ARTICLE

Micro-spectroscopy – shedding light on rock formation

Simon FitzGerald
Horiba Jobin Yvon Ltd, 2 Dalston Gardens, Stanmore, Middlesex HA7 1BQ, UK. E-mail: simon.fitzgerald@jobinyvon.co.uk

Introduction

Whilst there are many imaging techniques available to a research scientist, the information which is provided is often only of a visual/topographical nature. What they fail to provide is true compositional (chemical/elemental) analysis of the materials. However, micro-spectroscopic techniques such as Raman or X-ray fluorescence (XRF) can fill this gap, allowing highly detailed images to be generated based upon the sample's material composition.

The information the two techniques provide are quite different, but their application areas are strongly linked. Raman probes chemical bonding within a material using laser radiation, giving information on molecular functional groups, whilst XRF probes elemental composition by analysing fluorescence X-rays emitted following irradiation with a primary X-ray beam.

Raman is now routinely coupled with standard optical microscopes to yield spatial resolutions down to 1 µm, whilst the latest X-ray optical design allows ultra-narrow, high intensity beams with diameters down to 10 µm to be produced for XRF.

Both micro-Raman and micro-XRF provide convenient, non-destructive, microscopic analysis. For example, their non-destructive nature allows fragile museum/archaeological objects to be investigated, and forensic scientists can obtain fast characterisation whilst ensuring the trail of evidence is preserved – from samples as varied as polymers and fibres, explosives and narcotics, glasses and even fingerprints.

For materials research, the sensitivity of Raman to very subtle effects provides valuable insight into stress/strain in semiconductors, chirality/diameter of carbon nanotubes and crystallinity of polymers. The elemental characterisation of XRF, however, is ideal for micro-electronics, including analysis of circuit boards and soldering, and compliance testing for the forthcoming European WEEE/RoHS "lead free" legislation.

Other areas of interest for micro-spectroscopy include pharmaceuticals (crystal polymorphs, tablet formulation, well plates), coatings (homogeneity, thickness) and metallurgy (alloys, plating, corrosion). New applications continue to be developed, assisted by continued advances in instrumentation: for example, inverted (Raman) microscopes and high sensitivity micro-XRF analysis at atmospheric pressure open up new possibilities in biology/medicine (disease diagnosis, medicine efficacy, bacteria etc).

Shedding light on rock formation

Investigation of mineral and rock samples can gain strongly from Raman and XRF analysis. Raman allows fast identification of mineral forms, and with microscopic spatial resolution, can be used to study heterogeneity within rocks, probe inclusions *in situ*, and identify minute fragments.

At the Johannes Gutenberg-Universität in Mainz, Germany, Dr Lutz Nasdala and co-workers have extensively explored the use of micro-Raman in mineralogy, including an interesting study into the metamictisation of natural zircon.[1] Zircon ($ZrSiO_4$) is a common mineral in a range of rocks, and incorporates a number of trace elements, including uranium (U) and thorium (Th). These two radioactive elements cause self-radiation of the zircon, damaging its structure and lead-

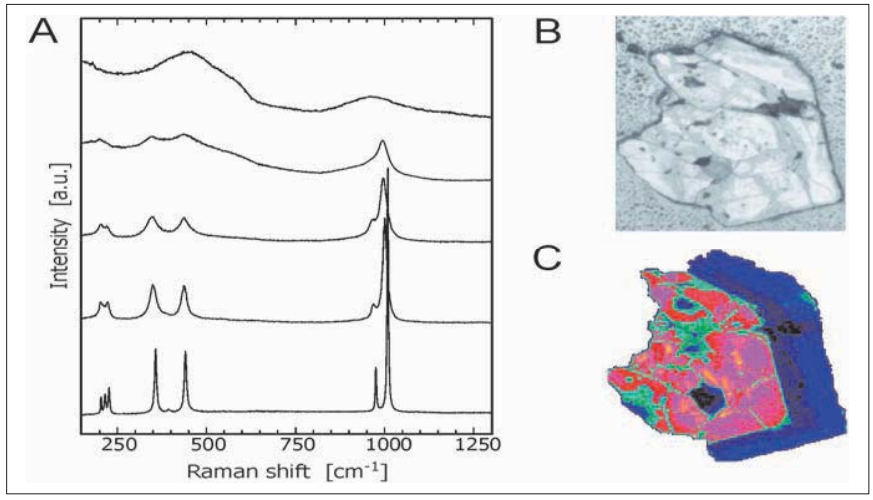

Figure 1. (A) Raman spectra of five zircon samples with different degrees of radiation damage, ranging from highly ordered (spectrum at bottom) to essentially amorphous (top). (B) Optical micrograph of polished zircon section. (C) Raman mapped image illustrating strongly damaged outer metamict zone (in blue) to moderately damaged inner area (red/pink/green).

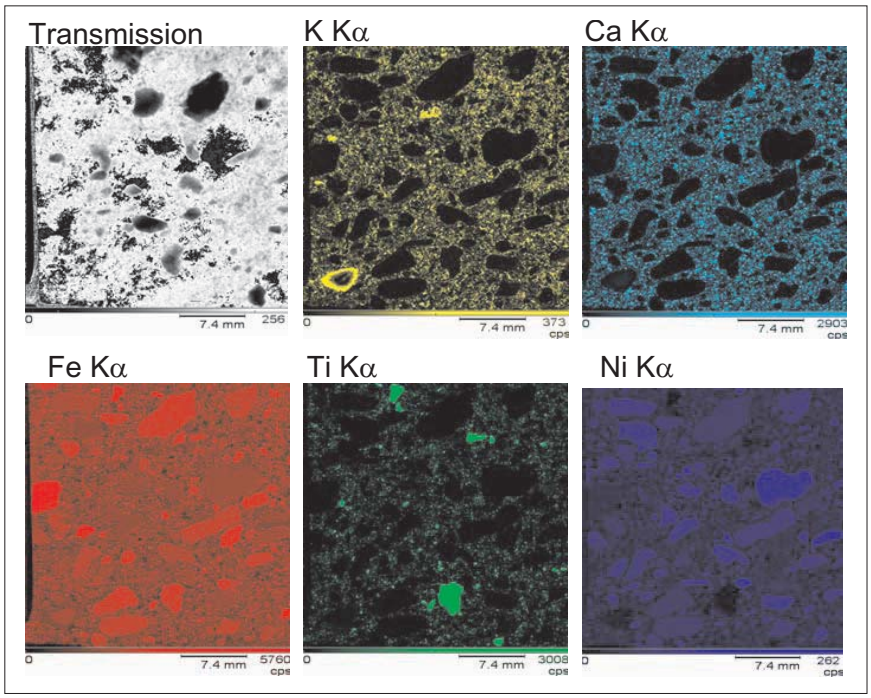

Figure 2. Mapped images showing transmitted X-ray intensity and elemental distribution in a kimberlite section. Total mapping area is $25 \times 25\,mm^2$.

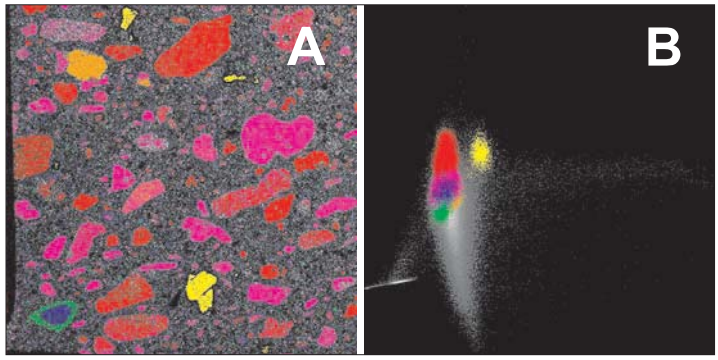

Figure 3. (a) Composite phase image of kimberlite section–see text for assignment of colours, (b) cluster diagram.

ing to a "metamict" form which is amorphous and isotropic. Investigation into such processes is aimed at understanding the cause and effect of the degradation of chemical and physical stabilities in zircon and other such minerals.

With micro-Raman, the extent of radiation damage can be quantitatively estimated – with increasing radiation damage the Raman bands decrease in intensity, become broader and show strong shifts to lower wavenumbers. Figure 1(a) illustrates typical spectra of zircon, from well ordered through to damaged and fully amorphous. The $1000\,cm^{-1}$ SiO_4 band provides a good indication of the level of metamictisation and can be used to generate highly resolved mapped images [Figure 1(C)].

As with Raman, the application of micro-XRF has been used to more fully understand rock structure and distribution of specific minerals. Dr Nicholas Arndt of the Université Joseph Fourier, Grenoble, France has reported many studies on kimberlite, the type of rock that is mined for diamond.[2] Recent work used micro-XRF to produce high spatial resolution elemental images of kimberlite sections. These contain abundant crystals of olivine $(Mg,Fe,Ni)_2SiO_4$ and one zoned, partially altered crystal of garnet. In the resulting elemental images (Figure 2), the garnet crystal is immediately identified by its alteration rim, which is rich in K-rich mica. High K content also identifies mica crystals within the matrix.

The olivine crystals are black in the K and Ca images but have various shades in the Fe and Ni images. These variations indicate the remarkable extent to which the compositions of these elements vary from crystal to crystal. In the Fe image, the olivine grains are seen to have thin Fe-rich rims. Notice also the additional information on physical structure provided by the transmission X-ray imaging.

Material phase analysis using principal components enables regions of similar elemental composition within the map to be grouped and imaged as one (Figure 3). In this manner, it is possible to visualise quickly where specific minerals and phases are located, and thus, olivine crystals (red/pink–varying composition), garnet with its outer mica region (blue/green), and titanium rich ilmenite (yellow) can be quickly identified.

These images provide valuable information about the origin of the olivine crystals and thus about the processes that formed this diamond-bearing rock.

Conclusion

The high information content of spectroscopic techniques such as X-ray fluorescence and Raman has been coupled with analysis on the micron scale to provide imaging techniques for scientists from many varied research fields. Micro-spectroscopy is leading the way in many novel applications, providing far more detail and contrast than is possible through more traditional techniques.

References

1. Lutz Nasdala, Marita Wenzel, Gerhard Vavra, Gert Irmer, Thomas Wenzel and Bernd Kober, "Metamictisation of natural zircon: accumulation versus thermal annealing of radioactivity-induced damage", *Contrib. Mineral Petrol.* **141,** 125 (2001).
2. Nicholas T. Arndt, "Komatiites, kimberlites and boninites", *J. Geophys. Res.* **108(B6),** 229 (2003).