

The Color Change of Natural Blue Sapphires by Heat Treatment

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ABSTRACT

This research aimed to investigate the effects of heat treatment on color and clarity of blue sapphires. The blue sapphires were heated at sequentially increasing temperature of 1300, 1400, 1500 and 1600 °C in nitrogen atmosphere. Each temperature, the samples were treated for 12 hours, before and after heat treatment at each temperatures, the color and clarity were measured by spectrophotometer. It was found that, when blue sapphires were heated at high temperatures, the color of the untreated sapphire crystal changed to darker blue at higher temperatures. Whereas, the clarity of all samples were not significantly found in the temperature range of 1300 -1600°C .

Key words: blue sapphires, heat treatment

INTRODUCTION

The structure of sapphire is related to that of corundum (Al_2O_3) and involves the Al^{3+} ions being distributed in an ordered fashion in 2/3 of the distorted (trigonal) octahedral sites within a frame work of hexagonal close-packed O^{2-} ions. Chains of face-sharing octahedra are directed along the c axis, and the Al^{3+} ions within each chain form pairs separated by an empty interstitial site as shown in Figure1.(Themelis, 1992; Winotai *et al.*, 2001) The color of blue sapphire results from a process known as intervalence charge transfer. Involved in this are traces of both titanium and iron (Hughes, 1990).

Iron and titanium both are substituted for aluminum in the sapphire crystal structure as shown in Figure 2. The iron may present either in ferrous (Fe^{2+}) or ferric (Fe^{3+}) state, while the titanium is found as Ti^{4+} . Should both Fe^{2+} and Ti^{4+} be present, they may interact with one another if located in close proximity. A single electron hops

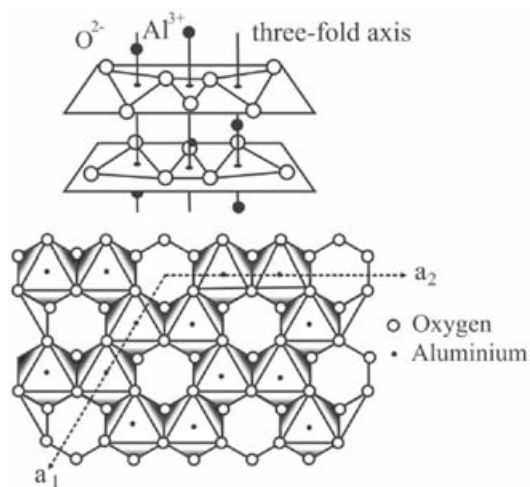


Figure 1 A polyhedral model of the structure of corundum (Hughes, 1990).

from the iron to the titanium ion when stimulated by light ray, in visible light absorbing process. This is illustrated by the following reaction (Hughes, 1990; Nassau, 2001)

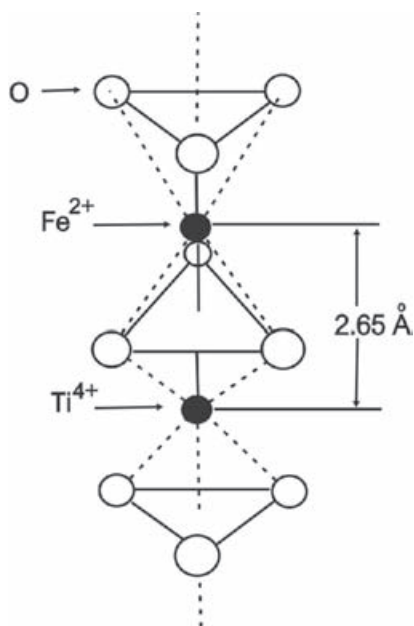
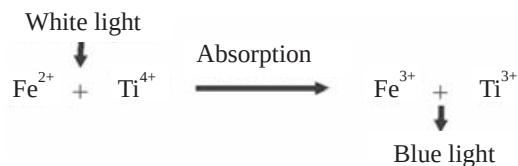


Figure 2 Fe^{2+} and Ti^{4+} replacing two neighboring Al^{3+} in sapphire (Nassau, 2001).



Natural, color and clarity of sapphires are not popular for market. Generally, the quality of sapphires may be improved by various processes, one of which is by the thermal process (Winotai *et al.*, 2001). So that, the purpose of this research is to investigate the effects of heat treatment on color and clarity of blue sapphires.

MATERIALS AND METHODS

The natural Vietnamese blue sapphires were cleaned thoroughly with acid and solvent to remove all stains and other impurities on their surfaces. Then, before and after heat treatment by electric furnace at 1300, 1400, 1500 and 1600°C sequentially in nitrogen atmosphere. The samples were treated 12 hours for each temperature. The

transmission spectrum of samples were measured by spectrophotometer (Perkin Elmer Instruments model Lambda 800). Then, the transmission spectra were converted to CIE color index. The CIE color index in Lab color space in three dimensions is shown in Figure 3 (a) and in two dimensions is shown in Figure 3 (b).

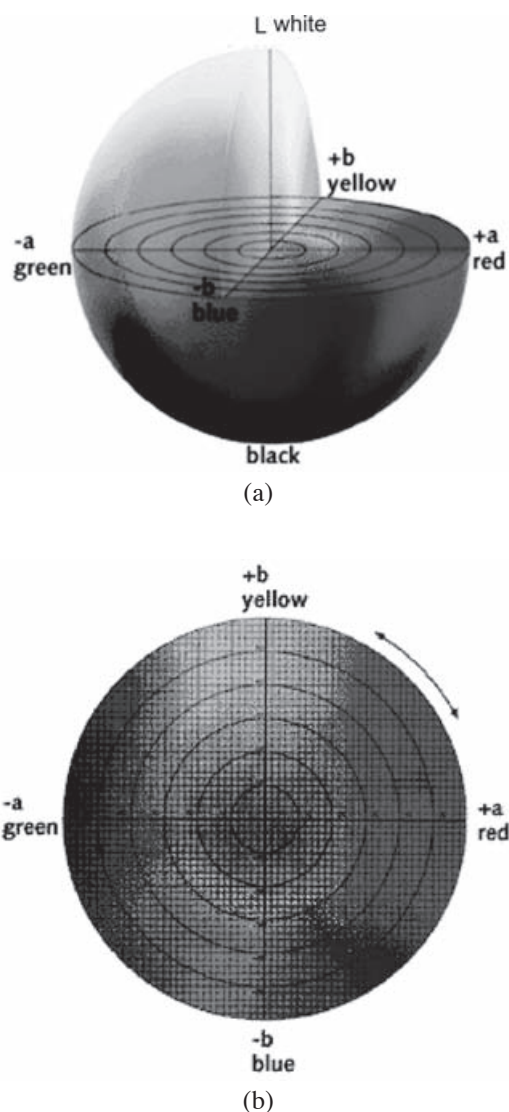


Figure 3 CIE $L^*a^*b^*$ color index, (a) in three dimensions and (b) in two dimensions.

RESULTS AND DISCUSSION

The results of color measurements of three samples for the study of color change and clarity before and after heat treatment are shown in Table 1 and the plotted results are shown in Figure 4.

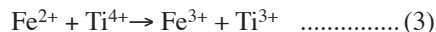
From Figure 4, the blue sapphires were heated at higher temperatures, the b^* index of samples decreases, or blue color of the untreated sapphire crystal (RT) changed to darker blue after heat treatment at high temperatures in nitrogen atmosphere. Consider what happens in our heat treatment, when a slight reduction is produced, say by a heat treatment using nitrogen. This converts some of the Fe^{3+} ion into Fe^{2+} ion. With both Fe^{2+} ion and Ti^{4+} ion now present, a new interaction becomes possible, this is called charge transfer and involves the hopping of one electron from the Fe^{2+} to the Ti^{4+} :



and:



or the combination of reactions (1) and (2):



The products on the right of reaction (3) are in a higher energy state than those on the left, as indicated in Figure 5, and the reaction only occurs when light is incident on the specimen and is absorbed, the reflecting light gives blue to the sapphire. The resulting absorption spectrum is shown in Figure 6, where the absorption band labeled 'b' produces blue (Nassau, 1994).

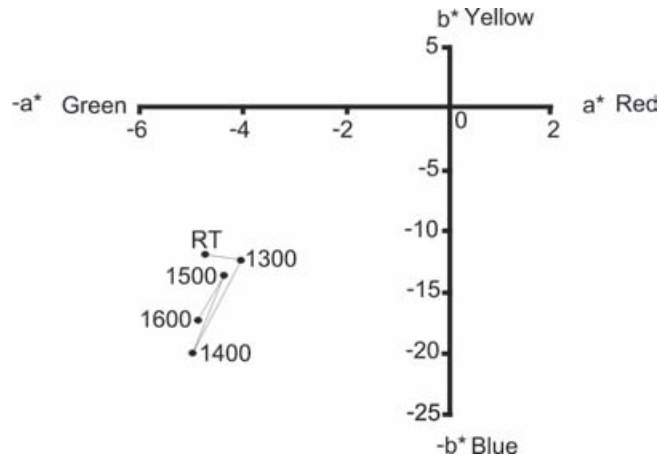
CONCLUSION

The investigation of the effects of heat treatment on color and clarity of Vietnamese blue sapphires by heated at 1300, 1400, 1500 and 1600°C sequentially in nitrogen atmosphere. Each temperature, sample were treated for 12 hours, before and after heat treatment at various temperatures, the color and clarity were measured by spectrophotometer. It was found that, when blue

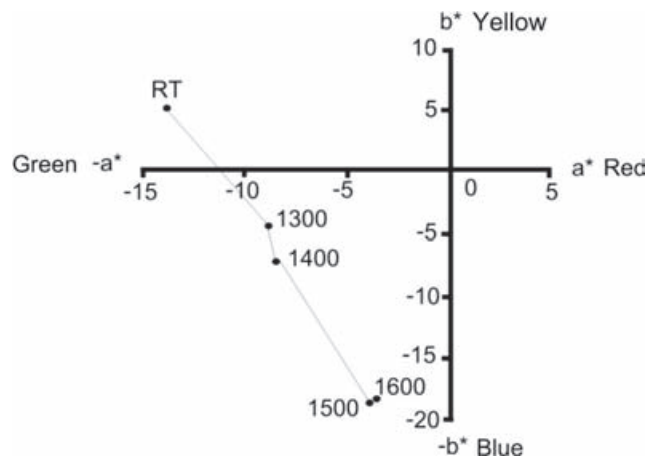
Table 1 CIEL*a*b* color index of three samples before and after heat treatment at the temperatures range 1300 – 1600°C.

Sample	Temperature(°C)	CIE L*a*b* color index		
		L*	a*	b*
1	RT	58.45	-4.74	-11.87
	1300	52.21	-4.02	-12.34
	1400	52.17	-4.96	-19.95
	1500	53.13	-4.35	-13.53
	1600	50.28	-4.87	-17.19
2	RT	52.64	-13.82	5.16
	1300	52.79	-8.86	-4.31
	1400	46.14	-8.40	-7.03
	1500	36.73	-3.79	-18.48
	1600	55.99	-3.54	-18.33
3	RT	54.85	-4.66	-11.18
	1300	46.55	-7.91	-11.25
	1400	49.47	-3.95	-17.30
	1500	49.37	-3.96	-16.44
	1600	50.33	-3.30	-15.39

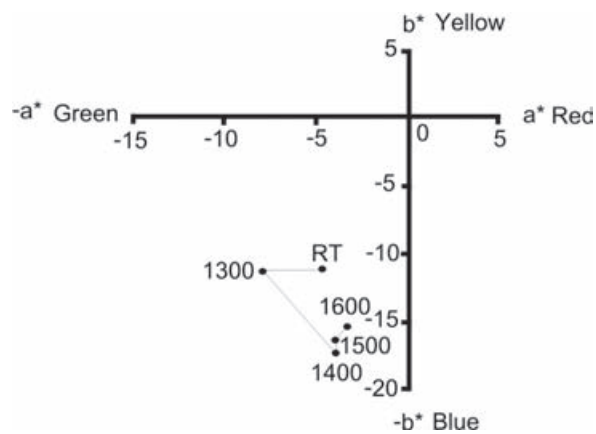
* RT = Room temperature (unheated)



(a)



(b)



(c)

Figure 4 Lab color space in two dimensions of three samples before and after heat treatment at the temperatures range 1300 – 1600°C, (a) sample1, (b) sample 2 and (c) sample 3.

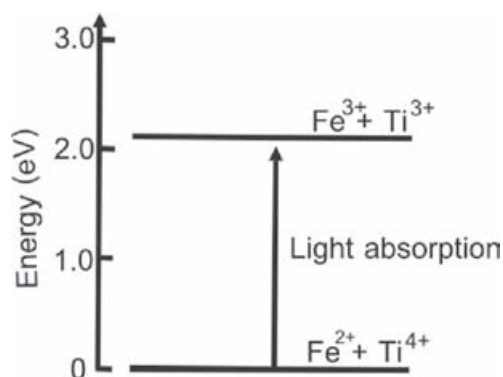


Figure 5 Energy levels involved in the charge transfer mechanism that gives the blue color in sapphire (Nassau, 2001).

sapphires were heated at higher temperatures, the color of the untreated sapphire crystal changed to darker blue at higher temperatures, because after heat treatment at high temperature in reducing atmosphere, Fe^{3+} ions were converted to Fe^{2+} ions. Whereas, the clarity of all samples was not significantly found in the temperature range of 1300 - 1600°C. In this work, the optimization of heat treatments of natural Vietnamese blue sapphires was at 1400°C.

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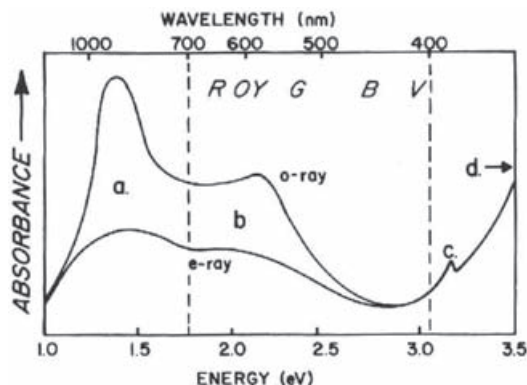


Figure 6 The absorption spectrum of blue sapphire (Nassau, 2001).

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