HORIBA
Scientific

Application Note

Mineralogy-Geology

XGT

XGT8

Micro-XRF reveals ruby structure and composition

X-ray fluorescence (XRF) has been widely used for many years in a variety of research fields for fast elemental characterisation with parts per million (ppm) sensitivity. More recent progress in micro-XRF techniques has seen these applications develop, combining single point qualitative analysis with high spatial resolution imaging of elemental distribution.
The XGT-5000 energy dispersive XRF microscope system presents the researcher with unique capabilities for micro-analysis, including unrivalled 10 µm spot sizes and simultaneous XRF and x-ray transmission imaging. For gemstone analysis, these features are ideally suited to analysing precise elemental composition, locating and identifying inclusions, and providing key information in quality assurance.
Rubies are a much sought after item for jewellery and decoration, and good quality examples fetch a high price. The principal component of ruby is aluminium oxide (Al_2O_3) with interspersed chromium ions within the lattice giving it the characteristic red colour.

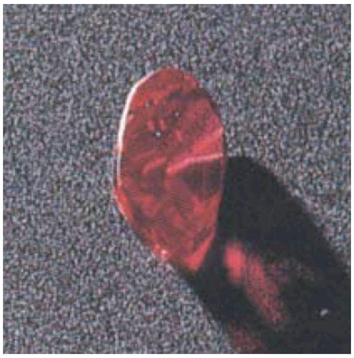

Figure 1: High quality, cut ruby

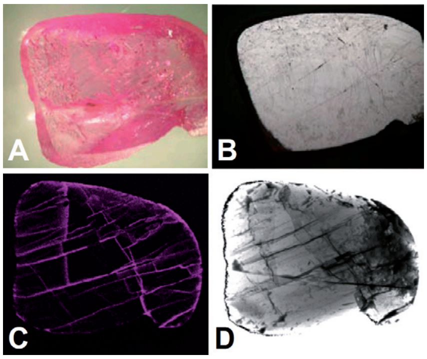

Figure 2: Analysis of ruby (A) optical image by reflection, (B) optical image by transmission, (C) lead XRF image, (D) x-ray transmission image

Filter analysis in treated rubies

Low quality rubies often show a complex array of fractures within the crystalline structure, and these can be filled to give an improved quality. By using a high refractive index material such as lead glass for the filler, it is possible to closely match the ruby refractive index (typically 1.76-1.77) – the result is filled fractures which are virtually indistinguishable by eye from the real ruby.

Elemental analysis is quite a different matter, and can very easily provide excellent contrast between the natural gemstone and the fillers (typically containing lead, bismuth and copper as additives to the silicate glass). Figure 2 clearly illustrates the difference between the XGT imaging technology and standard optical imaging.
Whilst the optical images show a number of visual features and defects, there is no clear evidence of filling. However, with x-ray imaging the presence of lead containing filler is obvious.

Phase analysis in cut ruby

Most applications of the XGT instruments concentrate on their unique ability for simultaneous XRF and transmitted x-ray analysis and imaging. However, at heart these instruments are simply x¬ray spectrometers, and thus can be used for other analyses involving x-rays.
X-ray diffraction (XRD) is a widely used technique, enabling researchers to characterise crystalline phases within materials by measuring the intensity of diffracted x-rays at varying angles to the incident beam. Whilst the XGT systems can't provide the same level of analysis and wouldn't be considered for complete crystal identification using XRD, they can nonetheless be used for fast imaging of phase differences across gemstones.

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The geometry of the XGT analysis beam and detector means that diffraction detection is limited to a Bragg angle of $2\theta = 135^{\circ}$. Diffraction peaks from the polychromatic incident x-ray beam are observed at varying energy positions within the acquired spectrum – by producing images based on these diffraction peaks, different crystalline phases can be visualised.
The images in Figure 3 are acquired from a high quality cut ruby. The transmitted x-ray image (A) clearly shows the presence of inclusions within the stone. However, it is the diffraction images which most clearly illustrate the structural features of the ruby, with three crystalline domains dominating

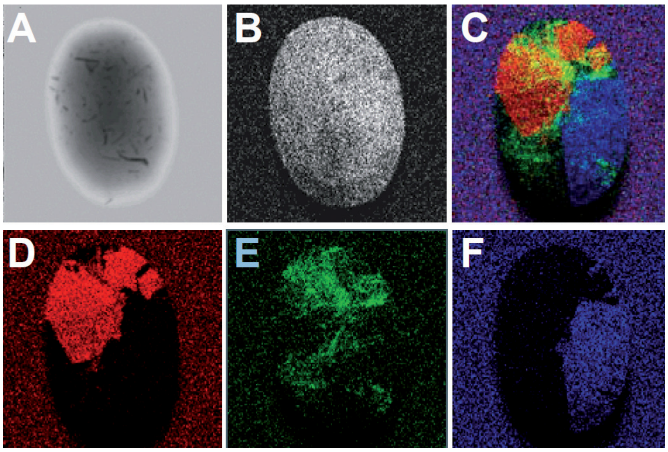


Figure 3: Analysis of ruby (A) x-ray transmission image, (B) chromium XRF image, (C) RGB superimposition of diffraction images D-F, (D) diffraction image 8.68 keV, (E) diffraction image 17.44 keV, (F) diffraction image 10.52 keV

Conclusions

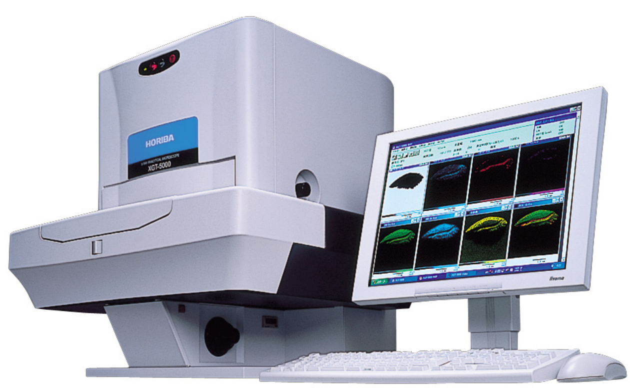
The fast mapping capability of the XGT-5000, with simultaneous XRF and transmission detection, allows gemstones to be analysed for composition, structure and quality.

Lead glass fillers used to repair low grade rubies can quickly be identified by their distinctive elemental signatures, and allow high and low quality stones to be easily distinguished using micro-XRF.

Moving beyond the more standard analysis, the XGT has also been used for high resolution imaging of crystalline phases in a ruby, by monitoring the intensity of specific diffraction bands within the EDXRF spectrum.

Acknowledgements

Data shown in Figure 2 was kindly provided by Petr Cerný of the General Directorate of Customs, Prague, and are reproduced with permission.



XGT-5000

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