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XRF

Glass-Filled Ruby Characterization with the XGT-9000, HORIBA's new micro-XRF

Application Note

Gemology XGT27

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Abstract: Gemstones for jewelry are treated by heating, irradiation, or filling of cracks to make them flawless. We performed imaging analyses using an XGT-9000 X-ray Analytical Microscope on a ruby provided by Mineralab. The transmission X-ray imaging revealed that the ruby included several internal defects, and the fluorescent X-ray imaging revealed that the ruby surface was treated by filling with Pb, Mg and Si which are representative of lead glass.

Keywords: Gemology, Gemstones, Treatment, Ruby, Jewelry, Micro-XRF

Introduction

Ruby is one of the most expensive gemstones on the market due to its increasing rarity. Like sapphire, it is a member of the corundum family. The name ruby is given to any natural corundum (Al_2O_3) with a red color. This color comes mainly from impurities of chromium in the form of Cr^{3+} and secondarily from impurities of Fe and V.[1,2] The best-known deposits are in Southeast Asia and East Africa.

High-quality rubies with little or no defects such as inclusions and/or cracks are becoming increasingly rare as the deposits have already been extensively mined. Moreover, these flawless pieces are often of low weight.

Figure 1: Gemstones for jewelry such as rubies and sapphires.

Producers have therefore sought to improve the quality of imperfect stones. Several techniques can be used: heating, irradiation, or filling of cracks. [1,2]

It is the latter technique that is illustrated in this note. The stones with defects are first heated to empty the cracks. They are then immersed in a mixture of metal oxide powders and heated again. Then they undergo various treatments such as heating in a reduced atmosphere, cutting, and polishing.

While stones with defects have an opalescent appearance, after treatment they have a brilliance comparable to a flawless ruby. However, the market value of these stones is much lower than a flawless natural ruby. Therefore, when such a ruby is sold, it must be accompanied by the words "treated" according to the CIBJO international regulation.[3]

It is therefore interesting to have tools to highlight these treatments. Among these tools, we present a micro-X-ray fluorescence analyzer (micro-XRF) from HORIBA, Ltd., called the XGT-9000 X-ray Analytical Microscope. Micro-XRF is a fast and efficient technique to characterize these treatments.

Instrument description and methodology:

The XGT-9000 (Figure 2) is the latest micro-XRF system from HORIBA. The versatility of the instrument makes it a perfect tool for industrial applications to detect failure problems or foreign particles as well as R&D.[4]

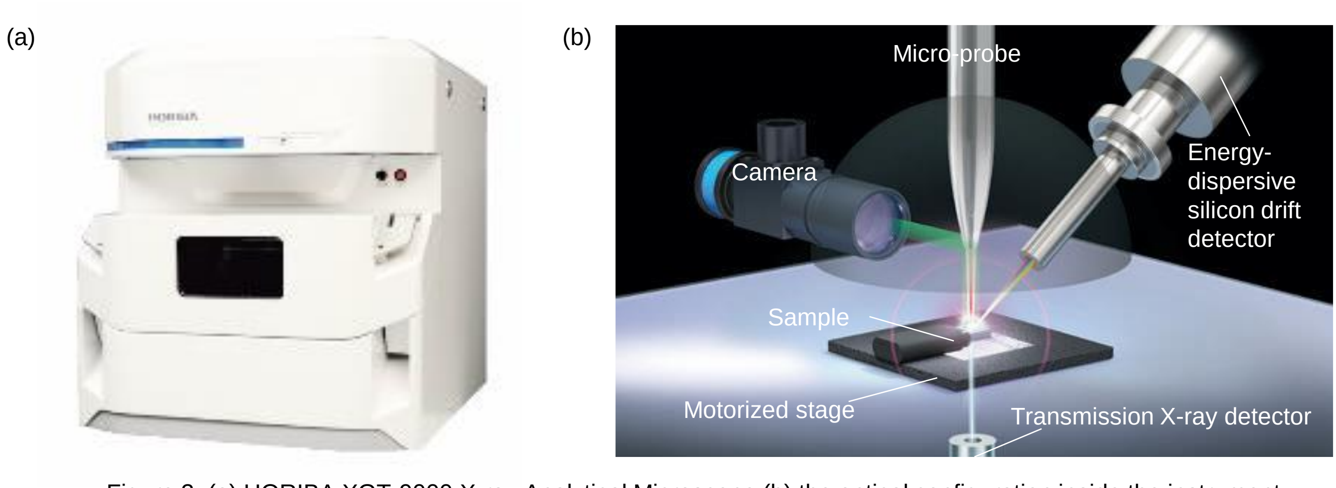

Figure 2: (a) HORIBA XGT-9000 X-ray Analytical Microscope (b) the optical configuration inside the instrument.

The principle of X-ray fluorescence is schematically represented in Figure 3. When materials are exposed to primary X-rays, as shown in Figure 3, the ejection of one or more electrons from the inner shell of the atom may occur. The removal of an electron makes the electronic structure unstable and in order to re-establish neutrality, electrons in the outer shells "fall" into the lower ones to fill the hole left behind. In falling, energy is released in the form of a secondary X-ray photon (fluorescent X-ray), the energy of which is equal to the energy difference of the two orbitals involved ($K\alpha$, $K\beta$, $L\alpha$, etc., in Figure 3). Thus, the material emits radiation with an energy characteristic of the atoms present.

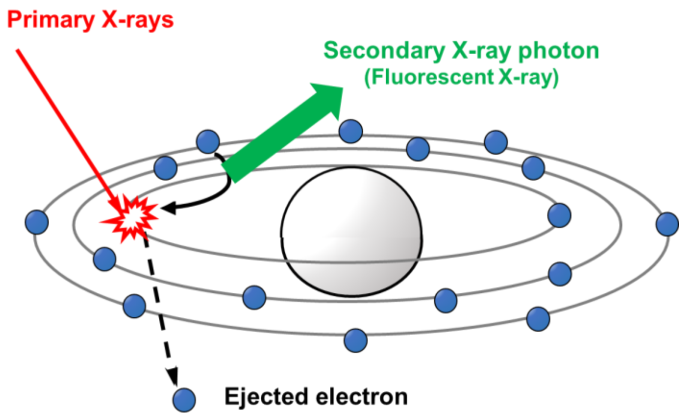

Figure 3: The principle of X-ray fluorescence

As shown in Figure 2 (b), the XGT-9000 detects the secondary X-rays with an energy-dispersive silicon drift detector with high count rate and good energy resolution. Furthermore, no liquid nitrogen is needed as Peltier thermoelectric systems are used for the detector cooling. Compared with conventional XRF analysis, micro-XRF systems are additionally equipped with a motorized XY stage and microprobes to focus the primary X-rays (Figure 2(b)). It is then possible to obtain elemental distribution images of the sample, by acquiring individual spectra across the sample, from which XRF element images can be reconstructed and used to characterize local heterogeneities of composition. In addition, the XGT-9000 is also equipped with a transmission X-ray detector. It is therefore possible to correlate compositional heterogeneities with defects revealed by transmission X-ray imaging. Areas as large as 10 cm x10 cm can be imaged in a single mapping.

Sample information

Figure 4 shows a ruby (5 mm x 7 mm) which Mineralab provided for this test. At first glance, this ruby had a nice brilliance and could be considered as an untreated natural stone of great value. However, using suitable lighting, cracks and inclusions are visible and treatment is suspected. The micro-XRF was then used to determine if any treatment to hide the defects had been applied.

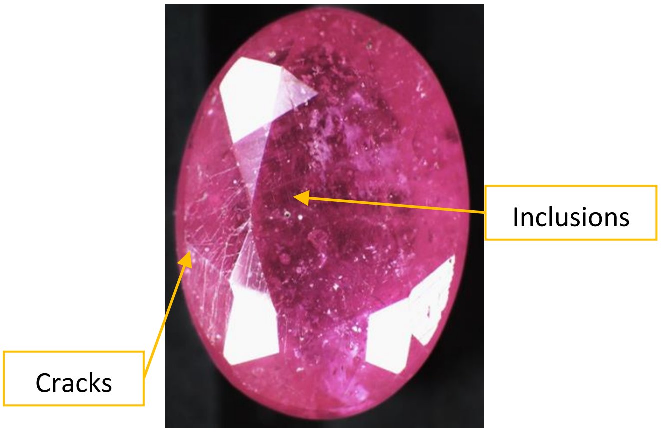

Figure 4: Optical picture of the studied ruby in this application note.

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Measurements and results

This ruby was introduced into the XGT-9000's analysis chamber without any prior treatment. The test was carried out under whole vacuum condition, at an X-ray tube voltage of 50 kV and a current of 800 µA. The primary X-ray beam was focused using a poly-capillary microprobe to obtain a high intensity beam of about 100 µm diameter. The following mapping images were acquired simultaneously in approximately 1 hour. The mapping size in pixels is 512 x 246 and the acquisition time per pixel is 10ms with 10 successive scans.

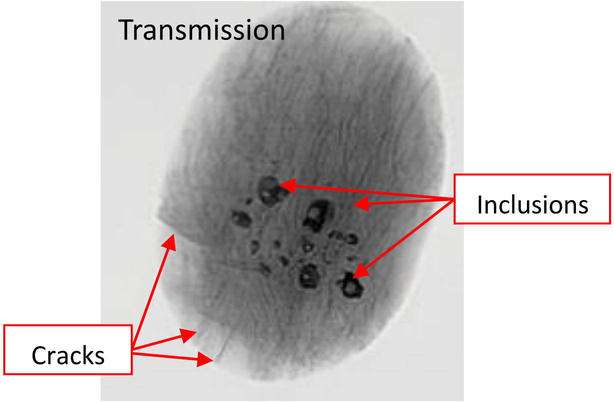

Figure 5: Transmission X-ray image of the ruby obtained by the XGT-9000.

On the transmission X-ray image (Figure 5), two kinds defects are detected: cracks and inclusions. The contrast is due to the differences in density derived from the compositions of the ruby, the mixture used to fill the cracks, and the inclusions.

In the fluorescent X-ray images of the ruby's constituent elements (Al, Cr, and Fe) in Figure 6, the cracks are clearly visible. However, unlike the transmission X-ray image which is representative of the entire thickness and density of the sample, the fluorescent X-ray images of these elements can only give a superficial view. The fluorescent X-ray images of Pb, Mg and Si are representative of the glass used to fill the cracks. Pb has a very good fluorescence yield and gives the best resolved image. Finally, Figure 7 (in the next page), which superimposes the major element of rubies (Al) with that of lead glass (Pb), shows the complementarity of these two elements in the ruby.

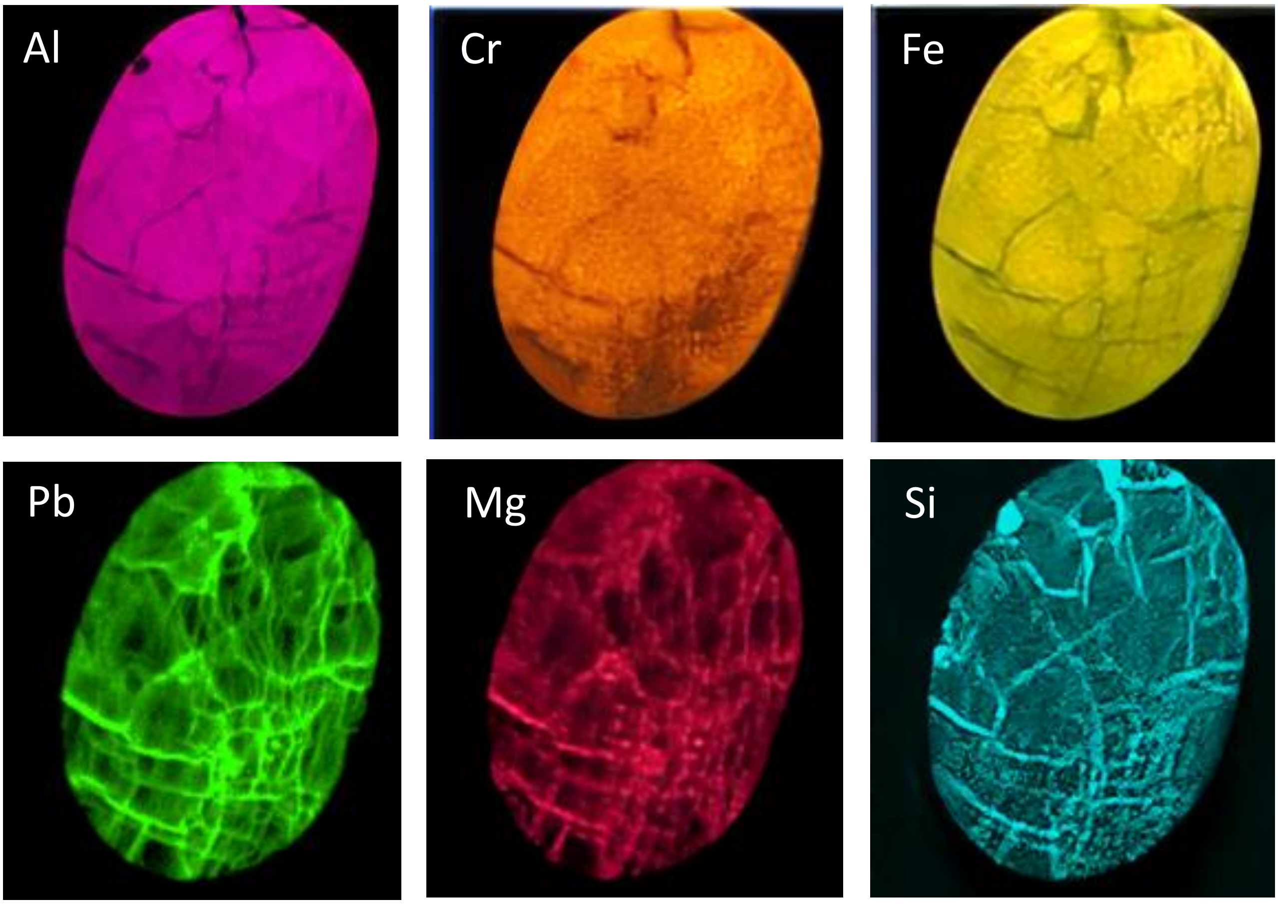

Figure 6: Fluorescent X-ray images of the ruby obtained by the XGT-9000 with a standard detector. (Al, Cr, and Fe are constituent elements. Pb, Mg and Si are representative elements of the glass used to fill the defects.)

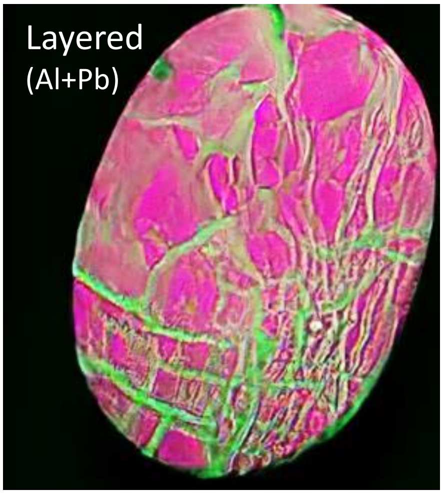

Figure 7: A layered image of the major element of rubies (Al) and that of lead glass (Pb) in the ruby

Conclusion:

The XGT-9000, HORIBA's latest micro-XRF system, has been used for the gemstone analysis. Its detector allows the elemental analysis of any type of solid sample. Combined with a motorized XY stage and a transmission X-ray detector, elemental images of samples up to 100 mm x 100 mm are obtained in record time. Moreover, thanks to the various spot sizes (from 10 µm up to 1.2mm), the spatial resolution can be adapted to the size of the area studied.

In this application, a ruby was without any pre-treatment and without any alteration of the sample. It could be imaged entirely and with a resolution adapted to the details to be observed using a 100 µm ultra-high intensity probe (poly-capillary).

The images obtained, both transmission X-ray and X-ray fluorescence, made it possible to highlight the treatment undergone by this ruby which was not apparent to the naked eye. Indeed, the transmission image revealed networks of cracks and chemical inclusions which differ from natural rubies without any treatment. The fluorescent X-ray images showed that these defects were enriched in Pb, Mg and Si.

Through analysis with the XGT-9000, this ruby can therefore be classified as "treated“, ensuring it can’t be mis-sold for an untreated natural ruby whose price is considerably higher.

Acknowledgement

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References:

[1] Padzunass S. (2010) - Étude des Rubis Traités au Verre dit « Enrichi en Plomb» et Mise en Évidence des Principales Caractéristiques d’identification – Rapport de stage du Diplôme d’Université Gemmologie – Université Claude Bernard Lyon 1, 50p.

[2] McClure S.F., Smith C.P., Wang W., Hall M. (Spring 2006) . Identification and Durability of Lead Glass-filled Rubies. Gems and Gemology, VOLUME XLII, 22-34

[3] The Gemstone Book 2020-1, CIBJO/Coloured Stone Commission, Viewed 10 Sep 2022. http://www.cibjo.org/wp-content/uploads/2020/04/20-12-22-Official-Gemstone-Book.pdf

[4] HORIBA Scientific Product, XGT-9000 X-ray Analytical Microscope (Micro-XRF)–Application, viewed 10 Sep 2022. https://www.horiba.com/int/scientific/products/detail/action/show/Product/xgt-9000-1909/