

The nature of Ti-rich inclusions responsible for asterism in Verneuil-grown corundums

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Abstract: Verneuil-grown star corundums, with variable zoning and colour (ruby and sapphire), host three sets of acicular inclusions at 120°. Inclusions are up to 20-30 µm long and 0.1-0.4 µm wide. Their cross-sections match the visible-light wavelength and explain the optical diffraction responsible for sharp six-arms stars in cabochon gemstones. Inclusions are elongated parallel to corundum {110} faces, and they are {110} polysynthetically twinned.

Electron diffraction and high-resolution transmission electron microscopy show that inclusions are almost isostructural with the corundum matrix, even if slightly distorted to a monoclinic lattice with $a = 5.00$ Å, $b = 4.63$ Å, $c = 13.08$ Å, $\gamma = 118^\circ$. Nanochemical data point to a TiO_2 stoichiometry, thus indicating the occurrence of Ti^{4+} cations, coupled with vacancies, within the distorted corundum-like structure (having just 1/2 of the octahedral sites occupied).

Close to the apical terminations of TiO_2 needles, local stoichiometry is consistent with the presence of Ti^{2+} cations, formed by redox disproportionation during post-growth thermal annealing.

Key-words: Verneuil corundums, asterism, Ti-rich inclusions, HRTEM, twinning.

Introduction

Natural gems, such as corundum, quartz, garnet and diopside, may display a special optical feature, consisting in the appearance of a bright star over the cabochon curved surface (*e.g.*, Nassau, 1968; Wüthrich & Weibel, 1981). This feature is called asterism and, like chatoyancy and silky, is due to isororiented acicular inclusions within the gem. The inclusions are oriented according to the host symmetry and have size in the order of the visible-light wavelength. The incident light is scattered by the inclusions, giving rise to star-like optical Fraunhofer diffraction (Moon & Phillips, 1984), with number of arms depending on host symmetry and cut orientation. Long, thin precipitates give a sharper star than do their shorter and wider counterparts (Eppler, 1958; Nassau, 1981).

Black star diopside from Nammakal shows four-arms asterism, when cut perpendicular to its 2-fold axis; the angle between the two sets of arms is 104°. Diopside asterism is due to acicular magnetite or amphibole inclusions (Woensdregt *et al.*, 1983; Doukhan *et al.*, 1990). In quartz cabochon, cut perpendicular to the ternary axis, the star has six arms and is due to oriented «asbestos» fibers (Gübelin, 1968) or sillimanite needles (Woensdregt *et al.*, 1980). Star garnet may show six-arms asterism when observed down a 3-fold axis, or four-arms asterism when observed down a 4-fold axis. In the Idaho star garnet, acicular inclusions are voids or rutile (Gunter *et al.*, 2005).

Asterism in ruby and sapphire is due to acicular rutile inclusions or, rarely, to hematite, mixed $\text{FeTiO}_3\text{-Fe}_2\text{O}_3$ and $\beta\text{-Al}_2\text{TiO}_5$ (Nassau, 1968; Phillips *et al.*, 1981; Weibel & Wessicken, 1981; Sahama, 1982; Barot *et al.*, 1989). Acicular inclusions are elongated parallel to the trigonal prism faces; perpendicular to the 3-fold axis, the corundum cabochon exhibits a six-arms star.

Asterism can also occur in synthetic corundum. The industrial growth of corundum is based on the Verneuil method (Nassau, 1980), which allows the obtainment of large monocrystals («boules») used for gemstones, watch glasses, axe bearings and other technical applications. Typical characteristics of Verneuil monocrystals are curved colour bands, subgrains boundaries and tiny gas inclusions. Cracks and longitudinal fractures may occur as well (Rinaudo *et al.*, 2002). According to Rinaudo *et al.* (2000), boules have a macromosaic structure, with slightly misoriented domains, possibly responsible for the mechanical weakness of Verneuil corundum.

The synthesis of star corundum is a complex, multistep process. Technical details are rarely disclosed, due to obvious industrial secrets, but the basic steps still are those reported in the U.S. patent by Burdick & Glenn (1949). 0.1-0.3 wt.% fine grained TiO_2 is added to the Al_2O_3 feeding; larger amounts of TiO_2 hamper the growth of high-quality corundum monocrystals, whereas lower amounts are not enough for asterism production. The boule, grown in an hydrogen reducing atmosphere, consists of corundum with

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