Blue sapphire enhanced by atmosphere with graphite powder

Sun-ki Kim[1], Hyun-min Choi[1], Young-chool Kim[1], Thanong Leelawatanasuk[2], Thanapong Lhuaumporn[2], Nicharee Atsawatanapirom[2] and Papawarin Ounorn[2]

1: Hanmi Gemological Institute & Laboratory (GIG), 20, 10-gil, Donhwamun-ro, Jongno-gu, Seoul, Korea

2: The Gem and Jewelry Institute of Thailand (Public Organization), 140 ITF Tower, Silom Road, Suriyawongse, Bangrak, Bangkok, Thailand

Abstract: The atmosphere control is very important in the corundum heat treatment. This is why it affect s the color expression of corundum depending on whether an oxidizing atmosphere or a reducing atmosp here is used. Generally, in the conventional corundum heat treatment method, a gas such as oxygen, hydr ogen, nitrogen, or the mixed gases is used for atmosphere control. In this study, graphite powder was used for atmosphere control to enhance a blue sapphire color and the result was confirmed through UV-Visible spectra before and after treatment. It was observed clearly that the Fe^{2+}-Ti^{4+} IVCT band related to the blue color, through the UV-Visible spectrum.

Key words: blue sapphire, atmosphere control, graphite powder, IVCT

Corundum has been heat treated with poor color and clarity improvement since antiquity. Today's modern heat treatment techniques produce dramatic results when compared with the subtle changes of the past. The historic turning point was the discovery, apparently in the 1960s, that the translucent milky white to yellow to brown and bluish white sapphire from Sri Lanka, known as geuda, could be transformed to a fine transparent blue by atmosphere-controlled high temperature heating. The outstanding color change in the geuda material was caused by the dissolution of rutile inclusions in the stone, and by the inward diffusion of hydrogen from the reducing atmosphere (Emmett et al., 2003; Shor and Weldon, 2009).

One of the most important things in corundum enhancement is that of furnace atmosphere. When any oxygen containing material is heated in an enclosed space to high temperature, a little oxygen gas is either emitted or absorbed. An oxidizing atmosphere can be obtained by adding more free oxygen than that given off by the material at a given stabilized temperature, causing extra oxygen to enter the crystal. The strongest oxidizing conditions are obtained by introducing pure oxygen into the chamber. Reducing conditions are generally obtained by inserting a gas which reacts with free oxygen, and in doing so, removes it from the reaction (Hughes, 1997; Nassau, 1981 and 1994; Themelis, 1992).

In 2009, a Korean company had attempted to refinement high temperature technology by using a belt press machine which is very well known to produce a synthetic diamond (Kim et al., 2016). They had modified some important parts of the machine, such as crucible and the metal frame and conducted various experiments to obtain optimum conditions for their treatment technique. The temperature of the treatment likely to be in the range of 1,200 ~ 1,800℃ and the treatment process took less than 20 minutes.

In this process they used graphite powder to create a reducing atmosphere. The stone was placed in the center of a crucible made from refractory clay. Then the crucible was filled up with graphite powder. The graphite has been used because its good thermal conductivity can transfer heat from electric heating element to the stone directly and it is also capable of producing a strong reducing atmosphere. Charcoal and carbon-containing substances allow a reducing atmosphere (Nassau, 1994), resulting in carbon monoxide, as follows:

$2C + O_2 \rightarrow 2CO$

Also, reducing atmosphere can be obtained by adding some water to graphite at a given stabilized temperature, resulting in carbon monoxide and hydrogen, as follows:

$C + H_2O \rightarrow CO + H_2$

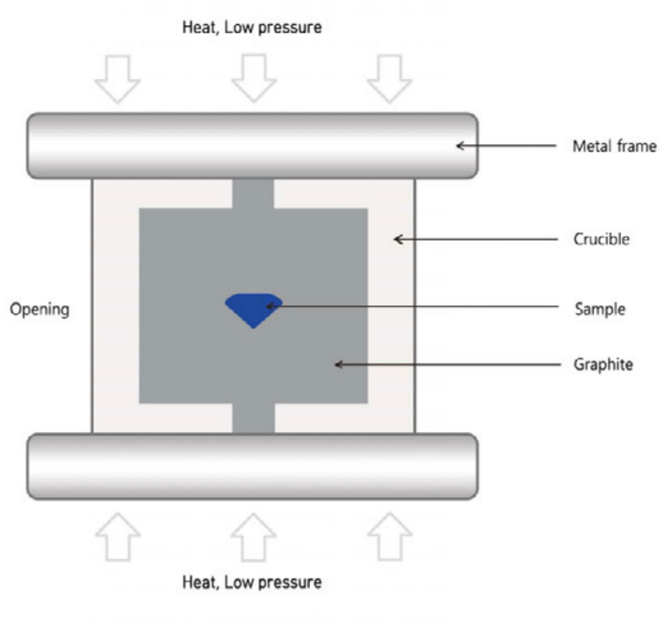

Figure 1. Schematic diagram of heat enhancement in this process.

12 faceted stones were tested for this study. The stones were treated in modified apparatus, and the gemological features of the stones before and after treatment were studied,

Pale blue color of untreated sapphires before treatment turned to intense blue after this process. Some fissures and cracks developed from their internal inclusions such as crystals and negative crystals. The milky cloudy appearance before treatment was removed after treatment.

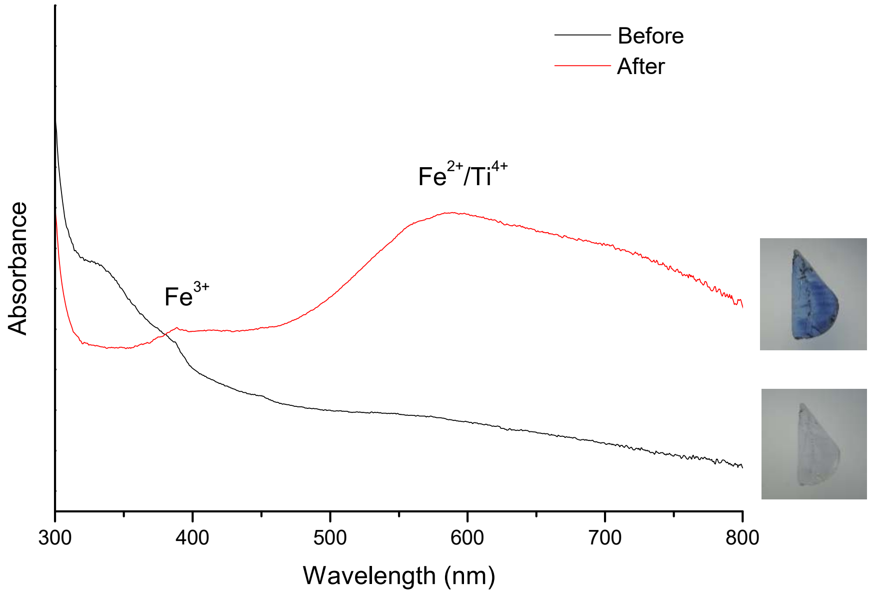

Figure 2. This non-polarized UV-Visible absorption spectra of an untreated blue sapphire before (black) and after enhancement (red).

UV-Visible spectrum of originally unheated pale blue sapphire sample gave a small absorption band due to Fe^{2+}-Ti^{4+} intervalence charge transfer (IVCT) and Fe^{3+}-related peaks at 388 and 450 nm. The Fe^{2+}-Ti^{4+} IVCT band responsible for the blue coloration have been obviously enhanced after this process.

Since graphite is directly in contact with the sample, it can act as a powerful reducing agent as well as transfer heat supplied from the outside. Therefore, even though the treatment time is short, the absorption band due to Fe^{2+}-Ti^{4+} IVCT can be enhanced. Nonetheless, further study is require for better understanding of the change mechanism and also the exact role of pressure in this process.

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