

SPECTRA OF GEM MATERIALS

Grant Pearson
Mt Waverley, Victoria

ABSTRACT

In this paper the usefulness of the gemmologist's hand-held prism spectroscope, as an instrument suitable for identifying gemstones, is questioned. Research conducted by the author, on the relationship of spectrophotometrically derived transmission spectra in the UV-Visible range to the spectra observed with the assistance of a prism spectroscope, indicates discrepancies that raise questions about the visibility of claimed identifying absorption spectra that have been long-published as being identifying of many gemstones. By defining and illustrating the Relative Luminous Efficiency curve for the human eye, and then deriving a parameter the author terms the *RLE Corrected Transmission*, that is based on the relative intensities of the various wavelengths (colours) that could be expected to be seen by human vision of average sensitivity, the author produces evidence that some absorption spectra that are specified in textbooks of gemmology, as being identifying, can't be seen with the gemmologist's hand-held spectroscope.

INTRODUCTION

The following discussion is an adapted excerpt from the author's thesis titled *Gem spectra* that was for the Research Diploma in Gemmology of The Gemmological Association of Australia. The research characterises the colour reactions of various gem materials and filters. Spectra were recorded with a spectrophotometer for the purpose of comparing the recorded spectra with those observed through the gemmologist's hand-held spectroscope. The project was undertaken for the purpose of assembling a reference compilation of spectrophotometrically derived transmission spectra of actual gem materials; and to attempt to clarify the value of their application to gem identification and characterisation. This was especially true since the results of this research have been derived instrumentally, and objectively, rather than on a visually interpretative instrument such as the hand-held spectroscope that, of necessity, yields mostly subjective results.

It was intended to avoid the idealised and interpretive responses, that are often reproduced in many gemmology texts as representative spectra of particular species and which may bear only slight similarity to those of the actual gem materials. This circumstance probably arises because many prized varieties of coloured gemstones are allochromatic, so that the chromophore responsible for much of their observed visible spectra may have a widely varying composition and concentration that is dependent, for instance, on the stones' source-geology, its formation conditions, and serendipity—consequently leading to widely variable spectra. If any of the absorption bands or lines considered to be characteristic or diagnostic for that species were absent, or of only weak contrast and difficult to detect, the reliability of spectroscopic examination could be considered to be less than totally satisfactory.

The influence of the human visual *Luminous Efficiency Curve*^{1,6,19}, which charts the sensitivity of the eye with wavelength, has also been considered with regard to the detectability of characteristic features or of colours actually perceived in comparison to the wavelength-passbands present in the transmitted spectrum.

The value of spectral examination and characterisation of a gem material can then be better appreciated, since spectrophotometry consists of the analysis of that very attribute to which a coloured gem owes much of its appeal and value, that is, its colour. The compilation of a library of objectively-derived instrumental gem spectra can also overcome the difficulty of critically comparing different spectra. This past inability to adequately compare spectra may have led gemmologists to neglect the value of spectroscopic examination, except for a limited range of stones for which well-established and consistent diagnostic spectral-features are easily detected. The following commentary includes some of the writer's observations and speculations on the causes and significance of various gem spectral features.

DERIVATION OF DATA

The data were collected as digital-files of pairs of values of Absorbance (A) at the corresponding Wavelength (nanometres, or nm) on a computer-interfaced UV-Vis Varian Cary-3 spectrophotometer that scanned from the short-wave ultraviolet (SWUV) limit at 200 nm through to the long-wave ultraviolet (LWUV) band from 300 nm, the visible range from violet-blue at about 400 nm through to red at about 700 nm, and just into the near infra-red to 900 nm.

DESCRIPTION & INTERPRETATION OF SOME SPECTROPHOTOMETRY TERMS

Absorbance is a function much used in spectrophotometric colorimetric analysis⁷; where an absorbance of zero represents no change in the intensity of the transmitted light, while an absorbance of 1 represents a 10^1 diminution of intensity at that wavelength. That is, the transmitted intensity is only one-tenth of that of the incident light at that wavelength. Similarly, an absorbance of 2, or of 3, or 7 say, represents a transmitted intensity of one part in 10^2 , or 10^3 , or 10^7 of the initial incident light. That is of one hundredth, or one thousandth or even of one ten-millionth, respectively. The instrument employed for this evaluation was a dual-beam spectrophotometer reading the absorbance range from zero to 10, enabling the collection of even very attenuated signals not accessible to many older spectrophotometers designed for routine chemical-analysis. Often these older instruments could accurately register only to an absorbance of about 3 or 4. The spectrophotometer used for this investigation also recorded its output digitally to facilitate computer manipulation of data.

Absorbance, earlier known by the now-obsolete term *optical density*, is related to *transmittance* (or *specific transmission*), by the Beer-Lambert **Law**⁷, which states:

“...when monochromatic light passes through a transparent medium, the rate of decrease in intensity with the thickness of the medium is proportional to the intensity of the light...” and that “...the intensity of a beam of monochromatic light decreases exponentially as the concentration of the absorbing substance increases arithmetically...”.

These statements, which are easily formulated and manipulated mathematically, especially by computer, infer that an absorbance of zero corresponds to a transmittance of 1 which translates as 100% transmission of the incident light; 0.5 transmittance represents 50% transmission (i.e. 50% absorption); and a transmittance of 0.02, for example, infers 2% transmission (98% absorption) of the initial incident light. The Beer-Lambert Law holds especially well for liquid solutions, which are quite homogeneous, and in general it is also applicable within limits to solid solutions of chromophores in matrices such as glasses and most crystals.

Absorbance is primarily of interest to chemical analysts, since the concentration of a coloured species is directly proportional to absorbance; but light transmission rather than absorbance is probably more recognisable by most gemmologists, since the brightness of particular features seen in the spectral image are proportional to the intensity of the transmitted light or transmission at a particular wavelength. Surprisingly, most graphical spectra currently presented in gemmological journals are still formatted as absorbance, which can be rather difficult to mentally reconcile with the spectral transmission image observable through the hand spectroscope.

Transmission, mathematically-generated by computer from absorbance using the Beer-Lambert relation, has therefore been graphed against wavelength and formatted to be a graphical representation directly comparable with the images observable through the direct vision hand spectroscope for the visible range from 700 to 400 nm. Spectra have actually been determined for the full wavelength range from 200 to 900 nm. This range of wavelengths includes the two ultraviolet ranges (SWUV of 200-300 nm, and LWUV of 300-400 nm) and the very-near infra-red (700-900 nm) as well as the visible region, thus displaying additional features that may not be detectable with the hand spectroscope, but may be useful for more advanced characterisation.

These factors are illustrated below for the examples of a neodymium-doped YAG (yttrium aluminium garnet), and the neodymium-doped glass 'alexandrium', so-named because of its spectacular colour-change perception from pink to blue that is analogous to that of alexandrite or chromiferous chrysoberyl. Neodymium, and its inevitably accompanying partner of almost identical chemistry, praseodymium, constitute the pair of rare-earth elements known as 'didymium'. This pair of elements are occasionally encountered in low concentrations in minerals such as apatite, as well as being deliberate chromophores (colourants) in various simulant and synthetic gem materials, such as glasses, YAG, YAP, CZ, GGG, where they impart a variety of sharp absorption lines and bands that serve as easily detected features for a convenient illustration. The key point to remember is that the higher the line (or locus) is on the graph of Transmission (vertical axis) against Wavelength (on the horizontal axis), the brighter will be the observable spectrum at that wavelength. The spectra have been deliberately formatted in the transmittance or transmission mode, so that they will be directly comparable with spectra observable through the hand spectroscope when viewed in the British/Australian convention of the longer (red) wavelengths to the left and shorter (blue) to the right. This convention is reversed in the USA. The spectra are then compared with the digital photographs of the same specimens viewed through a small prism hand spectroscope using incandescent illumination.

SPECTROPHOTOMETER FUNCTION

A scanning dual-beam spectrophotometer⁷ for the UV-Visible range is really just a more sophisticated version of the hand spectroscope in that it has a monochromator-module, with its appropriate lenses transparent to the UV, the visible and the NIR, adjustable slits and a dispersive component that is usually a diffraction grating, but may occasionally be a prism assembly in older instruments. It generates a monochromatic beam from an appropriate light source. The beam cannot be truly monochromatic (of a single specific wavelength), of course, but it has only a very small wavelength spread that is determined by its slit width. This narrow band of wavelengths is then split (intermittently chopped) into two equally intense rays. One is the reference beam, and the other traverses the specimen. A photosensitive detector then senses the relative-intensities of the transmitted and reference light beams to electronically calculate their ratios as absorbance values. Appropriate mechanical devices permit the wavelength to be progressively scanned between pre-selected limits.

COLOUR AND WAVELENGTH CORRESPONDENCE

Different bandwidths of particular wavelengths in the visible spectrum give rise to the sensations visually construed as different colours, as viewed in the spectroscope. Since the determination of the wavelength of a particular absorption in the direct-vision spectroscope during the identification of a gem-material is usually accomplished by the visual perception of a decreased brightness of a particular spectral colour, it is important to define which wavelengths are understood to be represented by specific colours. However, it is known that colour perception is to some extent an individualised and subjective interpretation of the wavelengths observed. The conversion table (below) of wavelengths, their corresponding frequencies, and the accepted range of associated spectral-colours, is given in many optics^{1 - p.13, 4 - p.115} and physics texts^{6 - p. 358}.

Wavelength (nm)	Frequency Range (Hz x 10 ¹⁴)	Colour Sensation
750 – 620	4.0 - 4.8	Red
620 – 590	4.8 - 5.1	Orange
590 – 580	5.1 - 5.3	Yellow
580 – 500	5.3 - 6.0	Green
500 – 460	6.0 - 6.5	Blue
460 – 450	6.5 - 6.7	Indigo
450 – 400	6.7 - 7.5	Violet

RELATIVE LUMINOUS EFFICIENCY CURVE

The human eye is not equally sensitive to all wavelengths throughout the visible spectrum, peak-sensitivity occurring mid-spectrum in the green at about 550 to 560 nm and tapering off to zero as the limits of the visible band at 400 and 700 nm are approached^{1,4,5,10}. In fact, it is estimated that 66 per cent of the visual stimulation

occurs in the green, about 30 per cent in the red, and approximately only about 3 per cent in the blue-violet^{10 - p. 197}. This is represented in a graph (Fig. 1) known under the various names as the ‘Luminous Efficiency Curve’ or ‘Relative Eye Sensitivity’^{8 - p. 902, 10 - p. 197} or ‘Spectral Luminous Efficiency’^{5 - pp. 371, 372}. Published numerical values^{6 - p. 73} for this graph were converted into a simple wavelength-dependent algorithm factor using linear smoothed interpolation between the discrete values.

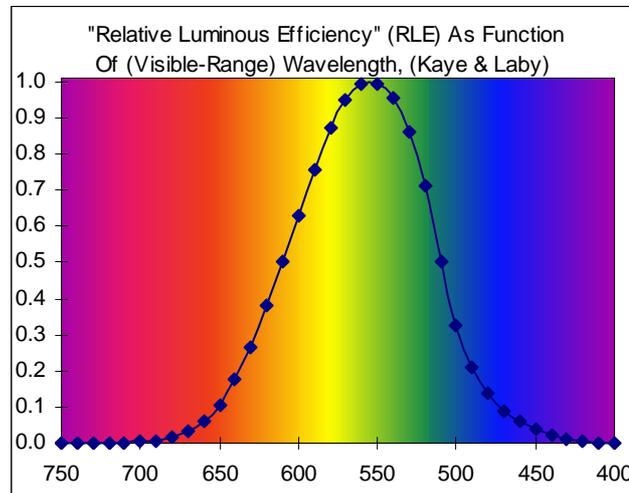


Fig. 1 Typical human ‘Relative Luminous Efficiency’ curve, describing the average sensitivity of the human eye to the various wavelengths in the visible spectrum

RLE CORRECTED TRANSMISSION

This relationship was then used for modifying the spectrophotometric transmission values, between 400 and 700 nm, for a number of gem materials into a parameter that has been called the *RLE Corrected Transmission*. The resulting parameter (Fig. 2) then actually becomes a representation of the relative intensities of the various band passes that could be expected to be seen by human vision of average sensitivity, as the perceptibilities of features at the extremities of the visible wavelengths are severely diminished relative to their presentation through the spectrophotometer.

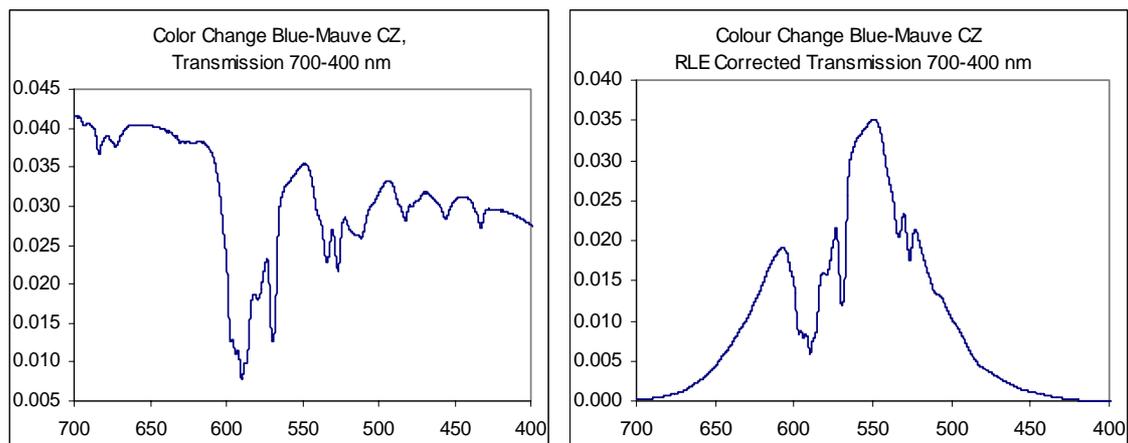


Fig. 2 Transmission spectrum (LHS) and the derived ‘Relative Luminous Efficiency’ (RHS) of a neodymium-containing Cubic Zirconia, illustrating the loss of visual sensitivity towards the wavelength extremities.

Note that the Relative Luminous Efficiency curve (Fig. 1) represents the human-visual sensitivity to continuous 'white' light just touching its peak-maximum at about 555 nm. This could, perhaps, be ideally portrayed as a straight horizontal line across the spectrophotometric transmission graph (with no absorptions) from 400 to 700 nm. The RLE Corrected Transmission is therefore a representation of the apparent visual brightnesses of different parts of a gemstone spectrum, when either viewed directly or through a direct-vision spectroscopy by a person with a visual response corresponding to the Relative Luminous Efficiency curve, and using continuous incident light visually interpreted as perfectly 'white' light. White light usually is considered to be equivalent to a colour temperature of about 5500 °C, about the surface temperature of the sun, unless alternative simulated illuminations are used.

Figure 3 compares the spectrophotometer recording (superimposed on an image of the visible spectrum) of a Nd-doped YAG (A) with its spectrophotometer derived 'RLE Corrected Transmission' parameter (B), and a photographic image of the absorption spectrum produced by a prism spectroscopy (C).

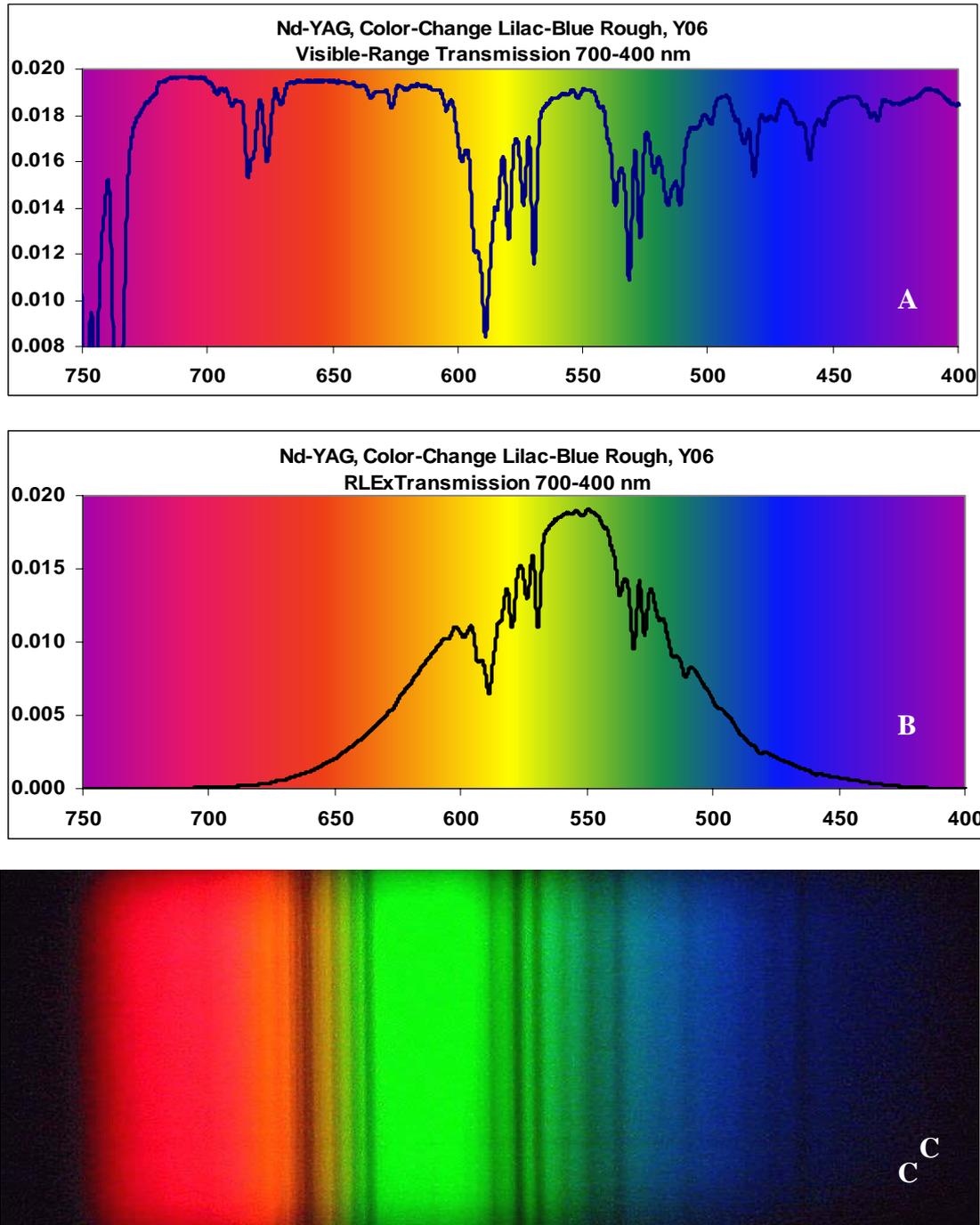


Fig. 3 Comparison between transmission spectrum of Nd-YAG recorded with a spectrophotometer (A), the derived RLE Corrected Transmission (B), and a digital camera photographic image of the spectrum produced by a prism spectroscope (C).

Inspection of the photographed spectral image (Fig. 3C), taking into account the non-linear distribution of the wavelength scale caused by this prism-based instrument, and comparing it with the RLE-corrected spectrophotometric image (Fig. 3B), reveals a clear correspondence between various well-defined line-absorption features. These include the very weak line in the orange-red at 598 nm adjacent to the intense absorption band centring at 589 nm with its weaker shoulders at 591 and 584 nm, the triad of lines including the moderate intensity line at 579 nm, the weak line at 573 nm, and the stronger line at 569 nm. Contiguous to this triad is a broad transmission-band in the green without significant absorptions, bounded by a weak line of another triad

at 536 nm, a stronger line at 531 nm, and a moderate intensity line at 527 nm. Adjoining these is another weaker group of three lines at 520 nm and 514 nm, and a moderate intensity line at 511 nm. The RLE-corrected transmission suggests that there is minimal visibly detectable detail at shorter wavelengths, which is also quite consistent with the writer's direct observation—although the digital photograph of the spectrum in the prism spectroscope indicates the camera's recording of a number of additional lines in the blue-to-violet. This is taken to indicate that the sensitivity of the digital camera used (Canon A-40) is quite closely adjusted to correspond to that of human vision; although its sensitivity in the blue-indigo-violet is actually somewhat greater than that indicated by the RLE.

A parallel pattern of absorption is observed (See figure 4) with the spectrum of the colour-change neodymium-glass, known commercially as 'alexandrium', and its photographed spectrum.

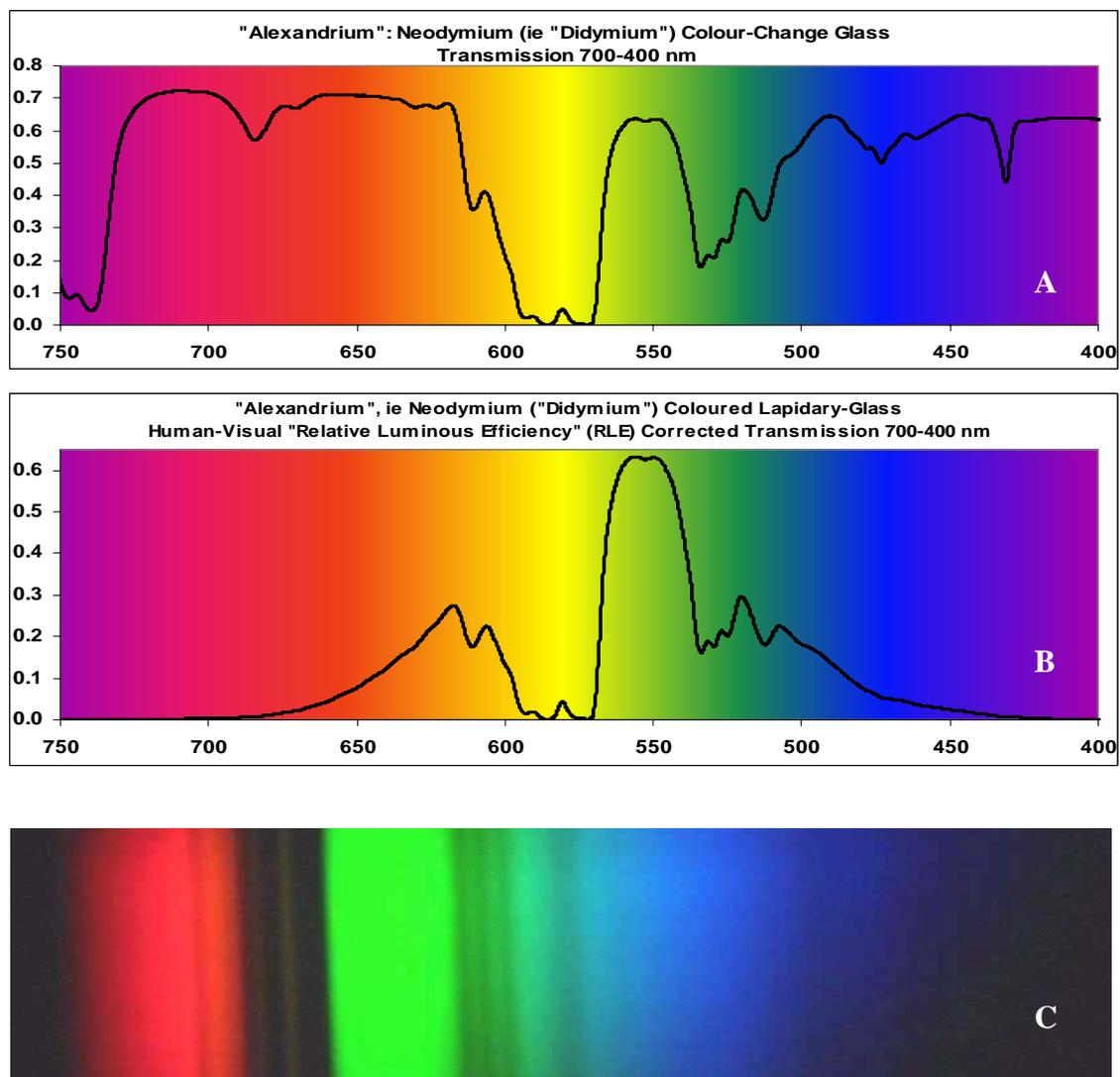


Fig. 4 Comparison between the transmission spectrum of 'alexandrium' Nd-doped glass recorded with a spectrophotometer (A), the derived RLE Corrected Transmission (B), and a digital camera photographic image of the spectrum produced by a prism spectroscope (C).

APPLICATIONS OF RLE CORRECTED TRANSMISSION

Sapphire

A conspicuous example of the use of the discussed method of spectral investigation is the detection of the presence of the intense absorption band in many natural blue (and yellow) sapphires at 450 nm in the deep-blue/indigo that has been attributed to ferrous (Fe^{2+}) iron, but which has not yet been observed by this author in any of the many specimens of synthetic corundum of Verneuil origin, or of flux/hydrothermal derivation he has examined. Yet, conversely perhaps, it may not be commonly appreciated that the occurrence of this specific feature, presently a 'hallmark' of natural occurrence, can be at least partially responsible for the obliteration of a large proportion of the blue-violet transmission of many such natural sapphires—especially in those dark blue-green stones of basaltic origin. When the absorption is intense, it can cause them to assume the less blue-saturated 'inky' greyish blue-green colours that contrasts them against most of their more deeply blue saturated synthetic counterparts that do not display this absorption. This contention is illustrated (Fig. 5) in the following overlain spectra of a typical Australian natural blue sapphire and Verneuil flame-fusion synthetic blue sapphire. Interestingly, no evidence has been observed in any of the examined specimens of sapphire, natural or synthetic, of the supposed three diagnostic absorption bands at about 450, 460 and 470 nm, reportedly attributable to iron. Nor, incidentally, were these corresponding three supposedly diagnostic 'iron bands' detected in any of a selection of peridot (idochromatic ferrous magnesium orthosilicate) recovered from a variety of locations around the world).

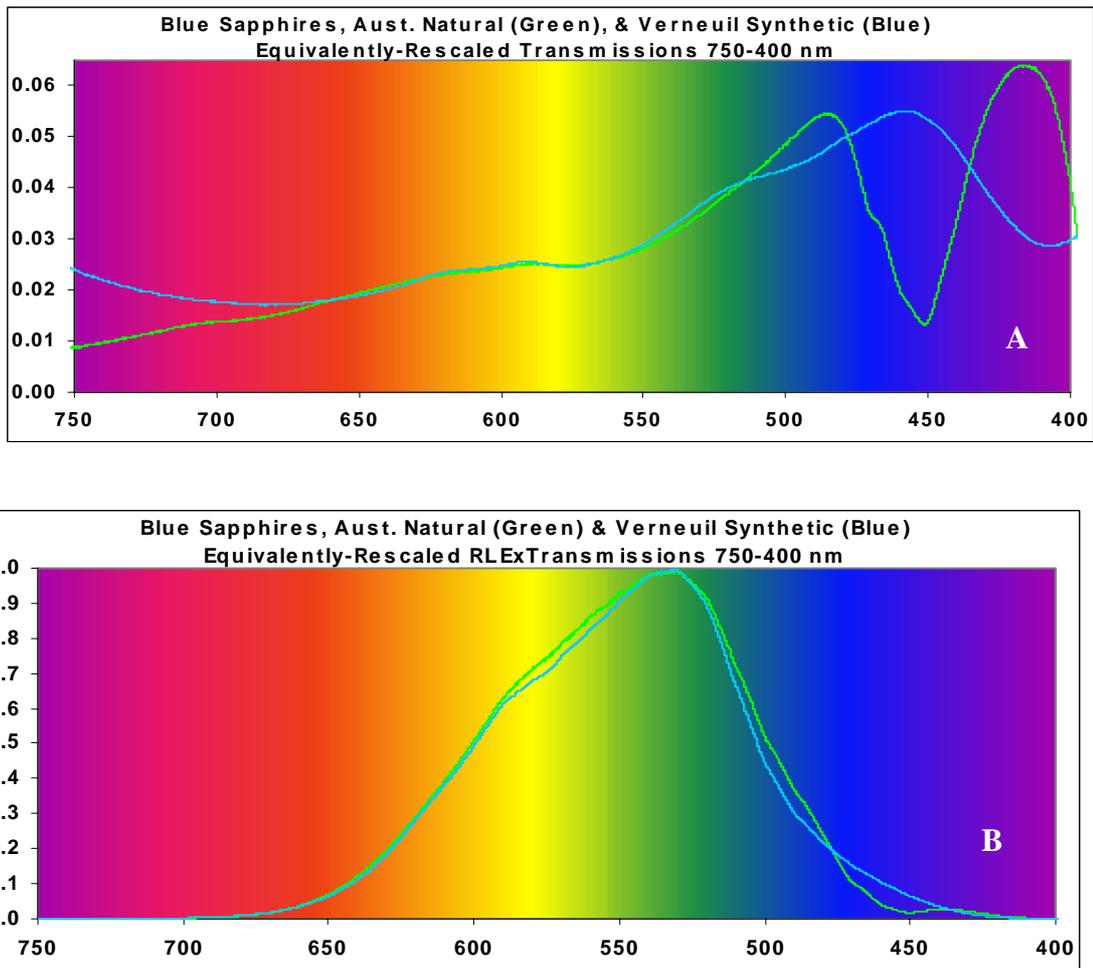


Fig. 5 Comparison between the spectrophometric spectra (A) and RLE Corrected spectra (B) of a typical natural deep blue sapphire of Australian origin (green spectrum) and Verneuil synthetic blue sapphire (blue spectrum) that was scanned perpendicular to the c-axis of the boule from which it was cut, demonstrating the reason for poor detectability of the 450 nm absorption. Note that the 450 nm absorption of the natural sapphire is conspicuous compared to its RLE corrected spectrum in which the 450 nm absorption line is almost visually undetectable. This difference, which explains the difficulty in observing this absorption in a Verneuil synthetic blue sapphire, may also be used to discriminate natural from Verneuil synthetic blue sapphire

The major consequence of the luminous efficiency response, then, is that the red and especially the indigo-violet spectral extremities of the directly-observable spectrum are far less visible than the mid-spectrum¹⁰. This explains why the abovedescribed characteristic absorption band at about 450 nm in iron-rich natural corundums is seldom positively detected visually, despite its being so prominent in a spectrophotometric scan that is not subject to any human visual 'Relative Luminous Efficiency' modifications. This fact is well illustrated in the above illustrated transmission spectra of a natural blue Australian sapphire and a Verneuil synthetic blue sapphire. Their RLE-corrected spectra, in which the initially very obvious 450 nm line of the natural specimen becomes almost obliterated due to the RLE-loss of human visual sensitivity in the deep-blue, consequently accounts for the difficulty of its detection with the hand spectroscope. The enhanced sensitivity of a digital camera

at these wavelengths might be exploited to advantage for detection of such absorptions.

Peridot

Peridot, like most sapphires, owe much of their colour to iron. Like sapphire, no evidence has been observed to support the earlier supposition that the diagnostic spectral indication of iron in this gemstone also consists of three absorption bands.

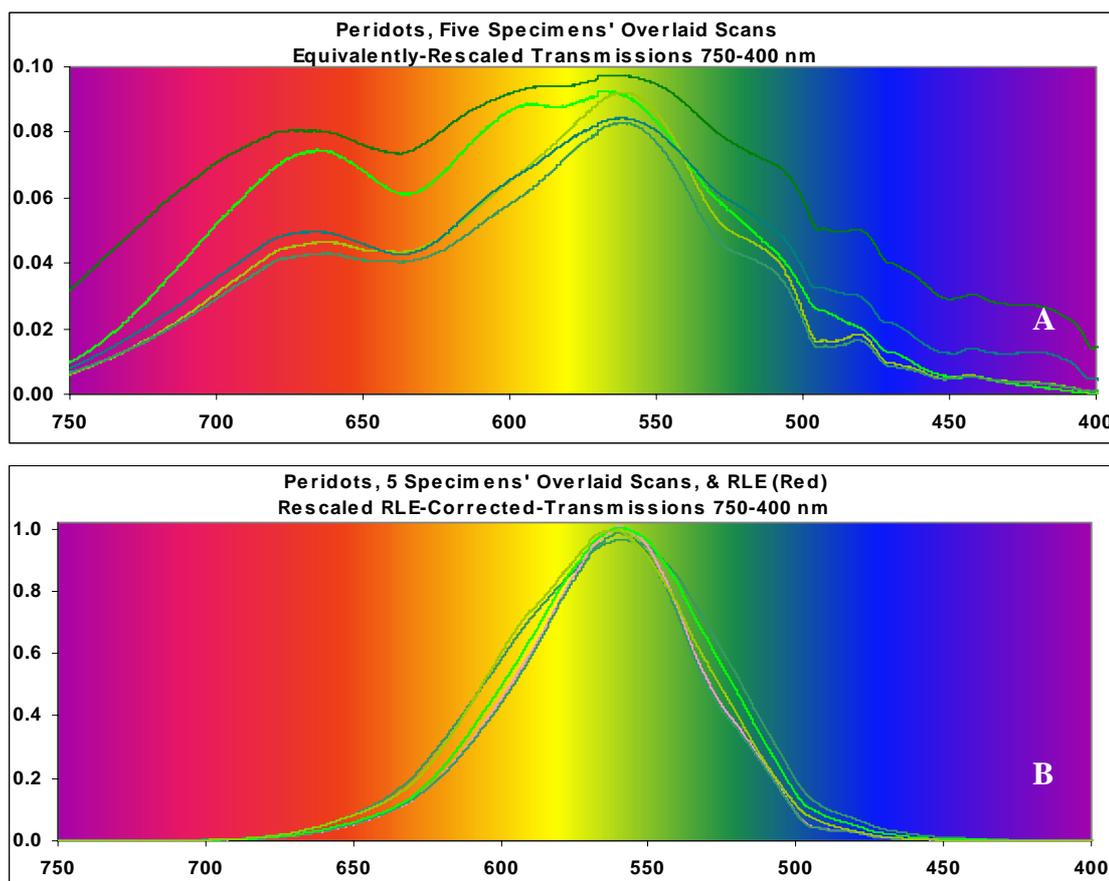


Fig. 6 Comparison between the spectrophotometric spectra (A) and RLE Corrected spectra (B) of peridots from various world-wide locations.

Inspection of the RLE-corrected transmission spectra of five different peridots from various locations around the world (Fig. 6) indicates that there are no clearly-defined absorptions that serve as unique or diagnostic distinguishing markers for discriminating this gemstone from others. Visual spectroscopic examination of these specimens was also consistent with this conclusion, despite the widespread belief of the presence of three bands in the shorter wavelengths, attributable to ferrous-iron.

Consequently, it appears that at least some gem spectra that have long been considered diagnostic or at least characteristic of particular species of gemstone may

need some revision in order to maintain their reliability for modern gem identification and authentication purposes.

Polarisers

Typical Polaroid™ plastic and glass-enclosed filters, as variously used to achieve polarisation in polariscopes, camera-filters, and refractometers were also examined. The absorption spectra of the glass and plastic polaroid filters were initially of especial interest, as it had been hoped to investigate the differences in absorption spectra of pleochroic gem materials as a function of their orientation by utilising a polarising filter to isolate specific rays. However, it was considered that the rather complicated polarising filter spectra would have made a detailed comparison of the different rays of pleochroic materials rather confusing, since the numerous absorption features in the filters (Fig. 7) could have been readily misinterpreted as arising from the specimen unless tedious and careful processing was used eliminate these features.

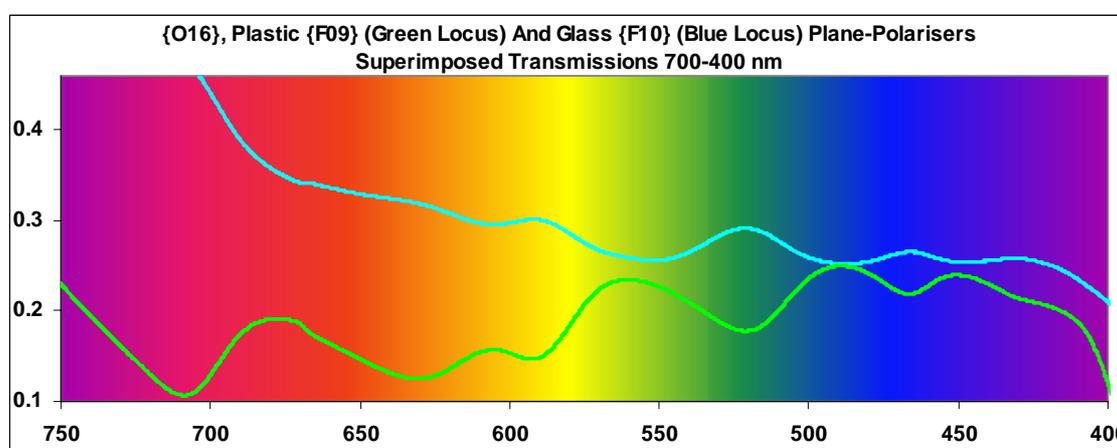


Fig. 7 Comparison of the transmission features of plastic and glass encapsulated polarising filters, that clearly demonstrate their different, complicated absorptions that interfering potentially with superimposed gemstone spectra isolated by these filters.

However, less critical comparisons of polarised spectra were feasible, enabling some general deductions to be drawn about the relationships between the various rays of many pleochroic materials. But for the majority of pleochroic materials, that were investigated, the visibly different pleochroic colours do not result from fundamentally different spectra, which are orientationally dependent. Instead, the spectral absorption and transmission bands are generally at the same wavelength-locations when the specimen is viewed from the differing directions. However, these bands have different relative strengths when viewed in different directions. It is these different proportions of wavelength band pass contributions that stimulate the visual receptors and so induce perceptions of different colours. The consequence of this finding, for the hand-spectroscope examination of pleochroic gem materials, is that the visible spectra will generally only differ marginally with change of specimen orientation—despite the differently coloured appearances of the pleochroic gemstones.

CONCLUSIONS

The spectrophotometric determination of a wide range of UV-Visible spectra of natural, synthetic and simulant gem materials has revealed that there is probably a pressing need to review and revise the spectra presently accepted as being typical or diagnostic of many gemstones and other related materials. There may also be significant opportunities for exploitation of the spectrophotometric technique for confirming the identities of so many of the burgeoning array of natural, treated-natural and synthetic or simulant gems currently available in the marketplace, and also for monitoring many enhancement treatments. It is also hoped that the appropriate formatting of spectrophotometric graphical spectra, for direct comparison with the images detectable in the hand spectroscope, together with the compilation of a gem-spectra library, might enable practising gemmologists to more effectively utilise the spectroscope.

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Address for correspondence:

Grant Pearson
5 Cora Court
Mt Waverley Vic 3149
email: gpearson@netspace.net.au