

This is the 4th and last article in this series on Birefringence by Dr. Brad Amos. Originally scheduled as a 3 part series Dr. Amos realised that it would be incomplete without reference to colour change aspects, which this 4th part now addresses. Our sincere thanks to Brad for enlightening us. Ed

Birefringence for facetors 4: Gemstones that change in colour.

Dr. Brad Amos

This article is concerned with some aspects of colour, and particularly with gemstones that change in colour according to illumination or angle of view.

The Absorption Law

Absorption colour is completely different from the **interference colours** which may be produced by viewing birefringent crystals between polarising filters, and the iridescent **diffraction colours** that arise from periodic structures, as in opal.

Absorption in a gem means the conversion of some of the light energy into heat. A gem looks red if it absorbs green and blue light, and the gem material becomes slightly warmed in the process. The red light is transmitted unchanged and, if able to emerge from the gem, can enter the eye.

Whereas the retardation produced by birefringence is simply proportional to thickness, absorption obeys a different rule, called **Lambert's Law** which states that **equal increments of thickness produce the same fractional decrease in light intensity**.

If you have a tiny, brightly coloured gem, in which the average total light path is 1mm, and half the light is absorbed, and you make a large gem of the same material, Lambert's Law tells you how much light will emerge from the large gem.

If the new average light path is 10mm, the emerging light will be only a tiny fraction (one half multiplied by itself ten times, i.e. one thousandth) of the light that

went in. In other words, the gem will look almost black. This is why, for example, dark garnet rough may come to life, showing a bright colour if it is cut to a very small size.

The mathematical expression of Lambert's Law is:

$$I_x = I_0 e^{-kx}, \text{ where :}$$

I_0 is the intensity of the light entering the material,

I_x its intensity after passing through a thickness x , and

k is a constant called the absorption coefficient.

Two Types of Colour-Change

Basic information on the origin of the colours of gem materials can be found in the textbook on:

'The Spectroscope and Gemmology' by Anderson and Payne and more recent knowledge at the Caltech website.

This article is concerned only with the phenomenon of colour change. There are two completely different types of colour change, which are often confused in gem advertisements, perhaps because the classic example (alexandrite) shows both.

The first is a change in colour according to the ambient illumination (**Fig.4.1**). The second is colour that changes according to the direction of view through the material. The correct word for this is **pleochroism**. Pleochroic materials are invariably birefringent.

Fig 4.1 on page 12

Colour Change Dependent on Illumination Spectrum

This type of colour change has no connection with birefringence, and is included here merely because it is so often confused with pleochroism. It arises from an interaction between the absorption spectrum of the gem and the emission spectrum of the illumination. The strongest changes are found in materials containing rare earth elements such as holmium or neodymium (present in mined alexandrite and as an additive in many synthetic gem materials). These elements produce sharply-defined absorption bands in the spectrum, which is a key to their colour-change property.

The human eye is adapted to sensing the colours of leaves, of ripe or unripe fruit, or flesh, which are produced by pigments with simple broad spectral bands. The eye cannot distinguish the complicated multiple and narrow absorption bands produced by, for example, neodymium (**Fig.4.2**). For that, a spectroscope is necessary.

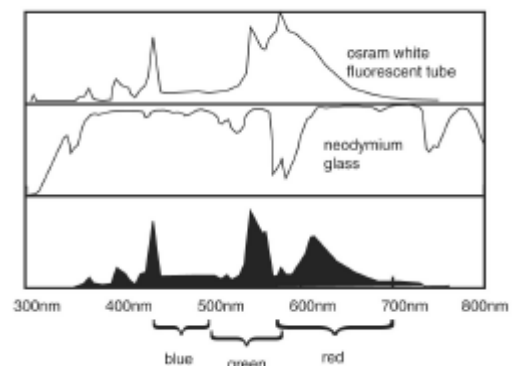


Figure 4.2. Emission spectrum of fluorescent tube, absorption spectrum of neodymium glass, and the effect of subtracting the neodymium absorption from the tube light: the result with this particular tube is colourless.



Figure 4.1. Six gems illuminated with tungsten halogen light (left) and fluorescent tube light (right). The gems are (clockwise from top left) hydrothermal emerald, 'tourmalike' glass, coloured cubic zirconia, neodymium glass, amethyst preform and red CZ

Some fluorescent tubes make the gem look blue, because they are not so rich in far-red emissions, and their near-red emission is almost completely eliminated by the neodymium.

The most remarkable colour change material is a proprietary glass called 'tourmalike' (Figs 4.1 and 4.3), which goes from wine-red in incandescent to grass green in fluorescent light. The spectrum shows that tourmalike contains neodymium, but there is something else, which increases the absorption in the blue near to the 430nm mercury emission of the fluorescent tube. The result is that tourmalike stimulates green sensation in fluorescent tube light. In the continuous spectrum of an incandescent light tourmalike transmits plenty of the intense deep red light, and the absorption bands at shorter wavelengths cause a slight red bias, hence the wine-red colour.

These colour changes depend on the precise spectrum of the incident light. This varies with the filament current in an incandescent light, and with the composition of the phosphor in a fluorescent tube. Lesser colour changes were seen in alexandrite and other gems long before the advent of fluorescent light, because the absorption bands can also tip the balance of sensation when, for example, red-rich candlelight is compared with daylight.

Pleochroism



Figure 4.4. Faceted oval of andalusite (left) with the same gem immersed in oil and viewed at three different angles.

Pleochroism is much more relevant to these articles, since it is closely related to birefringence.

A pleochroic gemstone is one which changes colour, or changes from coloured to transparent, according to the direction of view.

One of the best examples is andalusite (Fig 4.4), in which a single cut stone, with an overall grey colour, shows suffusions of brown and green, with occasional flashes of red and yellow. Immersion of a cut stone of andalusite in refractive-index matching oil renders the colour uniform throughout the stone, but variable according to the angle of view (Fig 4.4). This shows that the absorption changes according to the direction of the light rays passing through the crystal. (The effect of the

As is shown in Figure 4.2, neodymium produces good transmission throughout the visible spectrum except for a strong, sharp band in the orange and a little reduction in the blue.

In figures 4.2 & 4.3 the spectrum of the light source is shown at the top, the transmission spectrum of the gem material in the middle and the spectrum of the light from the source after transmission through the material (obtained by multiplying the corresponding values in the two curves together) at the bottom. Absorption in the material subtracts specific regions from the spectrum.

When a neodymium-doped stone is viewed in an incandescent lamp, it has a pinkish or pinkish-purple colour, resembling amethyst. This is because the emission of an incandescent lamp is strongest in the red, peaking towards the infra-red. Neodymium allows the red and the blue ends of the spectrum to pass freely, giving purple.

However, as Fig. 4.2 shows, the situation is completely different with a fluorescent lamp. Such a lamp has quite sharp peaks in the spectrum, and their heights are carefully adjusted to give equal stimulation of the eye-plus-brain in the blue, green and red. The effect of neodymium is to absorb the orange and light red emissions, bringing the light into a balance which is interpreted by the eye as white, and the impression is of a colourless gem (see Fig 4.1).

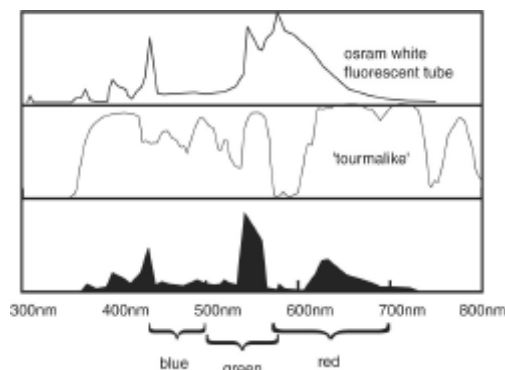


Figure 4.3. As for Figure 4.2, but showing the way in which the tourmalike subtracts all but the green emission from

immersion fluid is to eliminate the bending of light by refraction at the gem surface, so all the light goes through parallel to the line of sight). Pleochroism can be demonstrated effectively by cutting cuboidal specimens (Fig 4.5), selecting the angles of cutting so that adjacent faces show markedly different colours.

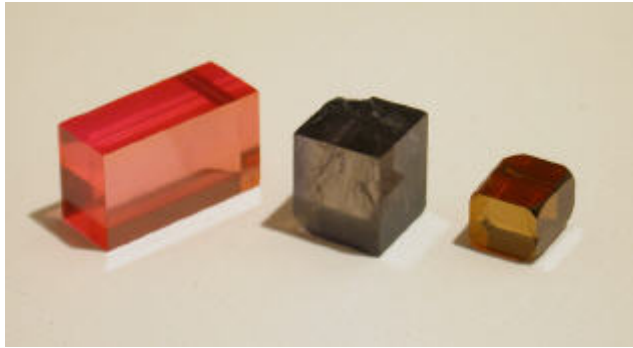


Figure 4.5. Polished cuboids of (from left) synthetic corundum, iolite and epidote.

chemical bonds have natural resonance (i.e. they can absorb energy) at the frequency of the incoming light wave. Instead of merely changing the wave velocity, these electrons can absorb the wave, converting its energy ultimately into heat.

The most familiar example of a dichroic material is Polaroid film, in which polymer molecules containing iodine atoms have resonant bonds along the direction in which the

Dichroism

A clue to the origin of pleochroism is provided by the phenomenon of **dichroism**, in which the brightness of a gem changes when it is viewed through a polariser.

The definition of **dichroism** is:

A change in the absorption coefficient according to the azimuth of polarization of the light beam passing through the crystal.

This means that when the direction of polarisation (i.e. of the electric field) of a light wave is parallel to a particular crystal axis, the absorption coefficient k_1 is different from that when the direction of polarisation is perpendicular to the axis (k_2).

Dichroism is defined numerically as k_1 minus k_2 .

All pleochroic materials turn out to be dichroic, and the origin of dichroism is the orientation of chemical bonds in the crystal structure.

As with birefringence, bonds that are oriented in the direction of polarisation can interact with the light. The difference from birefringence is that the electrons in the

film has been stretched during manufacture. If a light wave is polarised parallel to the resonant bond direction, it is absorbed: if polarised perpendicularly it is not.

Dichroism may be a useful property for identifying gems. The simplest way to detect it is to examine the gem through a linear polarizing filter, rotate the filter, and look for changes in colour or intensity. Special instruments known as dichroscopes are available (e.g. from the Gemmological Association) but can be improvised, as in (Fig 4.6).

Pleochroism in Uniaxial Crystals

As described in previous articles, in uniaxial crystals, there is one axis (the c axis) which is the axis of fourfold or sixfold rotational symmetry. This is also the optic axis, where the birefringence becomes invisible because the velocity of light along the axis does not vary according to the direction of

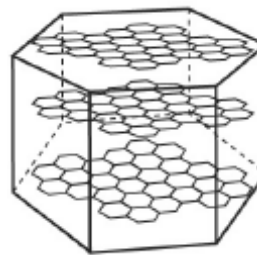


Figure 4.7. A possible model for the structure of corundum. Resonant bonds are imagined to run parallel to the sides of the small hexagons

polarisation. As mentioned before, the optic axis can also be defined as a direction perpendicular to any circular section of the index ellipsoid or

indicatrix..

Pleochroism of **corundum** is well known and relatively simple: the colour of rubies or sapphires is strongest when viewed along the c-axis of the hexagonal crystal and it is best to cut the table perpendicular to c.

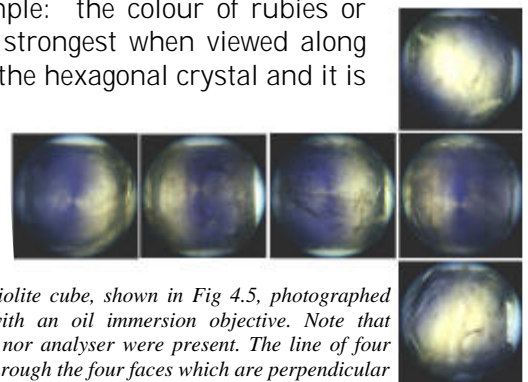


Figure 4.8. The iolite cube, shown in Fig 4.5, photographed conoscopically with an oil immersion objective. Note that neither polariser nor analyser were present. The line of four images is taken through the four faces which are perpendicular to the plane containing both optical axes. The top and bottom images are perpendicular to this plane. Note the four positions in which blue Brewster brushes are visible



Figure 4.6 Use of an improvised dichroscope to distinguish between immersed gems of green glass (left) and tourmaline (right). The dichroscope was made by attaching a piece of polythene at the 45 degree position to a polarising filter disk, and placing the disk inside the eyepiece of a microscope with the polythene towards the specimen. The plastic strip has to have a retardance of one half wavelength: such a strip can be identified from a number of samples by placing it between parallel polarisers, in which case it appears black, or nearly so. A similar result could be achieved with more difficulty by fitting together three pieces of polarising filter.

By contrast, in **tourmaline**, the **c**-axis, particularly in green crystals, is usually a muddy brownish-grey, and the best table orientation is *parallel* to **c**.

If corundum is viewed along the **c** axis through a linear polarising filter, the colour remains strong as the polarizer is rotated.

When viewed along a line of sight perpendicular to **c**, the colour is strongest when the polarizer is transverse to **c** and rather weak when its direction of polarisation is parallel to **c**.

The dichroism is particularly obvious in so-called 'padparadscha' synthetic corundum boules. In my experience, the **c**-axis is not necessarily along the longest dimension of a boule of synthetic corundum: it can be at 45 degrees to this axis. Some experiment, preferably with an immersed chunk of the rough material, may be necessary before the best direction for the table of a gem can be found.

The pleochroism of red corundum can be explained by a simple model (**Fig 4.7**) in which resonant chemical bonds for the absorption of green and blue light (and resulting transmission of red) are all oriented perpendicularly to the optic axis in a symmetrical arrangement, e.g. parallel to the sides of the hexagons of **Fig 4.7**.

When light is directed along the optical axis, there is strong absorption for all directions of polarisation and the emerging light is red. But when the light passes at right angles to the axis, only that fraction of the light that happens to be polarised parallel to the direction of the resonant bonds is absorbed, and the remainder passes through as white light, which, in combination with the red, gives a weak and unsaturated pink colour.

Pleochroism in Biaxial Crystals

Anyone who tries to optimise the colour by selecting the best table orientation in a biaxial coloured material such as iolite (i.e. cordierite) or epidote, notices that the process is not straightforward.

There seem to be several possible optima, and the colour may seem to change extremely rapidly over very small changes in angle. The behaviour of light in biaxial absorbing crystals is, in fact, very complex, and, unlike most aspects of optical crystallography, has only relatively recently been understood fully.

As previously explained, where one has a variation of colour or retardance with angle, the best method of study is by conoscopy, preferably by looking at the back focal plane of a microscope objective focused on a flat parallel-sided plate of the gemstone material. However, a rough-and-ready conoscopic view may be obtained simply by holding the plate close to the eye and viewing the non-polarised light scattered from **white paper** or a wall.

Brewster Brushes

It was discovered by Brewster in 1819 that the biaxial mineral iolite, viewed thus, appears in some orientations to be greyish white, with two strongly-coloured blue brushes, which appear to *almost* meet where their narrow ends are opposed. (**Fig 4.8**).

I have seen Brewster brushes also in epidote, where they appear bright green on a brownish ground. Further study shows that the brushes intersect near the two optical axes of the biaxial crystal. Since each optic axis has two ends, there are eight brushes in all.

In iolite, the brushes are angular regions in which the strongest and most beautiful blue colour can be seen, but where a small angular error produces a dull and unsightly yellow/grey, posing a baffling problem for the faceter.

Perhaps a cut could be devised to exploit this property?

Scientifically, the brushes raise many questions.

How can the birefringence, which governs the position of the optic axes, affect the absorption, as it clearly does in the case of the brushes? What determines the shape of the brushes, and why is it possible to see them without either polariser or analyser, whereas interference phenomena normally require both?

We now concentrate on iolite, which is an orthorhombic biaxial crystal with the blue colour due to iron, and also, in some specimens, a yellow/brown colour in other directions.

It is no surprise to find different pleochroic colours such as this in biaxial crystals, since the three crystalline axes (alpha, beta and gamma, **Fig 4.9**) are dissimilar and each axis can be imagined to have a different family of resonant bonds parallel to it. The three absorption spectra recorded for iolite with the plane of polarisation parallel to each axis in turn are completely different.

The strongest visible absorption (maximum at approximately 580nm) occurs when the direction of

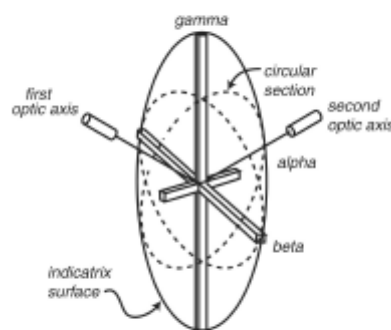


Figure 4.9. Indicatrix for iolite, with the differences in length between the three axes exaggerated for the sake of clarity. As with all biaxial crystals, there are two sections through the indicatrix which are circular, and these are perpendicular to the two optical axes, here shown with cylindrical 'handles' on them to distinguish them from the axes of refraction.

polarisation is parallel to the beta axis (**Fig4.9**): this is the source of the magnificent blue colour that is seen if the angle of view is just right.

To understand how the Brewster brushes arise, it is necessary to concentrate on the area of the conoscopic pattern around an optical axis (**Fig.4.10**).

In iolite, the angle between the optical axes is large (65° - 104°), so the area in the left-hand diagram of 4.10 shows only one optical axis, in the centre of the diagram.

Each of the ellipses in this diagram indicates the shape of the section of the indicatrix perpendicular to a line connecting the centre of the ellipse to the centre of the indicatrix.

The central ellipse is a circle, because the line is in this case the optic axis. If natural light, (consisting of a mixture of waves polarised in all directions) passes along any of these lines, it is split into two beams, each polarised at right angles to the other.

One of these beams, the slower one, is polarised parallel to the major axis of the ellipse, the other (fast transmission) is polarised parallel to the minor axis.)

This is physical reality, rather than merely a mathematical concept, as the basic demonstration of the two images generated by a calcite rhomb shows, each image being extinguished in turn as the polariser is turned through exactly 90°). But these 'index ellipses', as they are called, change shape according to their position on the conoscopic diagram.

Above the optical axis, the effect of the gamma axis is reduced, and the ellipses are flattened horizontally; below the optical axis, the gamma influence predominates, and the ellipses are extended vertically. To the left, the ellipses are rotated in one direction; to the right in the other direction. Thus, although the polarisations of the fast and slow beams are always mutually perpendicular, the angles that they make with the horizontal or vertical planes in the diagram vary from one region to another.

The oldest theory of the origin of the brushes is that the dichroism of the gamma axis is merely superimposed on the birefringence pattern.

Throughout the diagram the horizontal direction is parallel to the beta axis, and all rays polarised parallel to this axis will tend to be absorbed.

Now comes the key point: along the outer parts of the horizontal line passing through the optic axis both slow and fast beams have polarisation directions at equal angles (near 45°) to the horizontal. It can be shown

mathematically that the absorption in these cases is at a maximum, whereas cases such as the top and bottom of the diagram, where either the slow or the fast beam is polarised perpendicularly to the gamma axis, represent minimum net absorption.

According to this theory, Brewster brushes similar to the centre diagram in 4.10 are to be expected, by the combination of linear

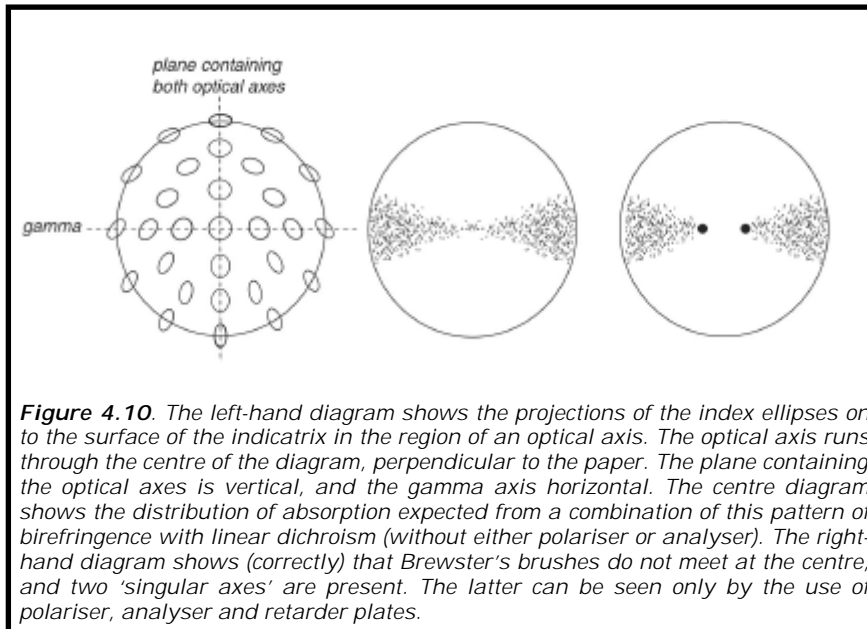


Figure 4.10. The left-hand diagram shows the projections of the index ellipses on to the surface of the indicatrix in the region of an optical axis. The optical axis runs through the centre of the diagram, perpendicular to the paper. The plane containing the optical axes is vertical, and the gamma axis horizontal. The centre diagram shows the distribution of absorption expected from a combination of this pattern of birefringence with linear dichroism (without either polariser or analyser). The right-hand diagram shows (correctly) that Brewster's brushes do not meet at the centre, and two 'singular axes' are present. The latter can be seen only by the use of polariser, analyser and retarder plates.

dichroism with birefringence.

It was not until 1955 that the defects of this theory were fully exposed and a better theory was presented by S. Pancharatnam of the Raman Research Institute (Bangalore).

It is impossible to explain Pancharatnam's theories here, but a few of the inadequacies of the above explanation can be mentioned. For example, *the region equivalent to the optic axis in a transparent crystal shows dichroism*, being not extinguished between crossed polarisers if their directions of polarisation are at 45° to the vertical (with reference to **Fig.4.10**).

Also, the use of polarisers and birefringent retarder plates shows that *instead of a normal optical axis there exist two 'singular axes'*, as shown by the dots in **Fig 4.10 (right)**, where the only means of passage of light is as a right-handed circularly polarised wave in one case, and a left-handed in the other. (Circularly polarised light is a form in which the electric field rotates continuously in direction, while remaining transverse to the direction of propagation.). Also, when a polariser alone is added, *interference rings*, of the type normally not seen without an analyser, become visible.

All of these phenomena were explained by Pancharatnam, who also laid the theoretical basis for modern liquid crystal devices before his tragic death in 1969, at 35 years old. The properties of absorbing crystals still continue to fascinate mathematicians: a comprehensive theory, with special notation, taking into account optical rotatory activity as well as linear birefringence and dichroism has recently been put forward by M.V. Berry and M.R. Dennis (2003).

Concluding remarks

This ends my treatment of birefringence, a journey which has passed from simple vectors to the frontiers of modern mathematics. The purpose was to reveal properties of gem materials which might be of value in the selection of best orientations and cutting angles, and might perhaps stimulate new gem designs.

My plea for a synthetic material of high birefringence but easier to work than calcite has already been answered by Dr G. Doughty of Glasgow, who has supplied me with large boules of lithium niobate (described by Arem and others under the name 'Linobate'). I have heard from one professional cutter that the earlier articles have helped him to improve his yield from natural zircon crystals.

If birefringence can be better exploited in gemcutting it will no doubt be the amateur worker with coloured stones who will do it: in this one respect diamonds, being cubic, are forever deficient.

Acknowledgements

I thank G. Mitchison for introducing me to the work of M.V.Berry, Professor Berry for recommending the work of S. Pancharatnam, and Professor G. Rossmann for helpful advice on cordierite (iolite).

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