

EXTENDED REVIEW

Schubnel, H.-J., Pinet, M., Smith, D. C. and Lasnier, B. *La Microsonde Raman en Gemmologie*. Paris (Association Française de Gemmologie), 1992. 61 pp. Price 200F (+ 50F postage).

The volume is presented in two parts. The first, by Schubnel, 'Une methode moderne d'identification et d'authentification des gemmes' describes the recent historical development of the technique paying particular attention to the determination of the nature of the gaseous, liquid or solid inclusions within the gemstones. The many advantages over the closely-related infrared absorption analysis are touched upon. There is no need for special sample cells or pressed halide powder discs. While not of immediate importance in gemmology, the strong absorptions of water and glasses make infrared spectrometry rather troublesome, but present no impediments for Raman spectrometry.

Thus small amounts of reference liquids or solids can be analysed in a glass tube of about 1 mm bore. Again a MOLE spectrometer can easily and quickly scan a vibrational spectrum from $\Delta\nu$ ($\nu-\nu'$) values of 40 to 4000 cm^{-1} .

The incident-light petrological microscope of the MOLE microprobe permits the effortless positioning of the laser beam on to individual inclusions or other features of natural or synthetic growth. Inclusions which either outcrop on the surface or lie at considerable depths and having dimensions as small as about 5 μm can be analysed. Unlike most other analytical techniques, the inclusion or the gemstone itself suffers no alteration or damage whatever, either in structure or even in discolouration. The results are highly reproducible when the laser beam is directed repeatedly at the same point in the gemstone. Occasionally, total internal reflections at sloping inclusion walls make many otherwise ideal inclusions inaccessible, but sample tilting can often overcome this limitation.

Schubnel points out the special ability of the instrument in the characterisation of inclusions to distinguish between natural and synthetic gemstones: in certain cases it can also provide useful indications of the artificial or 'enhancing' treatments of natural specimens. Since gemstone

solution synthesis usually leaves traces of the flux whose chemical constitution is quite unrelated to that of any natural growth environment, its analysis may unequivocally establish the origin of the sample. He gives an example of the *in situ* analysis of inclusion fluids and gases. Another striking example is the detection of gaseous nitrogen inclusions of the order of a micrometre in size associated with minute graphite lamellae in the interior of a diamond. He names five different types of solid inclusions found during the extensive course of studies of gemstones at l'Institut National de Gemmologie. They are monomineralic; multiphase; exsolution growths; secondary minerals formed from primary growth minerals, and secondary minerals deposited in open fissures or cavities. Illustrated examples are given of all five types.

The second part of this volume by Pinet, Smith and Lasnier has the title 'Utilite de la microsonde Ramman pour l'identification non-destructive des gemmes'. Its main object is the compilation of a selection of the Raman spectra of gemstone minerals.

It traces the history of the development of this photon microprobe since the announcement in 1975 but its inventors, M. Delhaye and P. Dhamelincourt at the Laboratoire de Spectrochimie Infrarouge et Raman at the University of Lille, France. Its invention followed shortly that the electron microprobe by Castaing in Paris.

The chapter headings consist of an introduction, followed by a description of the technique and instrumentation detailing the origin of Raman scattering and the production, treatment and identification of the spectra. Next, the factors relating to crystal physics and crystal chemistry are discussed. These are the crystalline structure and symmetry, the relation of intensity to the crystal's orientation, the chemical composition and wave number (cm^{-1}), colour and absorption, and the effects of heat and fluorescence.

Let it be imagined that one possesses a block of a transparent, non-selectively-absorbing material having no particles of included matter even below sub-micrometre size, and possessing two plane-polished faces inclined at a right angle to each other. If a narrow intense beam of monochromatic light is directed normally on to one of the faces, and a suitable microscope aligned with its

optic axis directed normally at the other face, then it is possible to detect two different kinds of faintly scattered light.

The first kind, known as Rayleigh scattering is perhaps about 10^{-5} the intensity of the incident beam. This radiation is independent of the nature of the scattering material and its intensity depends on the size of the atoms or molecules present and is strongly dependent on the wavelength of the incident beam.

The second kind is known as Raman scattering and is even weaker. Typically, one Raman photon is scattered for every 10^6 – 10^8 incident photons in about 10^{-12} seconds.

Neither should be confused with the strong Tyndall scattering which arises from small discrete particles rather than with atoms or molecules. Nor with Fluorescent/Phosphorescent scattering in which a photon is actually absorbed and another lower energy photon emitted at a later time. All four kinds are incoherently scattered in all directions.

The physics involved in Raman scattering is directly related to the excitation of vibrations in the infrared region. Because of the extreme weakness of this scattering, the effect is best observed using a moderately-powdered laser beam. Any visible frequency can be used, as long as it does not excite fluorescent scattering. An argon-ion laser with lines at 514.5 and 488.0 nm is often used.

Unlike the stronger Rayleigh ('elastic') scattering, the Raman ('inelastic') scattered light is shifted to either a lower or a higher frequency. This 'Raman shift', the difference between the frequencies of the exciting and the scattered light, depends on the nature of the bonding and fundamental vibrations of the atoms in the scattering substance. The substance can be a solid, a liquid or a gas. In a simplified picture of the Raman effect it may be imagined that some of the incident light quanta suffer inelastic collisions with molecules and either transfer some energy to a vibrational mode of the molecule or less frequently, gain energy from a molecule already in an excited vibrational state. Thus the scattered light contains the unchanged frequency ν (Rayleigh) and the $\nu - \nu^1$ and $\nu + \nu^1$ (Raman) frequencies. These latter are often referred to as 'Stokes' and 'anti-Stokes' frequencies respectively. It is the 'Stokes' radiation of lowered frequencies with which conventional Raman spectra are concerned. The 'anti-Stokes' spectra are very much weaker and are not used except with the more instrumentally complex coherent anti-Stokes Raman spectroscopy.

The Raman frequency shifts can easily be

recorded by a microscope-spectrophotometer arrangement having a back-scattering collecting geometry. Because of their relative simplicity, sharpness, narrowness, low-background and well isolated nature, the Raman spectral lines, with their highly distinctive, rich and unique patterns, serve as an admirable analytical fingerprinting technique. In this manner, the experimentally difficult middle- and far-infrared spectra can be moved to the much easier to observe visible region.

The sophisticated Raman instrument, known as 'MOLE' or RMP (Raman microprobe) is able to convert electronically the Raman scattered light into a spectrum stored on a computer. The primary function of its grating spectrometer is to ensure a clean rejection of the intense Rayleigh scattered radiation and to detect the weak Raman-shifted components.

The recorded spectral peak positions and intensities are characteristic of specific atoms in vibration in specific molecular environments. It is able to record at high speeds the Raman spectra of microscopically small volumes of solids, liquids or even gases lying *within* transparent materials. Most importantly, it can do this non-destructively, in air, and without any sample preparation, provided that the exciting laser beam can enter and leave the sample through a single flat-polished 'window' of the material. Therefore the sample can be gemstone 'rough', loose faceted stones or gemstones set in jewellery or other objects of cultural, historical or archaeological interest so long as they can be placed under a light microscope objective.

It is these features which make it an almost ideal tool for the characterisation of the inclusions in faceted gemstones. What has been missing is a systematic compilation of Raman spectra of those particular minerals which are associated with the conduct of any important gemmological testing service. This gap is one which other workers are only too aware of: these are the gemmologists and mineralogists wishing to keep up with this remarkable technique in gemstone and mineralogical investigations.

This special volume, published by the Association Francaise de Gemmologie, now overcomes the last obstacle to the ready use of this elegant micro-analytical procedure. It is the first presentation of the Raman spectra of a carefully selected series of some 80 minerals associated with gemstones. It permits the instrument's user to establish the identity of any gemstone and of any inclusion lying within the body of the stone. It does this by comparing the 'molecular' spectrum fingerprints with those of reference minerals.

These are standards whose crystal structures and chemical compositions have been determined by X-ray diffraction and X-ray fluorescent spectrometry or some other definitive method.

There follows the first ever catalogue of the Raman spectra of 80 natural gemstone minerals. Also included are the spectra of three synthetic materials used in gemmology as diamond simulants. They are cubic zirconia (CZ) gadolinium gallium garnet (GGG) and yttrium aluminium garnet (YAG).

The spectra are presented in the usual crystallochemical classification order (native elements, sulphides, halogens, oxides, leading to the silicates and their sub-classes of feldspars, feldspathoids, phenakite and euclase). An alphabetical list is given on the back cover. The spectra have been gathered from five different authors. There has been a careful conversion to the same scale throughout, with a Raman shift range of from about -100 to -1100 cm. This range is apparently sufficient for gemstone minerals, although the MOLE instrument range stretches from $+100$ cm^{-1} (embracing the Raman anti-Stokes region) up to -4000 cm^{-1} .

Each spectrum is accompanied by a list of the properties of each mineral. These are the ideal chemical formula, crystal structure and symmetry, unit cell dimensions and cell contents (Z), refractive indices for sodium light, density in g/cm^3 , Mohs' hardness, the most frequently observed colours and a list of all the peak wave numbers in cm^{-1} .

This catalogue is followed by illustrated examples of the differentiation of natural gemstones from their synthesised species purely by the Raman spectra of their inclusions. The photomicrographs, recorded by the integral camera of the MOLE, are in colour and like many of the others which accompany the catalogue entries, serve as an admirable insight into the complex inner world of gemstone minerals.

The final chapter of Part 2 shows how it is possible to determine semi-quantitatively the concentration of major elements in a solid-solution series. The two examples cited are of the garnet series (pyrope, almandine, spessartine and grossular) and the clinopyroxenes. Here, it was found possible in spite of their complexity, to evaluate the relative proportions of the elements present in the sites $M1$ (Mg, Fe^{2+} , Fe^{3+} , Al) and $M2$ (Ca or Na) in the structures, in particular for the solid solutions, aegerine-diopside-hedenbergite.

Reflecting on this volume this reviewer feels that there are several points worth touching upon. The first is concerned with the fact that opaque

minerals yield much weaker and broader bands, which are more akin to those encountered in conventional infrared absorption analysis. The semi-opaque minerals listed (hercynite, chromite, hematite, rutile and piemontite) are in this category. Because of the intense thermal impact of the focused laser beam, all the highly absorbing sulphide and sulphosalt minerals are prone to decomposition before their spectra can be recorded, unless very thin sections can be probed. This behaviour prevents the identification of such inclusions and so forfeits any claim for the technique to provide a complete analytical coverage.

The second point relates to the use of a Raman microprobe as an identification tool for the gemstone itself. This is pure overkill, or like to cracking walnuts with a steam-roller. If presented with a single, flat, polished surface on a piece of gemstone 'rough' or with a faceted gemstone, any graduate gemmologist in the jewellery trade would be able to identify with complete confidence any of the 80 minerals in the catalogue. The tools required for this task are a total internal reflectance refractometer, a hand-held pocket diffraction spectroscope, a 10-times magnification loupe, a pocket polariscope/ conoscope and a penlight-type light source. Such a set of simple instruments could also inform its user if the specimen was a glass, or was polycrystalline or if monocrystalline, whether it was isometric, uniaxial or biaxial, together with its refractive indices if these were less than 1.81. It would entail an expenditure of not more than £500. This is a very different sum from that of a MOLE microprobe, costing about £100,000. None but the few internationally-known gemmology schools or test centres could hope to possess one.

What the graduate gemmologist's instruments cannot do, but the microprobe, can, is to determine non-destructively the identity of an inclusion, whether outcropping or not.

This unique feature will become increasingly important to gemmologists and particularly to those in the gemstone industry. This is because it is now becoming a commercially fashionable and rewarding practice to attribute the provenance of a mined stone when issuing quality certificates of faceted stones: this was previously frowned upon. Again, it is very important to know if a gemstone is natural (an 'outdoor' stone) or is laboratory made (an 'indoor' stone). This fact becomes clear if a comparison is made of the relative prices which each commands in the marketplace. For example, a Burmese ruby of the finest colour, almost free of internal optical discontinuities (inclusions, fractures, colour zones), weighing

about five carats (one gram) and of impeccable cut and polish, was sold at an auction by Sothebys in New York in 1989 for \$400,000. A laboratory-made stone having properties indistinguishable to a none-gemmologist from this mined stone can be purchased today for as little as \$200. It is difficult for a mineralogist to understand why such an enormous price difference could possibly exist. It is equally difficult to comprehend the intense passion of an obsessional collector of rare gemstones. One has long suspected that professional mineralogists are often puzzled by the fact that such creatures as gemmologists exist at all. Now they know why.

Thus far, only the 'ordinary' Raman scattering effect has been discussed. Future developments in this field could well arise from the use of *Resonance Raman* spectroscopy. Here, if the laser frequency is permitted to fall near or become coincident with an electronic absorption frequency, a very significant intensity enhance-

ment may occur. The advantage for gemmological research may lie in its great sensitivity and selectivity as a probe of chromophore structure, since only vibrational modes directly associated with the chromophore are enhanced. There remains the intractable problem of trying to link the presence of different mixtures of the transitional or rare earth ions in a given host stone with the observed body colour of the stone. Raman Resonance spectroscopy might well be able to illuminate those dark gemmological corners where lurk the ions Ti^{4+} and Fe^{2+} in sapphires, the ions Fe^{3+} , Cr^{3+} and V^{3+} in alexandrites and those of Nd^{3+} , Sm^{3+} and Pr^{3+} in cubic zirconias.

While the MOLE instrument is beyond the financial reach of all but the most heavily-endowed laboratories, this volume is easily graspable at such a modest sum and should be snatched up before this print run is sold out.

J. B. NELSON