Introduction
Since late 2013, a variety of gemstone sold as “black sapphire” has entered the market. The result of our preliminary investigation on those stones were quickly reported to the gem community (see GIT’s LAB INFO by Leelawatanausk and Maneekrajangsang, January 2014; Leelawatanausk et al., 2014). This article is the update of our detailed investigation on this material.

Material and methods
Four “black sapphire” samples (two obtained in late 2013 and the other two in mid 2014) were selected for this study. They were faceted stones come in mixed cut, oval shapes, weighing from 1.44 to 1.91 ct. (Figures 1 and 2). All stones were recorded for standard gemological properties. Some specific spectroscopic data were also collected by advanced instruments; UV-Vis-NIR, FTIR, EDXRF spectrometers, Soft X-Ray radiograph and DiamondView™.

Results
General properties
The samples appear from extremely dark blue to almost black with low transparency under daylight (Figures 1 and 2). The stones standard gemological properties are generally consistent with natural sapphire. These four stones possess the RI values of 1.760 – 1.770 and SG values of 3.95 – 4.01. The stones show none to moderate dichroism from very dark blue to dark greenish blue through a dichroscope and inhibit under both LWUV and SWUV.

Microscopic features
Under magnification with normal illumination, the stones contain many healed fissures which made it difficult to find natural inclusions (Figures 3 and 4 left). However, fiber-optic lighting technique would be very helpful method to find blue to black color concentration along the healed fissures throughout the whole stones (Figures 3 and 4 right). Due to the lack of transparency of mid 2014 stones, one sample (1.54 ct.) was cut into 3 pieces in order to see more inclusions and provide better results from advanced testing (Figure 2). The polished slabs (~1 mm thick) reveal many features indicating the natural origin of raw material, such as cloud of silk pattern (Figure 5) and repeated (winning) (Figure 6).

Absorption spectra
The UV-Vis-NIR spectra of the late 2013 samples reveal iron-related absorption peaks at 377, 388, 450 mm, and Fe+/Ti³⁺ Intervalent charge transfer (IVCT) band at ~580 nm indicating the stone’s ‘metamorphic origin’ (Figure 10). By contrast, the UV-Vis-NIR spectra of the mid 2014 samples clearly give not only the Fe-related peaks at 377, 388, 450 nm and Fe²⁺/Ti³⁺ IVCT band at ~580 nm, but also the Fe²⁺/Fe³⁺ IVCT absorption bands at ~900 nm indicating the stone’s ‘basaltic origin’ (Figure 11). Notably the absorption spectrum of the blue zone shows higher intensity of Fe²⁺/Ti³⁺ IVCT absorption band near 580 nm than that found in the paler color zone of the same slab sample.

Discussion and conclusion
The late 2013 samples are blue to dark blue stones that were treated from starting raw material of metamorphic origin. By contrast, the mid 2014 samples apparently look much darker blue to almost black stones that were treated from starting raw materials of basaltic origin. The starting raw materials could be low-quality, near colorless to pale colored sapphire with abundant open fissures from both types of origins that were treated by a usual Ti-diffusion technique. Having been heavily fractured materials to begin with, the Ti compound could enter into the stone via open fissures and the Ti-diffusion could have been taken place from the fissures outward to the host corundum while those fissures were also healed during high temperature treatment. Hence, Ti-diffusion technique could create dark blue color zones extending outward from the fissures inside the stone and make them look very similar to a black sapphire. As such, these new products should be called “diffusion-treated black sapphire”, rather than “black sapphire” in the market.

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