Gem spinel in the Imperial Crown of the Holy Roman Empire: Evidence for very early gemstone heating?

L. Nasdala[1], T. Lamers[2], H.A. Gilg[3], C. Chanmuang N.[1], M. Griesser[2], F. Kirchweger[2], A. Erlacher[1], M. Böhmler[4], G. Giester[1]

[1]Institut für Mineralogie und Kristallographie, Universität Wien, 1090 Vienna, Austria
[2]Kunsthistorisches Museum Wien, 1010 Vienna, Austria
[3]School of Engineering and Design, Technische Universität München, 80333 Munich, Germany
[4]WITec Wissenschaftliche Instrumente und Technologie GmbH, 89081 Ulm, Germany
e-mail: chutimun.chanmuang@univie.ac.at

The Imperial Crown of the Holy Roman Empire, part of the Imperial Regalia, is the key exhibit in Vienna's Imperial Treasury. It is currently investigated within the three-year interdisciplinary project 'Crown' (www.projekt-reichskrone.at) led by Kunsthistorisches Museum Vienna. The research aims, among others, at issues regarding the Imperial Crown's materials, manufacturing technology and time, as well as its state of preservation. During the first measurement campaign in Spring 2022, we had the task to determine conclusively – and, if possible, to characterise further – all 172 (inorganic) gemstones in the crown, whereas studies of the pearls were planned for the second measurement campaign (2023).

Figure 1. The front plate of the Imperial Crown of the Holy Roman Empire (size 11.2 cm × 14.9 cm) contains two spinels, a pink stone (#A3) in the upper row, left side, and a large red stone (#A25) in the centre of the third row. Photo © KHM-Museumsverband (Christian Mendez); reproduced with permission.

Non-destructive spectroscopic analyses were done on site, using a fibre-coupled WITec confocal Raman probe system equipped with an alpha300 controller. Photoluminescence (PL) and Raman spectra were excited with a 457 nm diode laser (0.05–8.5 mW measured behind the objective). An Olympus 20× objective (free working distance 25 mm) was used.

Besides 71 blue sapphires, 50 garnets, 20 emeralds, 13 amethysts, four chalcedonies and 11 glass imitates, there are three spinels in the Imperial Crown, two in the front plate (Fig. 1) and one in the central cross (Nasdala et al. 2023). The analytical identification of spinel in the

Imperial Crown is of art-historical interest. So far the first appearance of gem spinel in European jewellery was known for the thirteenth century (e.g., Ogden 2021) whereas the central, large spinel in the front plate (#A25) seems to be original; that is, set into the Imperial Crown about 1000 years ago already. This stone hence represents one of the very earliest uses of spinel in jewellery. Furthermore, the stone has two drill holes that indicate an even older use.

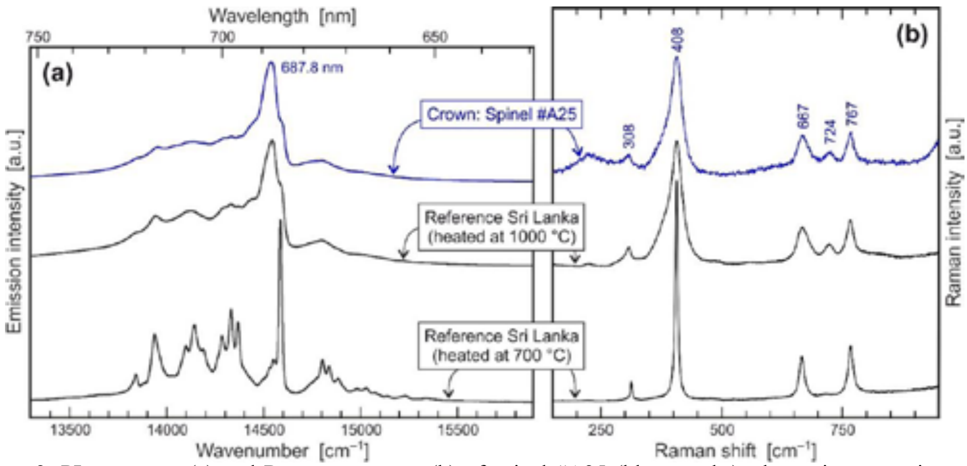

Figure 2. PL spectrum (a) and Raman spectrum (b) of spinel #A25 (blue graphs), shown in comparison with reference spectra (black graphs) obtained from a gem-quality spinel from Sri Lanka that was heat-treated in air.

The central spinel in the front plate (stone #A25) turned out to be of particular scientific interest, as it did not yield PL and Raman spectra that are typical of $MgAl_2O_4$ with (close to) normal occupation of cation sites. Instead, the PL spectrum (Fig. 2a) is characterised by loss of fine structure. Such spectra are obtained from natural Mg-Al spinel only after being heat-treated (Widmer et al. 2015; Liu et al. 2022). Similarly, heat-treatment results in significant broadening and asymmetry of Raman bands (Fig. 2b). These spectroscopic phenomena are assigned to heating-induced cation disorder; that is, increase of partial inversion of the cation occupation, according to ${}^{[4]}Mg\ {}^{[6]}Al_2\ O_4 \rightarrow {}^{[4]}(Mg_{1-x}Al_x)\ {}^{[6]}(Al_{2-x}Mg_x)\ O_4$ (with $x > 0.2$) (Widmer et al., 2015; Ma et al., 2022). The spectra obtained from spinel #A25 hence give strong indication that this stone was heated to close to 1000 °C. This is supported also by the presence of a multitude of healed fractures, 'lily pad' inclusions, and melted sulphides at the surface.

Heating of red 'yāqūt' to enhance colour and transparency is known back to the ninth century (e.g., Troupeau 1998). 'Yāqūt' (an Arabian term) has generally be assumed to refer to gem corundum, but the possibility cannot be eliminated that it – and hence also the early heating – may have included spinel as well. Our spectroscopic results indicate that, as early as about 1000 years ago, spinel #A25 may have been subjected to heat-treatment.

Liu Y, Qi L, Schwarz D, Zhou Z (2022): Color mechanism and spectroscopic thermal variation of pink spinel reportedly from Kuh-i-Lal, Tajikistan. - Gems Gemol 58, 338-353

Ma Y, Bao X, Sui Z, Zhao X, Liu X (2022): Quantifying Mg–Al cation distribution in $MgAl_2O_4$-spinel using Raman spectroscopy: An experimental calibration. - Solid Earth Sci 7, 60-71

Nasdala L, Lamers T, Gilg HA, Chanmuang N C, Griesser M, Kirchweger F, Erlacher A, Böhmler M, Giester G (2023): The Imperial Crown of the Holy Roman Empire, part I: Photoluminescence and Raman spectroscopic study of the gemstones. - J Gemmol 38(5), 448

Ogden JM (2021): Gem knowledge in the thirteenth century: The St Albans jewels. - J Gemmol 37(8), 816

Troupeau G (1998): Le premier traité arabe de minéralogie: Le livre de Yūḥannā Ibn Māsawayh sur les pierres précieuses. - Ann Islamologiques 32(6), 219

Widmer R, Malsy A-K, Armbruster T (2015): Effects of heat treatment on red gemstone spinel: Single-crystal X-ray, Raman, and photoluminescence study. - Phys Chem Miner 42(4), 251