TREATMENTS

Heated Sapphires with Unstable Colour Centres

Recently there has been a renewed focus on certain sapphire varieties that may exhibit a colour shift (or tenebrescence) as a result of unstable colour centres (Krzemnicki *et al.* 2018; American Gemological Laboratories [AGL] 2019; Krzemnicki & Cartier 2019). Over the past year, AGL has been collecting data on gem corundum that may display unstable colouration, specifically pink, padparadscha, orange and yellow sapphires.

The potentially unstable colour centre causing the colour shift is a trapped-hole centre related to Mg^{2+}. This is a naturally occurring phenomenon and is generally stable. However, in certain circumstances, trapped-hole centres are unstable for reasons that are not yet fully understood. When stable, the Mg^{2+}-related trapped-hole centre is active and responsible for the yellow colour in the vast majority of yellow sapphires (see, e.g., Emmett & Douthit 1993). Moreover, it is also an essential contributing chromophore in orange sapphires and in the orangey colour component of padparadscha sapphires. However, when the trapped-hole centres are not stable, there are two states: (1) the colour centre is inactive and therefore does not contribute to a stone's colour appearance, and (2) the colour centre is activated by exposure to UV radiation and then contributes to the observed colour. The trapped-hole colour centre can be returned to its relaxed (inactive) state by exposing the stone to the heat of a lamp (or otherwise warming it) for a brief period.

At the time of the April 2019 AGL press release, our data had shown that such changes in colour can occur in both unheated sapphires and in those that had been heated at relatively low temperatures. That release further indicated that the colour shifts had thus far not been observed in stones heated at relatively higher temperatures.

Recently, however, AGL examined five sapphires that displayed unexpected results when subjected to colour stability testing. They ranged from colourless to very pale blue and light yellow when they were first examined (Figure 36a). After exposure to short-wave UV radiation for 10 minutes, all five stones exhibited a distinctly stronger yellow colouration (Figure 36b). What was unexpected was that all five sapphires revealed clear evidence of having been heated at relatively high temperatures. This

Figure 36: (**a**) These heat-treated sapphires (2.63–4.19 ct) ranged from colourless to near-colourless (pale blue) and pale to light yellow when they were initially examined at AGL. (**b**) Exposing them to short-wave UV radiation for a period of 10 minutes activated unstable colour centres and caused a distinctly stronger yellow colouration. For each case, the stones are shown table-up (left) and from the side (right). Photos by Alex Mercado and Bilal Mahmood, AGL.

was apparent from the presence of heavily altered mineral inclusions, as well as thermally induced and altered stress fractures and partially healed fissures (Figure 37).

Previously it was thought that the heating process stabilised these colour centres, meaning that a colour shift would no longer be observed. The present discovery proves this is not always the case, which has direct implications for gemmological laboratories and the trade at large. Until now, colour-stability tests have been largely relegated to unheated sapphires. The more recent observations that unstable colour centres may be present in sapphires heated at relatively low temperatures—and now at relatively high temperatures—indicate that virtually all sapphires in the colour range of pink through padparadscha and orange to yellow, as well as colourless to near-colourless, should be tested for their colour stability regardless of their unheated or heated condition.

It remains unclear as to why a colour shift was not observed previously in sapphires heated at relatively high temperatures. However, one factor might be the kinds of sapphires that are typically submitted for laboratory testing, which consist of strongly coloured stones. Therefore, the potential influence of trapped-hole centre absorption may be minimised or reduced. Furthermore, the total trace-element composition (relative to Mg content) of more strongly coloured sapphires may provide a better environment to stabilise the trapped-hole centres than lighter stones with a reduced total trace element composition (again relative to Mg: see, e.g., Emmett *et al*. 2003).

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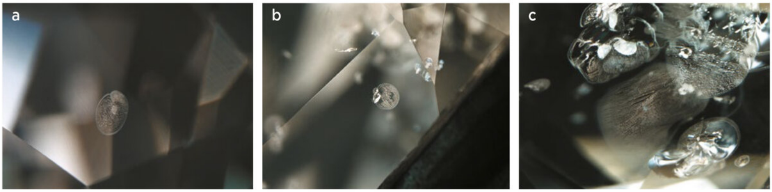

Figure 37: Each of the five sapphires with an unstable colour revealed clear evidence of relatively high-temperature heat treatment, including heavily altered mineral inclusions surrounded by tension fractures, thermally altered and induced stress fractures, and partially healed fissures. Photomicrographs by C. P. Smith; magnified 60× (a), 52× (b) and 48× (c).

References

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