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Luminescence of Beryllium heat treated corundum

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ABSTRACT

Corundum is a famous gem in jewelry market. The quality of the corundum depends on clarity and color. There are many heat treatment methods to enhance the color of corundum. A traditional way is to only treat the gemstones with high temperature to improve. Nowadays, chemical flux is also used in the heating process. Beryllium (Be) has been mixed with the flux for the very high temperature treatment. By this method, the enhanced stones appear brighter and yellowish brown color. Examining the Be heat treated corundum needs the advanced instruments which requires the gem samples to be destroyed. In this study, the luminescence spectrophotometer was applied to indicate the contamination of the Be in the heat treated corundum. Melted area on the surface of the Be treated corundum showed the luminescence spectra of chromium in the difference structure of corundum. The extra spectrum should be because of the melting of BeO and Al_2O_3 mixture. The luminescence method successfully identified the beryllium heat treated corundum which has the remnant of melted area on the surface.

Keywords: Corundum, Heat treatment, Beryllium, Luminescence

INTRODUCTION

Nowadays, the corundum (Al_2O_3) still be an important gems in the jewelry market because of the durability, hardness, and colorful. In nature, the gem quality with valuable color is rare. Almost of its have to be heat treated to enhance the color of the stone. A traditional way is to only treat the gemstones with high temperature to improve. Normally, chemical flux is also used in the heating process such as borax, lead glass and some light elements. Beryllium (Be) has been mixed with the flux for the very high temperature treatment. It is also a major element in chrysoberyl ($BeAl_2O_4$) that can be found associate with the sapphire in some origin. The first experiment of the Be treated corundum was an accident of the mixed of chrysoberyl in corundum crucible in the heat treatment process. The Be element from chrysoberyl has been diffused in to the corundum lattice and enhance the color of the corundum. Then, the heaters did the investigation of the Be element in the heat treatment process until they success. The process of heating is until now undisclosed by the heaters. In addition, the Be flux in the heating process is a toxic which the heater has to be careful while operating.

Be element is in the alkaline earth column in the periodic table. It is not easy to be analyzed by the non-destructive advance instrument such as Raman spectroscopy, FTIR spectroscopy and UV-Vis NIR spectrophotometer. The Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICP-MS) and Laser Induced Breakdown spectroscopy (LIBS) are

usually used to analyze the amount of Be on the surface of the treated corundum. The disadvantage of these instruments is the destruction of the sample by the laser ablation.

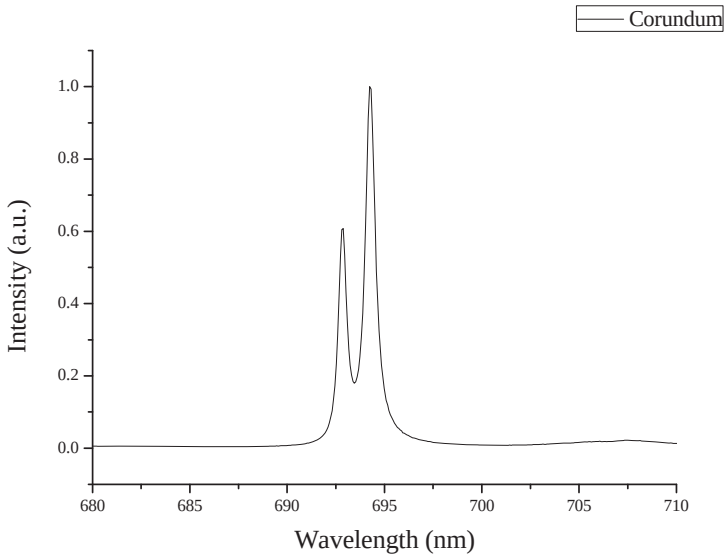

Fig. 1 Luminescence spectrum of Cr^{3+} in the corundum structure.

Commonly, the chromium is a major trace element in corundum. When there is much more enough amount, it is a cause of red color which can be called “ruby”. The other sapphire can also be contained a small amount of chromium. It is the cause of luminescence in corundum structure. The chromium emission lines at around 692.4 and 694.2 nm can be observed in the luminescence spectrum of the corundum (Nelson and Sturge, 1965; Wanthanachaisaeng et.al, 2006). The intensity depends on the concentration of chromium in the corundum (Fig. 1). The melting point of corundum is 2050^{o}C. The chromium can be also a trace element in chrysoberyl. When there is much more enough, it can be showed the color change which can be call “Alexandrite”. The melting point of chrysoberyl is 1870^{o}C The luminescence of the chromium structure shows the difference pattern when comparing to the corundum because of the difference crystal system (Trindade et al., 2011). These luminescence spectrums have been compared by Nasdala et al. (2004).

With the Be heat treatment at high temperature, the melted surface of the corundum can be presented various of mineralizers (Bukin et al., 1981; Alimpiev et al., 2002). Then, the luminescence spectrophotometer has been used in this study to investigate the phase change at high temperature of the Be treated corundum.

MATERIALS AND METHODS

The corundum (green sapphire) from Bangkacha, Chanthaburi was used in this study. The stone was polish in to a tablet perpendicular to the optic axis (Fig. 2). It was heated at high temperature by the heater in Chanthaburi with the mixed Be flux. The sample was heated in the electric oven with the temperature more than 1600^{o}C for 168 hours (personal communication with the anonymous heater in Chanthaburi). The Renishaw RM100 Raman spectrometer equipped with Leica DMLM optical microscope, a grating with 1200 grooves per mm, and a Peltier-cooled charge-coupled device detector with Ar-ion laser wavelength of 488 nm was used to investigate the luminescence of the heated corundum.

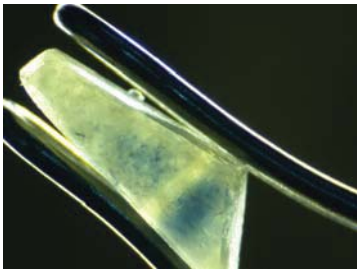

Fig. 2 The Be treated sapphire from Bangkacha, Chanthaburi

RESULTS

The unheated green sapphire from Bangkacha was used to investigate in this study. Normally, the luminescence of R1 and R2 emission peaks of corundum at the room temperature are at 694.2 and 692.8 nm (Wanthanachaisaeng, 2007). The luminescence of chromium in chrysoberyl structure has also presented in figure 3. After the Be heat treated, some part of the stone turn to yellow color by the influence of Be diffusion (Pisutha-Arnond et al., 2004). With the high temperature heated, some part at the surface of the stone showed the melted surface which should be the recrystallization between the Be flux and corundum host at high temperature (Fig. 2). The luminescence spectrophotometer has been applied to investigate this melting part at the surface of the stone to investigate the phase change after heat treatment. Not only the R1 and R2 emission peaks of corundum structure, but the extra luminescence spectrum emission also showed the broader peaks at 678.8 and 683.4 nm (Fig. 3).

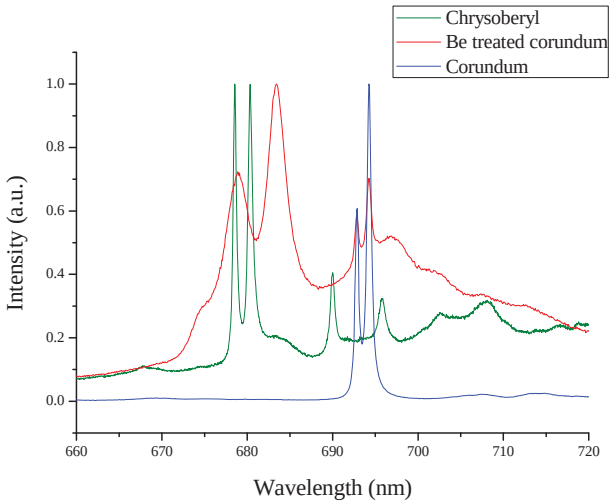

Fig. 3 Luminescence spectrum of chrysoberyl and corundum compared to the Be heat treated corundum at the melted surface

DISCUSSION

From the report of Atichat et al. (2008), they reported that the investigation of the beryllium-treated sapphire from Ilakaka, Madagascar by the Luminescence spectroscopy detected the three emission peaks at 688.9, 691.2 and 693.2 nm at the recrystallization on the surface which is not the normal luminescence spectrum from the Cr^{3+} in the corundum structure. These result is still under investigation to explain the extra peak after the Be heat treated. Also the Be treated corundum in this study, emission significant peaks at 678.8 and 683.4 nm have been detected at the melting surface instead (Fig. 3).

In the Be treated heating process, the beryllium diffused into the surface of Al_2O_3 structure at high temperature and at the surface of the host would be gradually transform to the $BeO+Al_2O_3$ mixture phase. Because of the reaction at high temperature (more than 1600^oC) between Be flux and the host corundum (Bukin et al., 1981), the $BeO-Al_2O_3$ compound melted at the surface of the stone. The recrystallization of the melting surface was just a short time cooling to room temperature. Therefore, the Cr^{3+} trace element was alternated to $BeO-Al_2O_3$ compound structure (orthorhombic structure) at the surface and some part still showed the luminescence peaks of corundum (Trigonal structure). As it is shown in the figure 3, however, the peaks at 678.8 and 683.4 nm are broader peaks when compared to the luminescence peaks of crystalline chrysoberyl. This result indicates that melted surface of the $BeO-Al_2O_3$ compound at Be heat treated corundum surface is not yet fully recrystallization because the final process of the heating, the stone must be taken out of the oven at high temperature immediately. The phase identification of the melted surface is still under investigation.

CONCLUSION

Because the problem to identify the Be heat treated corundum in the market has to use the advance instrument that has to destroy the sample, the luminescence technique can be used to indicate the Be treated corundum if there still has the remnant of the recrystallization at the surface of the stone without damaging the gemstone.

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