Investigation of Be-treated sapphire by luminescence spectroscopy

Wanthanachaisaeng, B.[1,*], Bunnag, N.[2], Sutthirat, C.[3,4], Atichat, W.[4], Ounorn, P.[4], Sripoonjan, T.[1,3], Lenz, C.[5], Nasdala, L.[5]

[1]*Gems Enhancement Research Unit, Faculty of Gems, Burapha University, Chanthaburi, 22170, Thailand*
[2]*Faculty of Gems, Burapha University, Chanthaburi, 22170, Thailand*
[3]*Department of Geology, Faculty of Science, Chulalongkorn University, Bangkok, 10300, Thailand*
[4]*The Gem and Jewelry Institute of Thailand (GIT), Bangkok, 10500, Thailand*
[5]*Institut für Mineralogie und Kristallographie, Universität Wien, 1090 Wien, Austria*
**e-mail: bhuwadol@yahoo.com*

Natural sapphire, nowadays, is commonly treated to enhance colour and clarity and hence to improve the quality of stones. There are several treatment methods including heat treatment, irradiation, and dying. The most famous and acceptable method is heat treatment because the change of the colour and clarity of the stone after treated is stable and permanent. Heat treatment has been developed from sole dry heating to high temperatures treatment to techniques which includes adding of a variety of chemical substances. Treatment of sapphire with Be has been discovered and developed recently by a heater in the town of Chanthaburi, Thailand. When the material to be treated is mixed with chrysoberyl ($BeAl_2O_4$), the colour of the sapphire is more favourably changed and becomes brighter. Pisutha-Arnond, et al. (2005) reported that beryllium has been diffused into the sapphire lattice influencing the initially brown colour in the Be-treated sapphire. The Be-treatment of sapphire is quite difficult identify. The LA–ICP–MS (laser ablation inductively coupled plasma mass spectrometry) technique well suitable to analyse Be and hence unravel the treatmnent, however samples are destroyed surficially (the analysis produces tiny holes about 50 µm in diameter). In this present study, photoluminescence spectroscopy has been applied to investigate traces of diffused Be without damaging of stone.

Luminescence of Cr^{3+} in the corundum structure has been widely studied, for instance to evaluate the amount of Cr or as pressure meter (Wanthanachaisaeng et al., 2005). Atichat et al. (2008) reported that Cr^{3+} luminescent peaks were found at 688.9 nm, 691.2 nm and 693.2 nm at the recrystallization area of Be-treated sapphire. This phenomenon has been described as recrystallization at the surface of heated sapphire. In this study, we have analysed a sapphire sample from the Bangkacha District, Chanthaburi Province, Thailand. The specimen was cut into three pieces (Fig. 1); two were heated with and without Be whereas the third was left unheated as. A Renishaw RM1000 spectrometer equipped with a grating with 1200 grooves per mm, and a Peltier-cooled charge-coupled device detector was used to analyse the luminescence. Spectra were excited with the 488 nm line of an Ar^+ laser.

We found that the unheated sapphire showed the normal emission spectrum of corundum, with Cr^{3+} peaks at 692.8 nm and 694.2 nm (Fig. 2). After (Be-free) heat treatment at 1650°C, Cr^{3+} luminescence was detected at 688.7, 690.6, 692.8, and 694.2 nm, which is assigned to the emission of Cr^{3+} in the boehmite structure (Gaft et al., 2005). The piece that was high-temperature heated with beryllium flux yielded luminescence peaks at 678.5, 680.4, 688.7, 690.6, 692.8, and 694.2 nm on the melted surface of the treated sapphire. The first two peaks are assigned to emissions of Cr^{3+} in the chrysoberyl structure (Gaft et al., 2005); this phenomenon is not known from untreated corundum of naturally orange colour. The preliminary results of our study indicate that the temperature and the chemical Be-flux in the heating process at high temperature affects a phase change on the heated sapphires' surface.

The photoluminescence technique can potentially be used to unravel Be-treatment, provided the facet stone has remnants of the melted area on its surface.

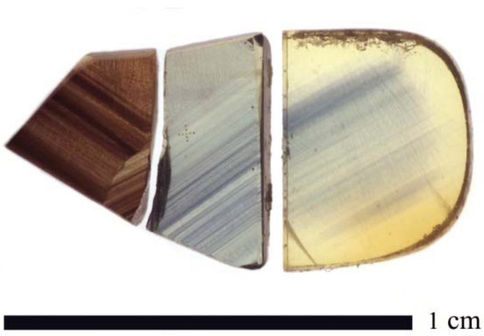

Fig. 1. *Sapphire from Bangkacha unheated (left), heated at 1650 °C (middle) and Be-heated (right; note the yellowish colour especially at the lower right side).*

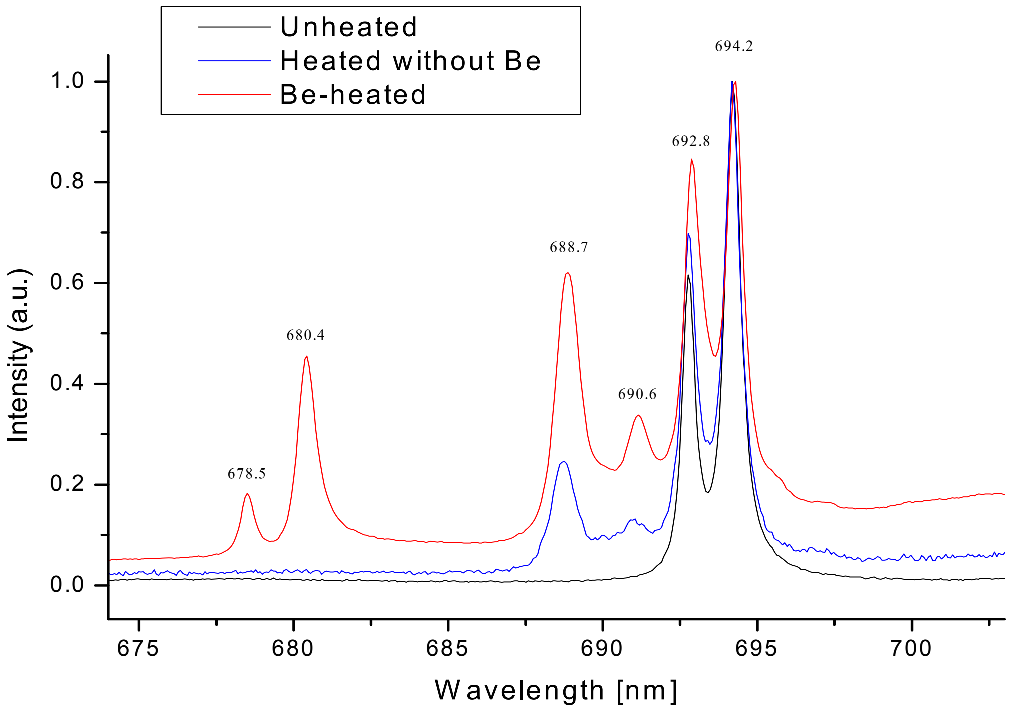

Fig.2. *Luminescence spectra of unheated sapphire (black; showing only the emission of Cr^{3+} in the corundum structure), heated at 1650°C (blue; Cr^{3+} also in the boehmite structure), and Be-treated sapphire (red; Cr^{3+} also in the chrysoberyl structure).*

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