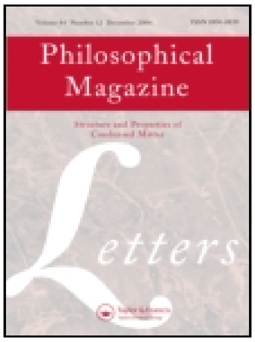

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COMMENTARY

Herapathite – the first man-made polarizer

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Recent research reported earlier this year in *Science* has now determined the crystal structure of the salt of quinine first described by William Bird Herapath in 1852 in *Philosophical Magazine* and subsequently given the name 'herapathite' in his honour by the scientific community. This relatively obscure and little-known biaxial material was the forerunner of Polaroid: it exhibits the property of pleochroism, to the extent that light is almost completely absorbed along one particular principal vibration direction of the crystal structure. The story of herapathite is a fascinating one, unfolding gradually over more than 150 years and involving low temperature chemical synthesis and structure–property relationships in materials.

Keywords: absorption; polarization; crystallography; optical microscopy; crystal structure; optical properties

1. Introduction

William Bird Herapath (1820–1868) was both a medical doctor and a chemist [1]. Elected Fellow of the Royal Society in 1859, his name was assigned by the eminent Austrian mineralogist Wilhelm Haidinger in 1853 [2,3] to the salt of quinine about which Herapath first wrote in *Philosophical Magazine* in 1852 [4]. Crystals of this salt, herapathite, appear a brilliant emerald green in reflected light. When viewed in transmitted light crystals they appear olive-green unless two crystals cross one another at right angles; under these circumstances the region where overlap occurs appears 'as black as midnight'. Thus, herapathite crystals act as polarizers. Herapath concluded his 1852 paper with the observation that the crystals he had synthesized were 'the most powerful polarizing substance known'. The figures used by Herapath to illustrate the behaviour of the crystals in the optical microscope are reproduced in the Appendix to this commentary as Figures A1–A12.

Polarized light is light that is polarized in a single direction, unlike a beam of unpolarized light in which each ray of light is vibrating normal to its propagation direction, and where each orientation of the vibration plane about the axis of the

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beam is equally possible. Prior to the discovery of herapathite, there were two ways of producing polarized light experimentally: the Nicol prism and tourmaline single crystals, the properties of which are described in a number of textbooks [5–10]. Nicol prisms produce polarization through double refraction, while tourmaline crystals produce polarization by absorption. Both make use of the way in which light propagates through anisotropic crystals. In general, in such crystals, a light wave of a particular polarization direction and wave normal entering a crystal is split into two waves polarized at right angles to one another and traveling at different velocities through the crystal [5–12]. In uniaxial materials with tetragonal, hexagonal or trigonal crystal structures, one of these waves is always termed the ordinary wave (or ray); the other is termed the extraordinary wave (or ray). Materials with orthorhombic, monoclinic or triclinic crystal structures are biaxial. For these materials there are no ordinary waves – both the light waves propagating through the crystal are extraordinary waves, although this is not a term used in practice to describe these waves [5].

In thin sections of most anisotropic materials, these two light waves (or rays) will propagate through the material with negligible absorption. However, in some materials, noticeable absorption of one or both of these waves can occur; the material is then said to exhibit pleochroism [5–10,13]. This manifests itself quite straightforwardly: pleochroic crystals change colour as they are rotated when observed in linearly polarized white light [5,7–10]. Uniaxial crystals exhibiting pleochroism are also referred to as being dichroic [5–10], because the change in colour is determined solely by the thickness of the crystal under examination and the absorption characteristics of waves vibrating parallel and perpendicular to the optic axis of the material [7]. For biaxial materials, absorption can be described in terms of absorption along three mutually perpendicular principal absorption axes, not necessarily all parallel to the three principal vibration directions, unless constrained to be so by symmetry considerations. The characteristics of the absorption along these three absorption axes will determine the nature of the pleochroism for a particular crystal [5,7,9,10].

The crystal structure of tourmaline, $(Na,Ca)(Mg,Fe,Mn,Li,Al)_3Al_6[Si_6O_{18}](BO_3)_3(OH,F)_4$, is trigonal, with absorption always such that the ordinary ray, the ray polarized perpendicular to the optic axis, is much more strongly absorbed than the extraordinary ray [10,14]. The effect of pleochroism (or dichroism) in tourmaline can be demonstrated with thin sections of crystals of tourmaline containing the triad or *c*-axis in the plane of the crystals [5,9,13]. When the *c*-axis is parallel to the polarization direction of the polarized light, it is usual for 30 μm thick sections of crystals to appear a deep yellow [5]. If, however, the *c*-axis is perpendicular to the the polarization direction of the polarized light, the crystals appear deep brown because of the strong absorption of the ordinary ray [5]. The reason that there is such strong absorption of the ordinary ray in comparison with the extraordinary ray in tourmaline is that the Si_6O_{18} rings and BO_3 groups within the crystal structure all lie in the plane perpendicular to the *c*-axis [10,15,16]. These rings and groups are able to interact strongly with light polarized in this plane so that visible light is strongly absorbed [10]. Thus, a knowledge of the crystal structure of tourmaline helps to rationalize why it exhibits pleochroism so well.

2. Herapathite, $C_{82}H_{120}I_6N_8O_{28}S_3$

The crystals studied by Herapath [4] were produced by dissolving the disulphates of quinine, $C_{20}H_{24}N_2O_2$, and cinchonine, $C_{19}H_{22}N_2O$, in concentrated acetic acid, warming the solution and then adding iodine. After leaving this solution for a few hours, brilliant plates of crystals, emerald-green in colour, were precipitated from the solution. Experiments undertaken by Herapath using tourmaline as polarizers showed how well these crystals absorbed light, to the extent that he comments in his paper that they were a factor of at least five times more effective than tourmaline. Additional experiments that Herapath reported in the 1852 paper showed that cinchonine disulphate was not necessary for the production of the crystals, and he concluded that only iodine, sulphuric acid and quinine were absolutely necessary for the production of these crystals. A further set of experiments reported by Herapath in *Philosophical Magazine* the following year specified a procedure whereby large plate-like crystals of herapathite could be grown for use as artificial tourmalines [17]. This procedure, but with the replacement of acetic acid for pyroligneous acid (which contains acetic acid as one of its ingredients, and is a source of acetic acid), was the one used by Kahr et al. [18] for preparing crystals of herapathite for their recent *Science* paper. Kahr et al. established the composition of the crystals they grew to be $4(C_{20}H_{24}N_2O_2H_2^{2+}) \cdot CH_3COOH \cdot 3(SO_4^{2-}) \cdot 2(I_3^-) \cdot 6(H_2O)$, in essence the chemical formula reported by Jörgensen in 1876 [19], but with the addition of an acetic acid molecule.

Since the work of Herapath and others in the 1850s, research on herapathite has been sporadic, to the extent that West [20] began his 1937 paper on its crystallography by commenting that herapathite was now technically important ‘after a century of obscurity’. The technical importance to which West referred was its use as a starting material for the production of ‘large area transmission polarizers (Polaroid, Herotar, etc.)’. Herotar was reported by Clark to consist of a single thin crystal of herapathite on glass [21]. Honty [22] stated that Herotar was made ‘by the Bernauer method’, the precise technical details of which seem now to be lost [23]. Bernotar filters were also made by this process [23–26], one which clearly required both great skill and patience [26], but was able to produce sheets of single crystal 10 cm × 10 cm in size [25]. Originally, Polaroid film was produced by embedding small herapathite crystals in a plastic sheet which was then extruded to align the crystals parallel to one another [5,7,21,26,27], but this method of production was replaced commercially in the early 1940s by the stretching of polyvinyl alcohol sheets and subsequent dyeing by iodine [6,21,28,29], still in use today.

3. Crystal structure of herapathite

West’s 1937 paper was the first one in which the crystallography of herapathite was considered. He showed that the crystals were orthorhombic, and that the unit cell was unusually large. In the description of the unit cell that he specified, crystals in the form of thin plates with [100] perpendicular to the plates formed readily. These plates were sometimes elongated along the [010] direction. Light vibrations parallel to [100] and [010] were freely transmitted, while light vibrations parallel to [001] were strongly absorbed. West observed that the absorption characteristics along [100] and [010] were similar. Therefore, although herapathite is biaxial, it can be said to be dichroic [18]. West hypothesized that the unusual optical properties of herapathite arose from linear configurations of the polyiodide ions parallel to [001], noting that ‘it should prove possible to test this supposition by an analysis of X-ray diffraction data’. Such an analysis has finally been undertaken some 70 years later by Kahr et al. [18]. They have shown that triiodide ions lie roughly parallel to the absorbing axis in herapathite. Delocalized excitations polarized along the absorbing axis from a number of the triiodide ions account for the dichroic nature of herapathite and confirm the essence of West’s hypothesis.

4. Concluding remarks

Herapathite has had an interesting history. In two distinct periods of time, the early 1850s and the mid-1930s, it became a material of intense fascination for a few scientists for its use as a man-made polarizer. As Land noted in his 1951 paper [28], Herapath found it extremely difficult to produce large crystals of herapathite to act as polarizers, and so while there was great interest in the early 1850s in herapathite, it remained no more than a curiosity, despite its promise. In the 1930s, Bernauer succeeded in producing large single crystals of herapathite [24,25] through careful and painstaking work, as a result of which Herotar and Bernotar filters were produced. At the same time, the precursors of modern Polaroid film were made using small herapathite crystals. However, once the modern sheet polarizers were invented, herapathite returned once more to being no more than a scientific curiosity. The recent paper by Kahr et al. [18] has now given it a third chance to be in the limelight. As Kahr et al. have noted, there is a rich clathrate chemistry to be explored in the family of materials of which herapathite is a member. Even though this has been known since the work of Herapath and Jörgensen in the nineteenth century [4,17,19,30], will the mantle now be taken up by the scientific community? Only time will tell.

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Appendix

The figures in the original paper by William Bird Herapath, Phil. Mag. Ser. 4 3 (1852) p.161, are reproduced here, together with a description of each figure provided by K.M. Knowles separately, because in 1852 it was not the custom to provide figure captions. Note that these figures are drawings rather than photographs: Herapath's work predated the widespread use of photography. The arrows in all the figures (excepting A4 & A12) mark the planes of the tourmalines. Herapath records that the magnification of the optical microscope he used was certainly less than 100; however, he made no comment on whether his drawings were to scale for the magnification that he used. The reproductions here are enlargements of the figures in the original paper where the outer circles in each figure were each 38 mm in diameter.

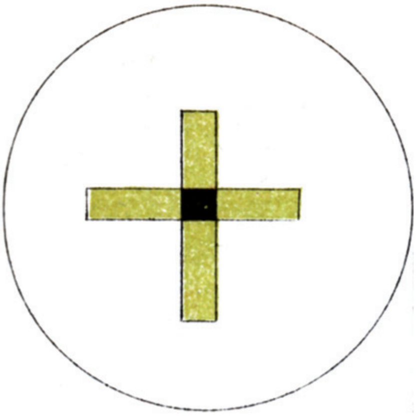

Figure A1. Two crystals of herapathite crossing at right angles to one another and viewed in transmitted unpolarized white light. The region where these two olive-green crystals intersect appears black because of the strong pleochroism exhibited by the crystals.

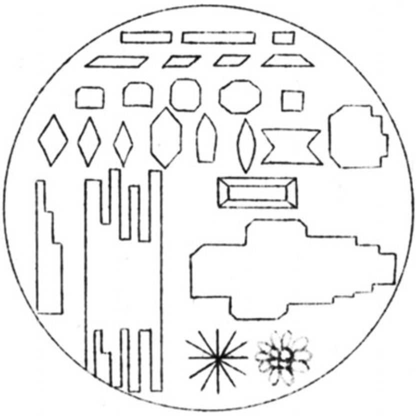

Figure A2. Crystalline forms exhibited by herapathite. Herapath noted that the various forms produced are very susceptible to slight changes in the production process.

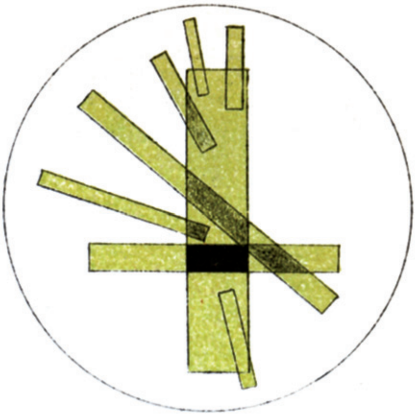

Figure A3. Thin rectangular crystals superimposed upon one another at various angles and viewed in transmitted unpolarized white light. Crystals with their long axes parallel remain an olive-green colour, while crystals at right angles to one another appear black in the region where they intersect, as in Figure 1. For an angle greater than 30° between the long axes, there is a perceptible polarizing effect produced which produces darkening, and which increases in darkness as the angle increases to 90°.

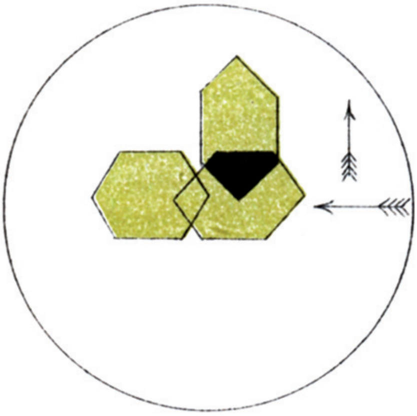

Figure A4. Overlapping elongated hexagonal-shaped crystals of herapathite viewed in transmitted unpolarized white light. Arrows denote the long axes of the elongated hexagons and the direction of polarization produced by the crystals. Extinction is apparent when crystals overlap and their long axes are orthogonal to one another.

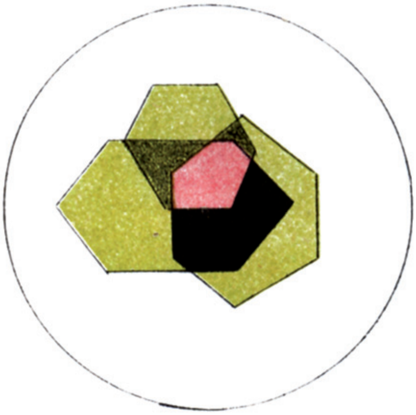

Figure A5. Three overlapping elongated hexagonal-shaped crystals viewed in transmitted unpolarized white light. Two of these are crossed at right angles, and therefore dark at their intersection. A third crystal introduced between them with its long axis at 45° to the other crystals enables light to pass through, in this case producing light of the sensitive tint (first-order red) colour. Herapath noted that this behaviour is the same as that of selenite (a colourless variety of gypsum, $CaSO_4 \cdot 2H_2O$) introduced in the same way between two tourmaline crystals at right angles to one another. Note that the overlap of the third crystal with just one of the crossed crystals produces a perceptible polarizing effect, as for the crystals shown in Figure 3.

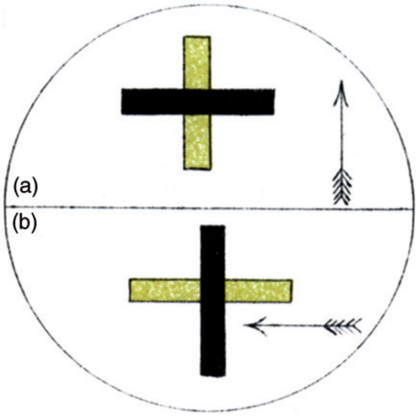

Figure A6. (a) Two crystals of herapathite crossing at right angles to one another and viewed in transmitted polarized white light produced by a tourmaline single crystal. The direction of polarization is indicated by the arrow. The crystal with its long axis parallel to the polarization direction appears olive-green, while the crystal with its long axis perpendicular to the polarization direction appears black. (b) As (a), but with the tourmaline single crystal rotated by 90° about an axis coming out of the plane of the paper. The crystal which was previously olive-green becomes black, while the one which was black now appears olive-green.

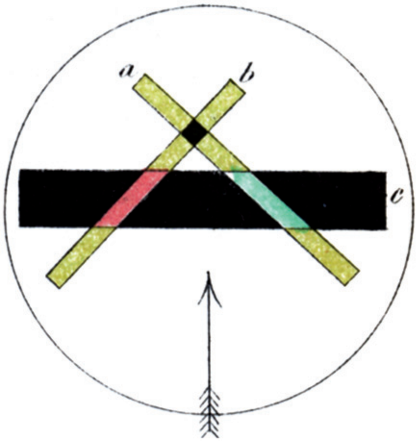

Figure A7. An arrangement of three crystals, *a*, *b* and *c*, in which *c* is below *a* and *b*, examined in polarized white light produced by a tourmaline single crystal placed over the eyepiece of the microscope. The direction of polarization is indicated by the arrow. Crystals *a* and *b* are at 45° to *c*. Where *b* and *c* overlap, a pink colour results; where *b* and *c* overlap, a green colour, complementary to the pink colour, appears. The crystals appear black where *a* and *b* overlap and where *c* is not overlain by either *a* or *b* because of the pleochroism exhibited by the herapathite crystals.

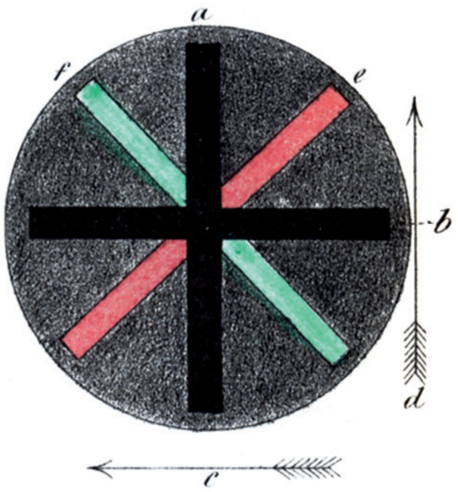

Figure A8. Herapathite crystals crossing at right angles viewed in crossed polars (in this case, crossed tourmaline crystals). The crystals both appear black when they are in orientations *a* and *b*. Rotating the crossed crystals by 45° while keeping the tourmalines stationary enables light to pass through the herapathite crystals, as shown in *e* and *f*.

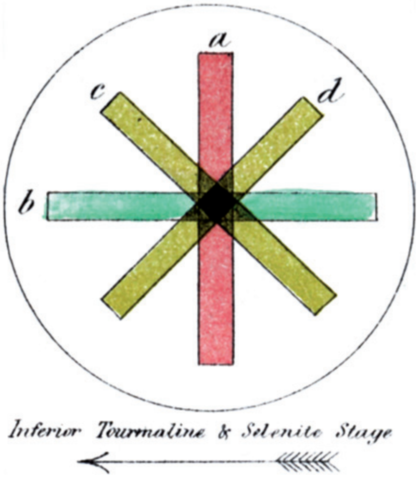

Figure A9. Observations made of herapathite crystals with a tourmaline crystal upon which there is a selenite stage which produces a pink colour (or sensitive tint colour) when viewed in crossed polars. For crystal *a*, the herapathite crystal acts as an analyzer in a polarizing microscope, and so the pink colour is seen. For crystal *b*, the herapathite crystal acts as a polarizer parallel to that of the tourmaline and so it appears green, the colour complementary to the pink colour. Crystals *c* and *d* are at 45° to the tourmaline and remain olive-green in colour.

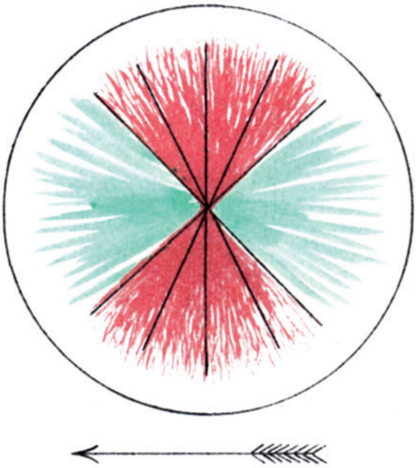

Figure A10. Tufts of cinchonine disulphate prisms placed on a pink selenite stage with a tourmaline beneath the stage. Prisms arranged at right angles to the tourmaline appear red, while those parallel to it appear the complementary green. These observations confirm that cinchonine disulphate can also act as a polarizer.

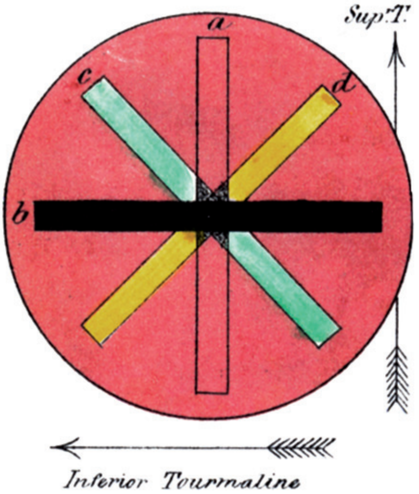

Figure A11. Herapathite crystals viewed in crossed polars with the pink selenite stage. Crystal *a* appears pink because it lets light through polarized in the same direction as the analyzer (the superior tourmaline). Crystal *b* appears dark because it only lets light through polarized perpendicular to the analyzer. Crystal *c* and *d* let light through and are complementary in colour to one another.

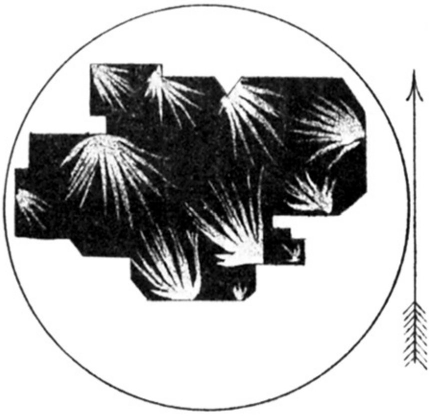

Figure A12. Plates of herapathite used as an analyzer mounted on glass on top of a herapathite crystal used as a polarizer. Quinine disulphate has precipitated on the glass in the form of radiating crystals. These crystals are anisotropic and are therefore visible between these man-made crossed polars.