Some Uncommon Sapphire "Imitations": Blue Co-zirconia, Kyanite & Blue Dumortierite

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筆者滙報數個瑞士珠寶研究院(SSEF)近期收到要求鑑證的藍色寶石，經檢測後確定其中包括一些非常罕見的藍寶石模擬石：含鈷氧化鋯、藍晶石及藍線石等。

Sapphires are among the most abundant gems we receive at the Swiss Gemmological Institute (SSEF) for testing. From time to time, however, we are quite surprised by the imitations which we find among the goods sent in and this can then be disappointing news for the clients. In the following short note, the author presents a few uncommon imitations identified recently at the SSEF. Identification of these imitations is straightforward and should be no problem for any experienced gemmologist.

The first case is that of an attractive blue faceted stone of approximately 1.4 ct, set in a ring with diamonds (Fig. 1). The stone was characterised by a high lustre and exceptional brilliance, combined with a vivid blue colour. Although sold to our client as a sapphire, the look of the stone was "too good to be true" and was thus a doubtful case even for our client. Gemmological analyses revealed immediately that this was in fact no sapphire. The stone in the ring showed a negative RI reading (above 1.79), an isotropic optical character (polariscope) and thus no pleochroism at all. Under the microscope, we saw no inclusions, however a slightly greenish reaction under the LWSW and there was a weaker similar reaction under SWUV lamps. Based on these properties and a chemical analysis by X-ray fluorescence (EDXRF), the blue stone was readily identified as cubic zirconia (ZrO_2). Having seen this artificial product in a wide range of colours, the author had not previously seen one of such a saturated and attractive blue. Based on literature (Nassau 1981) the analysed traces of cobalt in that stone have been identified as the colouring element in this specimen. The absorption spectrum of the stone (Fig. 2) – although superposed by several rare

Fig. 1 These two blue imitations of sapphire are cobalt-doped cubic zirconia (ZrO_2) and were tested recently at the Swiss Gemmological Institute SSEF. *Photo © Luc Phan, SSEF.*

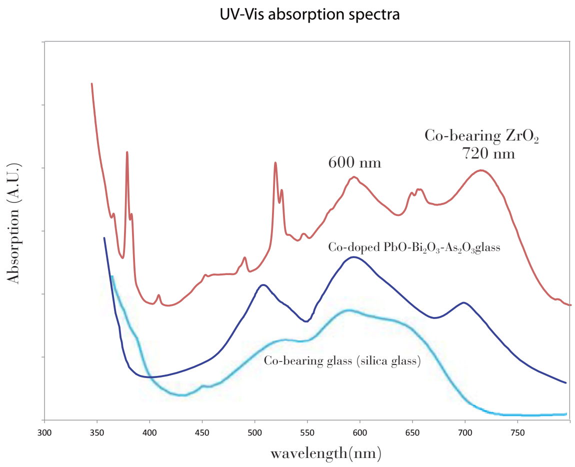

Fig. 2 The absorption spectra of Co-bearing ZrO_2 and Co-bearing glasses show similar broad absorption bands due to cobalt as colouring element. The spectrum of the blue cubic zirconia is further superposed by a series of rather narrow absorption bands at approximately 380 nm, 490 nm, 520 nm, 655 nm due to traces of rare earth elements.

earth element bands – is dominated by three broad absorption bands at approximately 520 nm, 600 nm and 720 nm respectively, which is interpreted as absorption of Co in accordance with similar broad Co-absorptions in Co-doped glass (Rao et al. 2012). Just a few days after testing that ring, an auction house sent in an even larger blue stone of 16.3 ct for testing. To our surprise and that of the client, this stone was also identified as Co-bearing cubic zirconia (Fig. 1).

The second case is that of a small parcel of six blue stones of 3.1-5.7 ct weight sent to SSEF for testing. Our analyses revealed that they were in fact kyanites except for one sapphire showing indications of heating (Fig. 3). Again, the five kyanites were easy to identify, based on their physical properties with an RI of 1.711-1.730 (DR 0.019) and a SG of 3.63. They showed distinct pleochroism with dark blue and light blue colours and distinct colour zoning and

Fig. 3 From this parcel of six blue stones, five were identified as kyanite and only one as sapphire.
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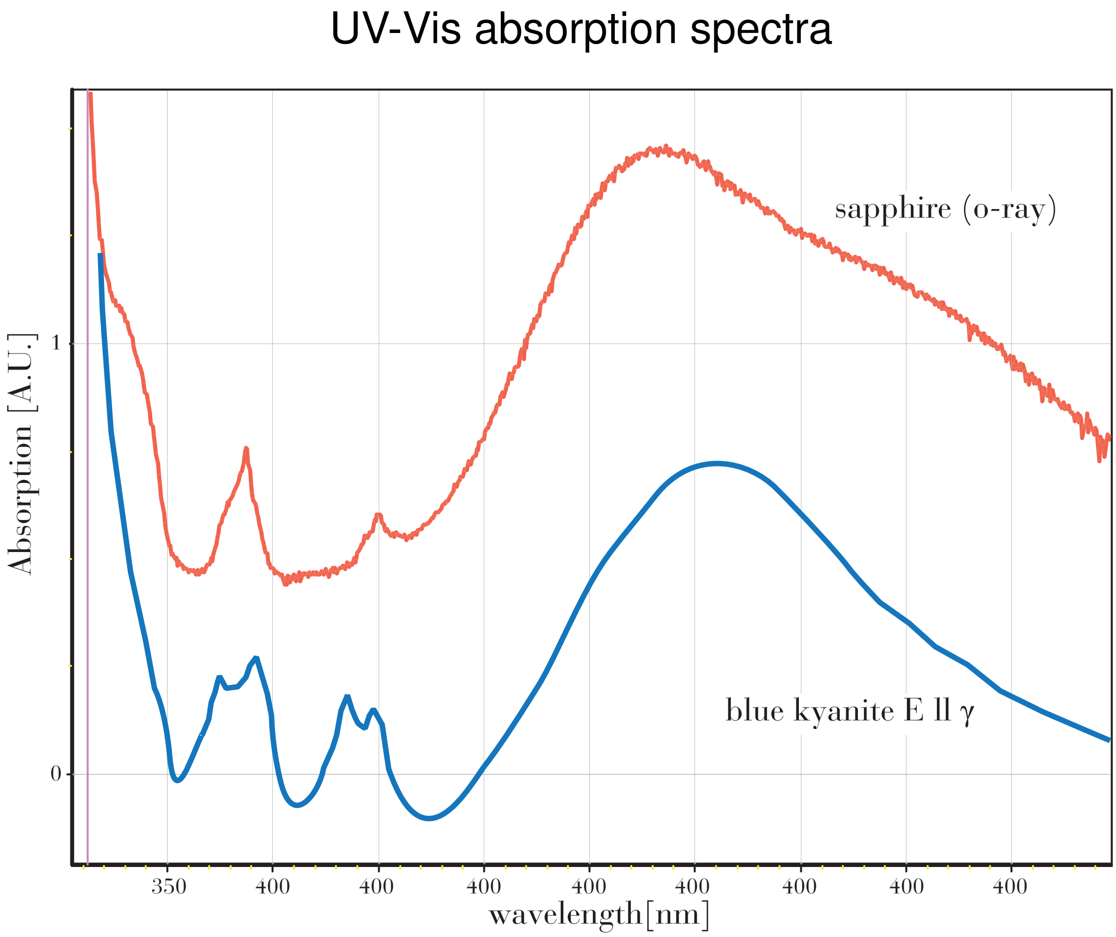

Fig. 4 The comparison of the absorption spectra of kyanite and sapphire shows a close similarity. The dominant absorption band at about 580 nm is due to Fe^{2+}-Ti^{4+} intervalence charge transfer. The small absorption bands at 450 nm and below are resulting from Fe^{3+} replacing Al^{3+} in the crystal structure.

Fig. 5 Blue dumortierite in different orientations showing distinct pleochroism from near colourless to dark blue. *Photo © M.S. Krzemnicki, SSEF*

parallel hollow channels under the microscope. Faceted kyanite of saturated blue colour and high purity has been on the market for quite a time, especially material from Nepal (Fritsch 2002, Henn & Schollenbruch 2012). Although the identification was straightforward and simple, the client was quite astonished to learn that most of his submitted "sapphires" were in fact kyanites. It is however quite interesting, that these intense blue kyanites owe their colour to Fe^{2+}-Ti^{4+} and Fe^{2+}-Fe^{3+} intervalence charge transfer (IVCT) and Fe^{3+} absorption bands, exactly the same as metamorphic sapphires (Platonov et al. 1998). Although different in crystal structure, this ultimately produces similar spectra to those of sapphire (Al_2O_3) and the alumosilicate kyanite $Al_2(SiO_4)O$ (Fig. 4). Even more interestingly, kyanite is often found with corundum, especially well-known from the ruby deposits within amphibolite rocks in Winza (Tanzania) and Mozambique.

The last case is that of a blue stone of 2.07 ct submitted to SSEF for testing some time ago. Again it was immediately evident, that it was not a sapphire but some other mineral. Based on classical testing methods (RI, polariscope, SG) and combined with chemical (EDXRF) and structural (Raman) analyses, the blue stone could be readily identified as blue dumortierite (Fig. 5). Dumortierite $Al_7BO_3(SiO_4)_3O_3$ is well known as a constituent of aluminium-rich and highly metamorphosed rocks and may present as dense translucent to opaque blue masses as an ornamental material. Single crystals of transparent blue dumortierite, however, are much more rare. The sample we investigated was characterised not only by an excellent purity, but also by a very strong pleochroism from near-colourless to deep blue to nearly black (Fig. 5). Interestingly, the colour of blue dumortierite is again linked to Fe^{2+}-Ti^{4+} intervalence charge transfer (Platonov et al. 2000) resulting in broad absorption bands in the visible range of the spectrum.

In conclusion, these three imitations were easy to detect, but intriguing in their optical properties and behaviour. For an inexperienced buyer, the Co-bearing zirconia and kyanite can make very convincing sapphire lookalikes and end up giving them quite a nasty surprise when their true nature is unveiled. Transparent crystals of blue dumortiertite are however such a rare material, that this will be only rarely be mistaken for sapphire.

References

Fritsch E. (2002) Blue, biaxial positive kyanite from Nepal. Gems & Gemology, Vol. 38, pp. 96-97

Henn U., Schollenbruch K. (2012) Saphirblauer Disthen (Kyanit) aus Nepal. Zeitschr. Der Deutschen Gemm. Gesellschaft (in German). Vol. 61, No. 3-4, pp. 91-98

Nassau K. (1981) Cubic zirconia: an update. Gems & Gemology, Vol. 18, 9-19

Platonov A.N., Tarashchan A.N., Langer K., Andrut M., Partzsch G., Matsyuk S.S. (1998) Electronic absorption and luminescence spectroscopic studies of kyanite single crystals: differentiation between excitation of FeTi charge transfer and Cr^{3+} dd transitions. Physics and Chemistry of Minerals, Vol. 25, No. 3, pp 203-212

Platonov, A.N., Langer, K., Chopin, C., Andrut, M., Taran, M.N., 2000, Fe^{2+}-Ti^{4+} charge-transfer in dumortierite. European Journal of Mineralogy, 12, 521-528

Rao N.S., Rao S., Rao Ch.S., Raghavaiah B.V., Kumar V.R., Brik M.G., Veeraiah N. (2012) Influence of valence states and co-ordination of cobalt ions on dielectric properties of PbO-Bi_2O_3-As_2O_3 : CoO glass system. Physica B: Condensed Matter, Vol. 407, No. 4, pp. 581-588