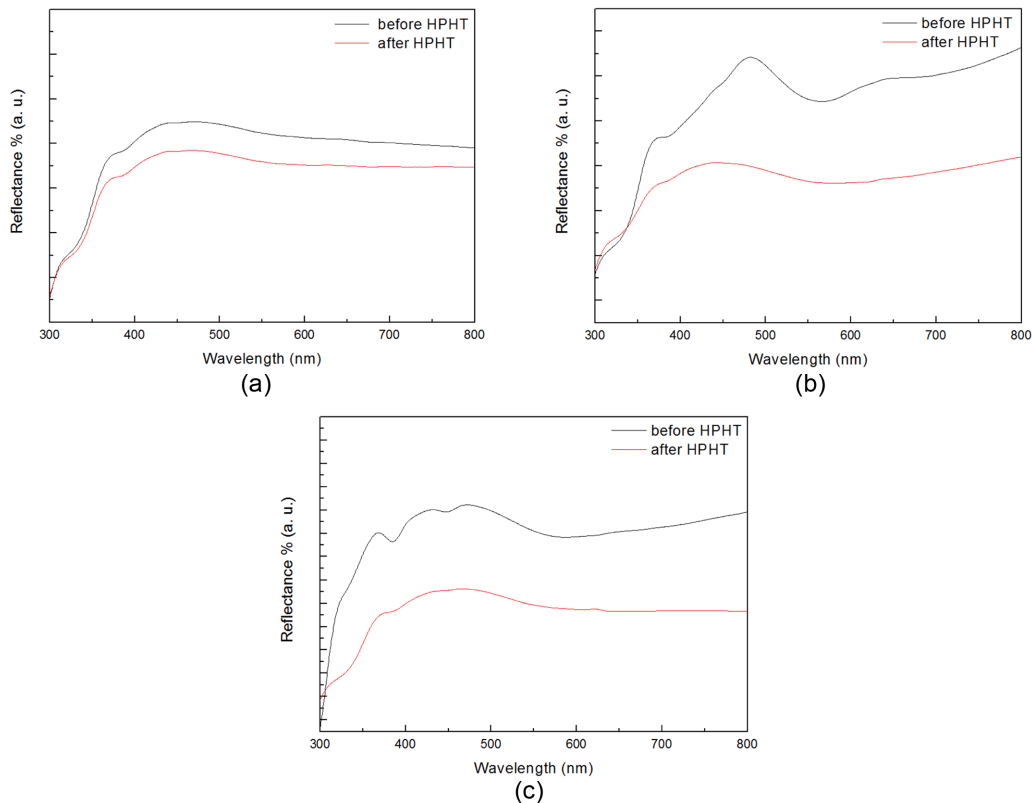


Fig. 2. UV-VIS-NIR spectra of sapphires before and after the HPHT treatment: (a) #1, (b) #2, and (c) #3 sample.

Table 3. Lab Color Scale of the Sapphire Samples

Sample		L	a	b	Color difference
#1	before	61	-2	-5	6.32
	after	55	-2	-7	
#2	before	69	-8	2	45.32
	after	42	2	-33	
#3	before	68	-6	4	23.94
	after	54	-2	-15	

lar trend with that of the #2 sample. The reflectance around 450 nm before the treatment decreased while the reflectance after the treatment showed peak did not decrease which maintaining the reflectance of the blue color peaks. This result lead us to confirm that, in agreement with the visual inspection, the HPHT treatment above 1750°C can achieve the color enhancement to blue.

Table 3 summarizes Lab color scale, color, and color differences based on the results of UV-VIS-NIR spectroscopy from Fig. 2. For the case of #1 sample, Lab color scale changed very little from 61 / -2 / -5 (light bluish grey) to 55 / -2 / -7 and its color differences is as minimal as 6.32.

For the case of #2 sample, Lab color scale markedly changed from 69 / -8 / 2 (light green) to 42 / 2 / -33 and its color differences is as high as 45.32 indicating definite color enhancement to blue. Note that the b-index responsible for

blue color turned on toward the negative direction which means blue color. For the case of #3 sample, Lab color scale markedly changed from 68 / -6 / 4 (light greyish green) to 54 / -2 / -15 indicating definite color enhancement to blue. Note that, like the case of #2 sample, the b-index responsible for blue color turned on toward the blue direction.

We, thus, confirmed that the quantitative analysis of color differences support the results obtained by visual and UV-VIS-NIR analysis and concluded that blue color can be developed for the lower quality sapphires via the HPHT process under the conditions of > 1750°C/1GPa/5 minutes.

Figure 3 is the results of Raman spectra for the samples before and after the treatment. Fig. 3(a) is for the #1 sample showing no characteristic Raman peak in the range we scanned. Although M. Kadleikova *et al.*¹²⁾ reported that synthetic sapphire produced sapphire's unique Raman peak in the wave number range of 300 ~ 750 cm^{-1} , we can not distinguish it from the strong Raman signals from the natural sapphire's fluorescent background. Fig. 3(b) and (c) from the samples of #2 and #3, respectively, also show no characteristic Raman peak or peak change by the treatment. We concluded that the Raman analysis is not a proper method to evaluate the characteristic changes by the color enhancement for natural sapphires.

Figure 4 shows the FT-IR analysis of each light-color sapphires before and after the treatment. Fig. 4(a) from the #1 sample shows no absorption peak change in the whole range of 400 ~ 4000 cm^{-1} . Fig. 4(b) and (c) from the #2, #3 samples,

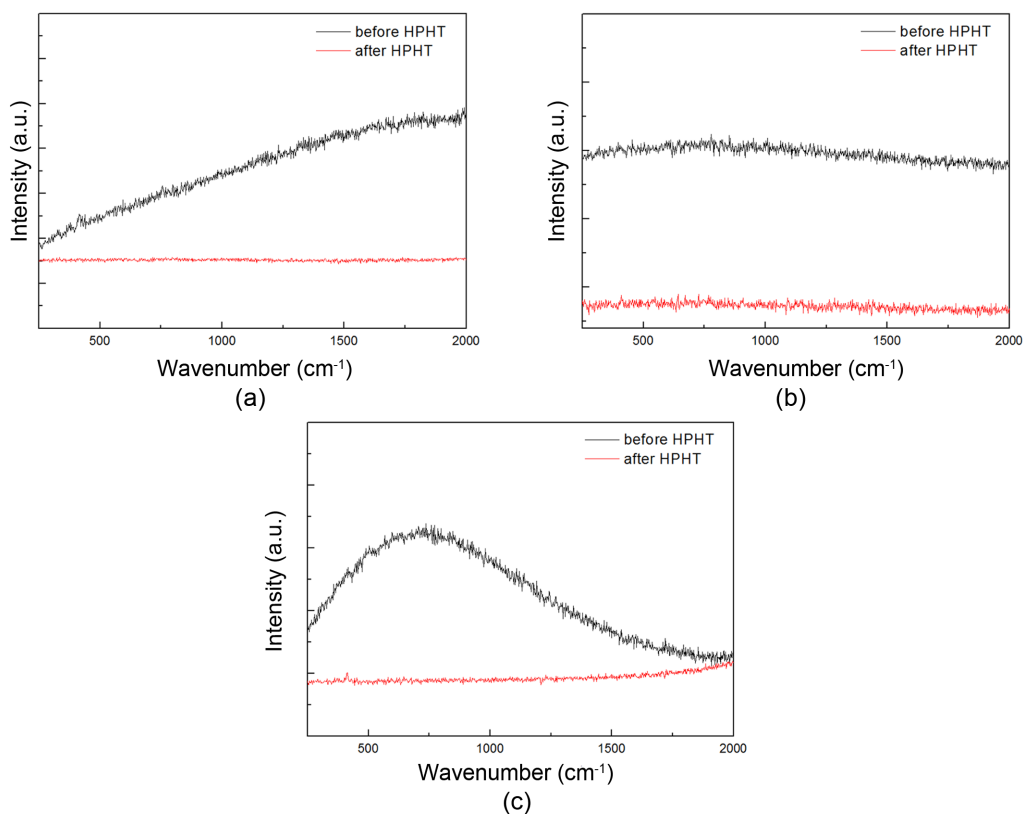


Fig. 3. Micro-Raman spectra of sapphires before and after the HPHT treatment: (a) #1, (b) #2, and (c) #3 sample.

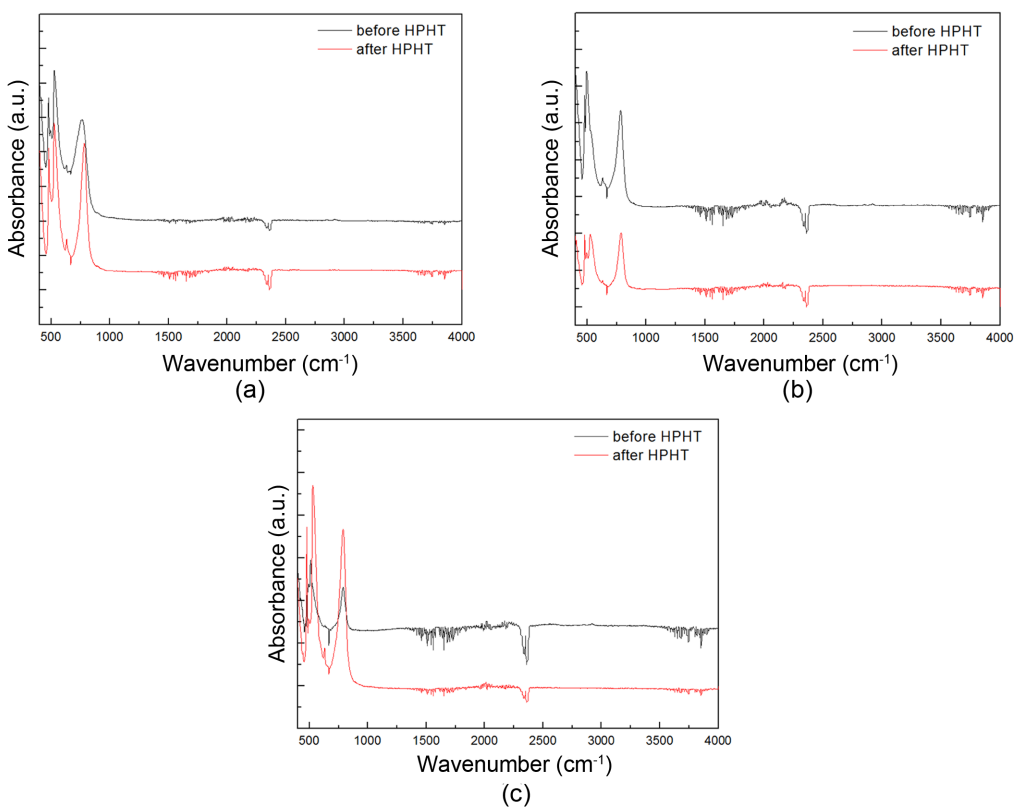


Fig. 4. FT-IR spectra of sapphires before and after the HPHT treatment: (a) #1, (b) #2, and (c) #3 sample.

respectively, also show no characteristic absorption peak change in the whole measured range. We, however, noticed that all samples of Fig. 4(a) ~ (c) showed ratio changes in absorption strength by the treatments in the range of $0 \sim 1000 \text{ cm}^{-1}$. This is in good agreement with the report by Song *et al.*⁷⁾ that claimed the ratio changes in adsorption strength are not directly related with color change for the translucent natural sapphire of low quality with enough amount of Fe_2O_3 and TiO_2 .

We, thus, concluded that the FT-IR analysis is not appropriate to measure color enhancement of sapphires after the HPHT treatments since the color centers are not in activated state under the mid-IR range. By the same reason, the FT-IR analysis is not proper to distinguish whether the stone is HPHT treated or not.

4. Conclusion

We confirmed that the color enhancement of colorless or light-blue natural sapphires can be achieved by the HPHT treatment at above 1750°C under pressure of 1 GPa, if the stones contain more than a certain amount of Fe_2O_3 . We successfully obtained blue sapphires in such a short time period of 5 minutes by the HPHT treatment. For both natural and synthetic blue sapphires, we adopted the WD-XRF analysis as a convenient and nondestructive method for the quantitative determination of Fe_2O_3 content, which is the decisive factor for the blue coloring.

Compared to the existing technologies of simple heat treatments, the newly-proposed approach of high pressure high temperature (HPHT) from this study enhanced the color of sapphires up to the blue level in such a short time period of 5 minutes. We emphasize the fact that, in addition to the visual inspection, the UV-VIS-NIR spectroscopy as an effective method to quantify the degree of color enhancement by providing Lab color scales and color differences data.

Acknowledgments

This paper was supported by Basic Science Research Pro-

gram through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (grant number 201405072011).

REFERENCES

1. Y. Chiang, D. Birnie III, and W. Kingery, *Physical Ceramics*; pp. 133-35, John Wiley & Sons Inc., Canada, 1996.
2. Y. K. Ahn, "Color Change by the Beryllium Diffused and Heat Treated Corundum from Various Deposits," pp. 48-58, Ph. D. Thesis, Hanyang University, Seoul, 2013.
3. T. Themelis, *Beryllium-Treated Rubies & Sapphires*; pp. 6-7, A&T Publishing, LA, 2003.
4. S. F. McClure and C. P. Smith, "Gemstone Enhancement and Detection in the 1990s," *Gems Gemol.*, **36** [4] 337-38 (2000).
5. R. E. Kane, R. C. Kammerling, and J. I. Koivula, "The Identification of Blue Diffusion-Treated Sapphires," *Gems Gemol.*, **26** [2] 115-33 (1990).
6. K. Chemetzer, H. A. Hanni, E. P. Jegge, and E. J. Chupp, "Dyed Natural Corundum as a Ruby Imitation," *Gems Gemol.*, **28** [2] 112-15 (1992).
7. J. H. Song, S. H. Moon, G. W. Jang, and O. S. Song, "Property Change of Sri-Lanka Milky Geudas with Heat Treatment," *J. Korean Gems and Jewelry*, **7** [3] 129-36 (2013).
8. J. H. Song and O. S. Song, "Color Enhancement of the Type II and Type IaB Brown Diamonds into Colorless by HPHT Process (in Korean)," *J. Korean Ceram. Soc.*, **49** [3] 221-24 (2012).
9. J. H. Song and O. S. Song, "Surface Graphite Formation of the Brown Colored Type I Diamonds During High Pressure Annealing (in Korean)," *J. Korean Ceram. Soc.*, **49** [6] 614-19 (2012).
10. E. Fritsch and G. R. Rossman, "An Update on Color in Gems. Part 3: Colors Caused by Band Gap and Physical Phenomena," *Gems Gemol.*, **24** [2] 81-102 (1998).
11. L. V. Nikolskaya, V. M. Terekhova, M. I. Samoilovich, "On the Origin of Natural Sapphire Color," *Phys. Chem. Minerals*, **3** 213-24 (1978).
12. M. Kadleikova, J. Breza, and M. Vesely, "Raman Spectra of Synthetic Sapphire," *Microelectron. J.*, **32** 955-58 (2001).