Effects of Gamma Irradiation on Corundum: Towards a Potential Detection Method

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Introduction

Corundum, encompassing the highly prized ruby and sapphire varieties, stands as a cornerstone of the global gemstone market. The allure and value of these gems have historically driven the development of various treatment techniques aimed at enhancing their colour and clarity. While many treatments are stable and widely accepted when properly disclosed, the emergence of new or less understood methods presents an ongoing challenge for the gemological community. Accurate detection and disclosure of all treatments are paramount for maintaining market confidence and ensuring fair trade. Gamma irradiation has been explored as a potential method to alter the colour of various gemstones, including corundum (Ashbuugh, 1988; Pardieu *et al.*, 2022). However, the effects of such irradiation on corundum, the stability of any induced colour changes, and robust methods for their detection remain areas requiring comprehensive investigation. This contribution builds upon our preliminary work, presented at the IGC Tokyo 2023 (Wang et al., 2023), to provide a more in-depth understanding of gamma irradiation effects on a diverse suite of corundum samples and to outline a potential detection method.

Materials and methods

• **Sample selection:** For this study, we carefully selected 29 natural and synthetic corundum samples. This selection was designed to represent a variety of colours, including colourless, pink to purple fancy sapphires, rubies and sapphires. The rationale was to assess how differing trace element compositions, which are fundamental to corundum's colour, influence the response to gamma irradiation. Four selected samples representing different initial colours and elemental concentrations (Mg, Ti, V, Cr, Fe) are presented in Table 1. Elemental concentrations were determined by LA-ICP-TOF-MS.

		Init. Colour	Mg	Ti	V	Cr	Fe
Sample 1	Nat. Crd.	blue	100	175	11	10	2800
Sample 2	Nat. Crd.	purple	25	50	10	400	540
Sample 3	Syn. Crd.	purple	-	60	0.6	360	95
Sample 4	Syn. Crd.	purplish red	-	5	1	1700	-

Table 1. Information and initial colours of the selected four corundums as well as their trace element composition. All numbers are in unit of ppm. "-" indicates that the concentrations are below detection limit ~1ppm.

• **Gamma irradiation:** The samples were subjected to gamma irradiation at FRM II Facility for a continuous period of 70 hours, achieving a total dose of approximately 33 kGy (Li, *et al.* 2022). This represents a substantially higher dose than in our preliminary investigations, intended to maximize any potential colour alterations.

• **Post-irradiation handling:** Immediately following irradiation, samples were carefully transferred into an aluminum container. This precaution was taken to shield them from ambient light exposure, thereby preserving any unstable colour centers that might have been restored until systematic laboratory analysis could start. Upon return to the laboratory, the initial post-irradiation colour of each sample was documented.

• **Colour stability testing:** To test the colour stability we followed an altered procedure based on the standard testing procedure as used also for client stones in the SSEF laboratory (Krzemnicki, 2022). The colour shift of 4 selected samples after each step are shown in Figure 1.

o Fading test: To assess the light stability of any induced colour, samples were exposed to a 20 W high-power LED light source, for a duration of 3 hours. Importantly, this LED source was characterized by the absence of long-wave UV (LWUV) component at 365 nm and only a negligible contribution of short-wave UV (SWUV) at 254 nm (Palke *et al.*, 2023).

o Activation test: Following the fading test, samples were exposed to standard gemological UV lamps to probe for the presence of colour centers that could be reactivated. This primarily involved exposure to LWUV (365 nm) for 10 minutes. For specific samples that showed no discernible colour shift after LWUV activation (e.g., Sample 3), more energetic activation methods were employed, including LWUV exposure for 2 hours, SWUV exposure for 1 hour and deep UV exposure using a DiamondView instrument for 10 minutes, to explore the potential activation of other types of colour centers.

o UV-VIS-NIR spectroscopic analysis: UV-VIS-NIR absorption spectroscopy was the primary analytical technique used to characterize colour and to identify specific chromophores or colour centers. Spectra were recorded over a range of 290 nm to 1600 nm. While the majority of analyses focused on polarized light through C-axis (O-ray), E-ray measurements were also conducted on select samples to further investigate anisotropic absorption features.

o Mild heat treatment: After the colour stability test, a mild heat treatment at 350 °C for 20 minutes was applied to all samples, in order to see the colour stability under heat condition.

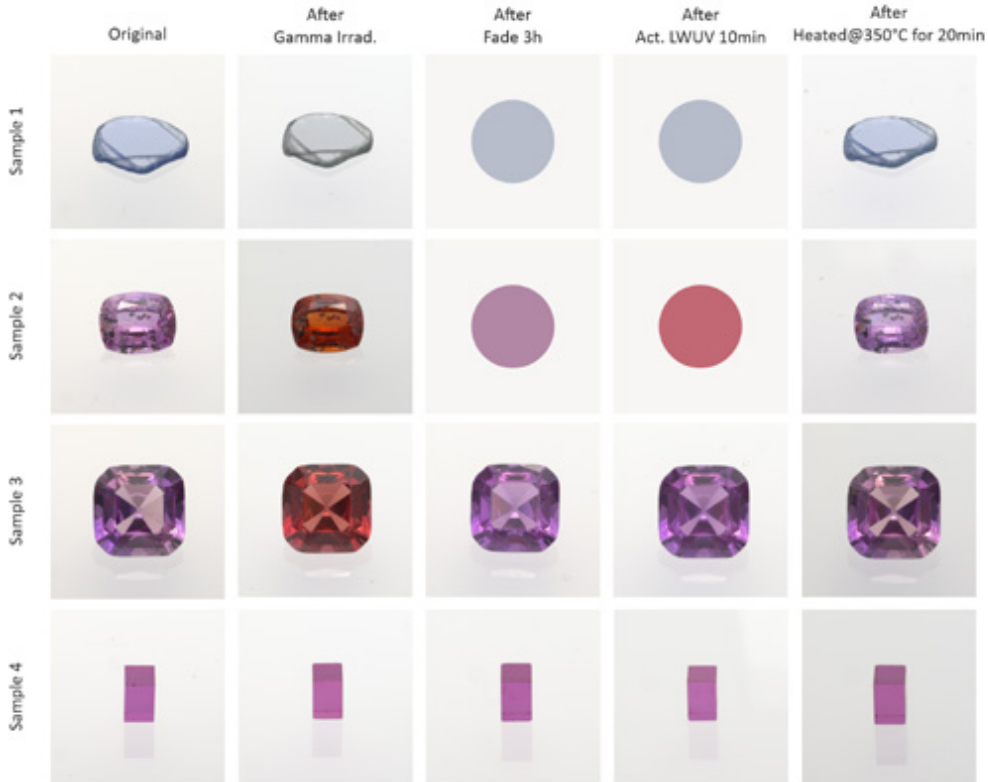

Figure 1. Photos of selected four corundums undergoing colour shift (except for sample 4 no obvious colour shift) after Gamma irradiation, colour stability test in the lab and a mild heat treatment. After fade and after activation photos of Sample 1 & 2 were unfortunately not properly taken, hence the colours are represented by the colour disks.

Results and conclusion

Gamma irradiation induces diverse, chemistry-dependent colour shifts in corundum, which we have categorized into four distinct groups based on their behaviours (Figure 1). These responses include irreversible (during fading or UV activation) blue colour reduction in Fe-Ti rich sapphires (Group 1), which might be one of the reasons that blue/purple hue can be reduced in some rubies. We also observed the development of unstable, light-sensitive, colour reversible orange hues in some natural pink/purple corundum (Group 2) and the appearance of semi-stable orange hues in certain varieties (Group 3) that are bleachable by intense light but not readily reactivated by standard UV sources, nor higher energy UV lights. Notably, high concentration Cr-only synthetic corundum (Group 4) showed an inert response to the irradiation. Those samples with colour shift after irradiation can be restored to their original colours after a mild heat treatment.

The variability and potential transience of these induced colour shifts require a detection approach beyond simple observation. We will propose a strategy based on differential UV-VIS-NIR spectroscopy, meticulously tracking spectral changes during colour stability tests (controlled fading and UV activation). This method involves comparing spectra taken before, during, and after these tests to identify characteristic patterns of colour centres which are unstable, or which can be activated again. We will also discuss spectral features serving as illustrative examples of ongoing investigations into diagnostic markers. This emphasis on the dynamic response of the stone offers greater diagnostic potential than static measurements.

In conclusion, while gamma irradiation effects in corundum are complex and present detection challenges, our methodology may hold promising potential. Future research will focus on expanding the sample database, refining stability testing protocols to enhance diagnostic spectral features, correlating these features with specific colour centres and defects, and validating the method through broader studies. This work aims to provide the gemmological community with more robust tools for identifying gamma-irradiated corundum, thereby supporting market transparency and consumer confidence.

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