

The structure of amethyst quartz and the origin of its pleochroism

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1. Introduction

By reason of the very beautiful colour which amethyst exhibits, this material has been used as a gem-stone since ancient times. Much interest therefore attaches to the problem of the origin of its colour, for a solution of which we need to know how amethyst and colourless quartz differ in respect of their structure. In the present investigation we have sought to elucidate the nature of this difference by a fact-finding study of those properties of amethyst which are calculated to throw light on its physico-chemical make-up. The results have led us to a view of the nature of amethyst which is altogether different from those which have found expression in the extensive literature of the subject, but which nevertheless appears to be both simple and natural.

2. The density of amethyst quartz

If the colour of amethyst were due to the presence of appreciable quantities of the oxides of heavy metals such as manganese or iron, as has sometimes been suggested, we may expect this to come into evidence in precise determinations of the density of the material. For such a test, it is clearly necessary to use specimens which do not exhibit visible cracks, inclusions or surface impurities. We have therefore chosen to work with selected material in the form of cut and polished gem-stones. A Sartorius analytical balance was employed and the density of each specimen was measured in the usual manner by transferring it from a cup in air to a second cup held suspended by a fine wire under water. Table 1 shows the densities thus determined of six pieces of colourless quartz, while table 2 shows the corresponding results obtained with thirteen different specimens of amethyst. Necessary corrections were made in each case for the temperature of the water and the buoyancy of air. The remarks made against each specimen in the tables indicate its optical behaviour.

Table 1. Density determinations with quartz

Description	Mass in grams	Density in grams per c.c.	Remarks
Quartz crystal with natural faces	3.9264	2.651	Very transparent and free from inclusions
—	0.595	2.650	—
Polished quartz sphere I	4.7197	2.652	A few needles inside but quite transparent
Polished quartz sphere II	3.7886	2.651	Very transparent and free from inclusions
Polished quartz sphere III	2.5042	2.653	Exhibits a weak star due to inclusions
Polished quartz sphere IV	2.4194	2.667	Exhibits a markedly diminished transparency and a bright star due to inclusions

Table 2. Density determinations with amethyst

Description	Mass in grams	Density in grams per c.c.	Remarks
Intensely coloured	2.3394	2.651	
—	1.8521	2.652	
—	1.3466	2.651	
—	1.0846	2.652	
—	0.7137	2.650	
Moderately coloured	2.2276	2.651	
—	1.4184	2.650	
—	1.2545	2.650	
Lightly coloured	3.1782	2.650	
—	1.1595	2.653	
—	1.1937	2.651	
—	1.0351	2.650	
—	0.7481	2.654	Visible inclusions

It will be evident from a comparison of the figures in the two tables that in the case of colourless quartz of the best quality, the density comes out consistently as 2.651, the uncertainty not exceeding one unit in the last decimal place. On the other hand, colourless quartz containing inclusions gives definitely higher values. The determinations for amethyst do indeed show variations in the third decimal place, but these deviations are in no way correlated with the depth of the colour exhibited by the specimen. The differences are therefore either purely experi-

mental or else arise from residual defects in the specimens which are indeed noticeable when they are critically examined under immersion in a liquid cell.

The data appearing in the two tables give no support to any explanation of the origin of the colour of amethyst as due to metallic impurities. On the other hand, *they show quite definitely that the density of amethyst quartz does not differ measurably from that of colourless quartz of optical quality.*

3. The scattering of light in amethyst

Colourless transparent quartz free from internal inclusions gives an observable scattering of a blue colour and of uniform intensity when traversed by a concentrated pencil of sunlight. But the effect is extremely weak and is observable only in favourable circumstances. Figure 1 in plate II shows a transparent crystal of quartz of optical quality immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. The track of the beam in the liquid appears in the photograph, but the track within the crystal is hardly to be seen by reason of its extreme weakness.

Figure 2 in the same plate shows a similar experiment with a crystal of smoky quartz immersed in a cell containing distilled water. It will be noticed that the Tyndall track within the crystal is conspicuously observable.

Figure 3 in the same plate is a photograph of a crystal of amethyst quartz immersed in carbon tetrachloride. The track of the beam in the liquid both before entry into the crystal and after emergence from it is very conspicuous. Within the crystal itself, there are two regions adjoining its rhombohedral faces in which no track is visible. These regions are precisely those which exhibit the amethystine colour, while the region midway between them exhibits a conspicuous Tyndall effect which is due to inclusions present in this colourless part of the quartz. The crystal had a density of 2.563, which is slightly higher than that of pure quartz, thus indicating the presence of such inclusions.

Figure 4 in the same plate is a photograph of a cut gem of amethyst immersed in a cell containing carbon tetrachloride and traversed by a beam of sunlight. Here again, the track of the beam is totally invisible within the crystal.

Visual observations with all the specimens of amethyst listed in table 2 yielded the same result. Hence we conclude as follows: *amethyst quartz does not exhibit the Tyndall scattering so conspicuously observable in the case of smoky quartz; its behaviour in this respect is comparable with that of colourless transparent quartz.*

4. X-ray diffraction studies

The experimental facts set forth in the two preceding sections appear very significant. It seems difficult to reconcile them with any explanation of the colour

of amethyst as due to impurity material present in a colloidal or even in a molecularly dispersed form. Nor does it appear easy to reconcile them with an attribution of the colour to defects or imperfections of crystal structure or to a stoichiometric deficiency or excess of either silicon or oxygen in the lattice. On the other hand, they fit in perfectly with the hypothesis that amethyst is a crystalline material very similar to colourless quartz but with a different electronic configuration. Such configuration might well belong to a lower symmetry class than that of α -quartz, and this would immediately account for the fact that amethyst is optically biaxial whereas colourless quartz is uniaxial. A different electronic configuration belonging to a lower symmetry type would necessarily involve an alteration in the electronic energy levels and hence also to an altered absorption spectrum. The pleochroism and the optical characters of amethyst would thus both find a natural explanation on the present view of its structure.

It is evident from the foregoing that a thorough study of the pleochroism of amethyst and of its absorption spectra should prove useful in dealing with the problem of its structure. Such a study has been carried out at this Institute by Mr S Pancharatnam and his results are reported in the paper following the present one in the same issue of the *Proceedings*. We shall not traverse the same field here but will proceed to describe the results of an entirely different technique for investigating the problem under issue.

If colourless quartz and amethyst differ in their electronic configurations, comparative X-ray diffraction studies may be expected to reveal the existence of such differences and even to indicate their nature and magnitude. In view of the near resemblance between the two structures, it appeared unlikely that the usual methods of X-ray structure determination would prove useful in this connection. We have therefore chosen to adopt a different technique which we shall now proceed to describe and which is based upon certain well-known facts regarding amethystine quartz.

A section plate of amethyst cut in any arbitrary direction often exhibits a variety of features. Commonly noticeable is the appearance of bands of colour alternating with clear quartz running parallel to the intersection of a rhombohedral face of the crystal with the surface of the section plate. Sectors exhibiting different colours are also noticeable on section plates cut obliquely to the trigonal axis of quartz. Thus, if a pencil of X-rays traverses such a section plate, the material over different parts of the area should exhibit differences in the X-ray reflection intensities corresponding to the optically observable features on the plate. In this connection, however, some important remarks are necessary. As is well known, any mosaicity or imperfection in crystal structure would reveal itself in a general increase in the intensity of X-ray reflection. Hence, what we have to look for in the present case is not an enhancement of reflection intensity corresponding to the areas of colour on the plate, but differences in X-ray reflection intensity which vary with the particular crystal planes giving the

reflections and hence connote real differences in crystal structure in the different areas on the plate.

It has also to be remarked that quartz often exhibits internal twinning. If such twinning be of the electrical type, areas on the plate in which the electric axis is oppositely orientated would, in general, give different X-ray reflection intensities. Hence it is essential to work with section plates in which electrical twinning is absent.

5. Technique and results of study

A plate about 1 millimetre thick and about 2 cm by 1.5 cm in areas was cut out from a large clear crystal of amethyst. The plate exhibited both the bands and sectors of colour described earlier. By fine grinding the surfaces of the plate and then etching with dilute hydrofluoric acid and examining them under a spot-light, it was verified that the area on the plate chosen for the study and which exhibited the bands and sectors of colour was completely free from both optical and electrical twinning. The absence of optical twinning was also independently verified by an examination of the plate between crossed polaroids when immersed in a cell containing benzyl alcohol which has very nearly the same refractive index as quartz.

The X-radiation from a rotating target tube run at 50 mA and 60 kV emerged through a 1 millimetre hole and was allowed to diverge until the area of the crystal plate was completely bathed by the beam at a distance of about 40 cm. A photographic film was placed at a distance of about 10 cm behind the crystal plate. This distance was found to be sufficient to avoid overlapping of the Laue reflections which in these circumstances are necessarily of rather large size. In effect, each Laue spot recorded on the photographic film presents a picture of the irradiated area of the crystal.

Figure 1 in plate I is a reproduction of the larger part of a Laue diagram obtained in the manner described above. At the centre of the picture has been placed in its correct orientation a photograph taken by transmitted sodium light of the area of the crystal plate actually employed in X-ray diffraction. It will be seen that the plate exhibits a set of parallel bands towards the left, while at its centre and towards the right appear a pattern of sectors which by ordinary daylight exhibit the different colours indicative of their pleochroism. Fainter bands are also visible towards the upper right-hand corner.

On a scrutiny of the pictures of the crystal appearing in the figure as Laue reflections, the following features emerge. All the pictures exhibit varying degrees of distortion, but this does not prevent us from comparing them with the optical picture of the crystal appearing at the centre of the figure. The latter, it should be mentioned, has been slightly enlarged to make the comparisons easier. Two irregular bright streaks appear in all the pictures; these arise from defects in the

crystal which were readily visible on a direct examination and are irrelevant for our present purpose. Some of the stronger Laue reflections exhibiting significant features have been numbered as a series from 1 to 9 for convenience of reference. Number 1 shows prominently the set of parallel bands appearing on the left of the crystal plate. The same bands can be seen faintly in some others of the numbered spots but are invisible in no. 6. The large sector appearing at the centre of the plate presents very different aspects in the different spots. Compare, for example, nos. 2, 3, 6, 8 and 9. The complex pattern of sectors on the lower right of the specimen can be made out in several of the pictures but presents altogether different aspects in them. Compare for example, nos. 3 and 8. The bands seen in the upper right-hand corner of the crystal are very conspicuous in nos. 2 and 3 but are weak in nos. 6 and 9. The record thus clearly establishes that amethyst is a crystalline solid which gives coherent X-ray reflections, the intensities of which differ from those of colourless quartz and are also different for areas exhibiting different colours by transmitted light. A correlation is thus established between the pleochroism of amethyst on one hand and its crystal structure on the other hand.

6. Acknowledgement

We wish to take the opportunity of expressing our gratitude to Sir Purshotamdas Thakurdas for his generous gift of the rotating-target X-ray set manufactured by Messrs. Newton-Victor which has been used in the present investigation.

7. Summary

Comparative measurements with clear quartz and amethyst show conclusively that these two materials do not differ measurably in their density. Amethyst and clear quartz also resemble each other in not giving any Tyndall effect of the kind so conspicuously observable with smoky quartz. These facts indicate that amethyst is a crystalline material very similar to colourless quartz in its make-up, but with a different electronic configuration belonging to a lower symmetry class. The optical biaxiality and the pleochroism of amethyst then follow as natural consequences. This view of the nature of amethyst is confirmed by X-ray diffraction studies made with a section plate of amethyst free from internal twinning but exhibiting colour bands and colour sectors over its area.

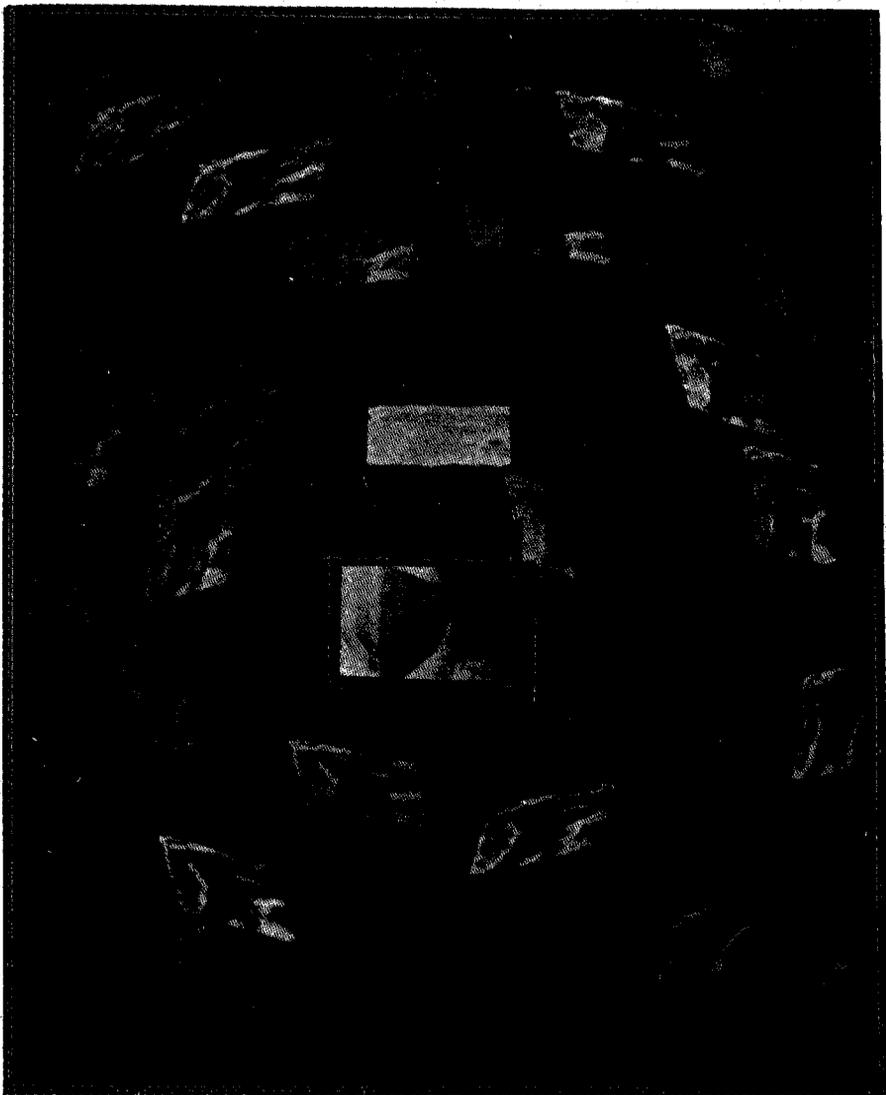
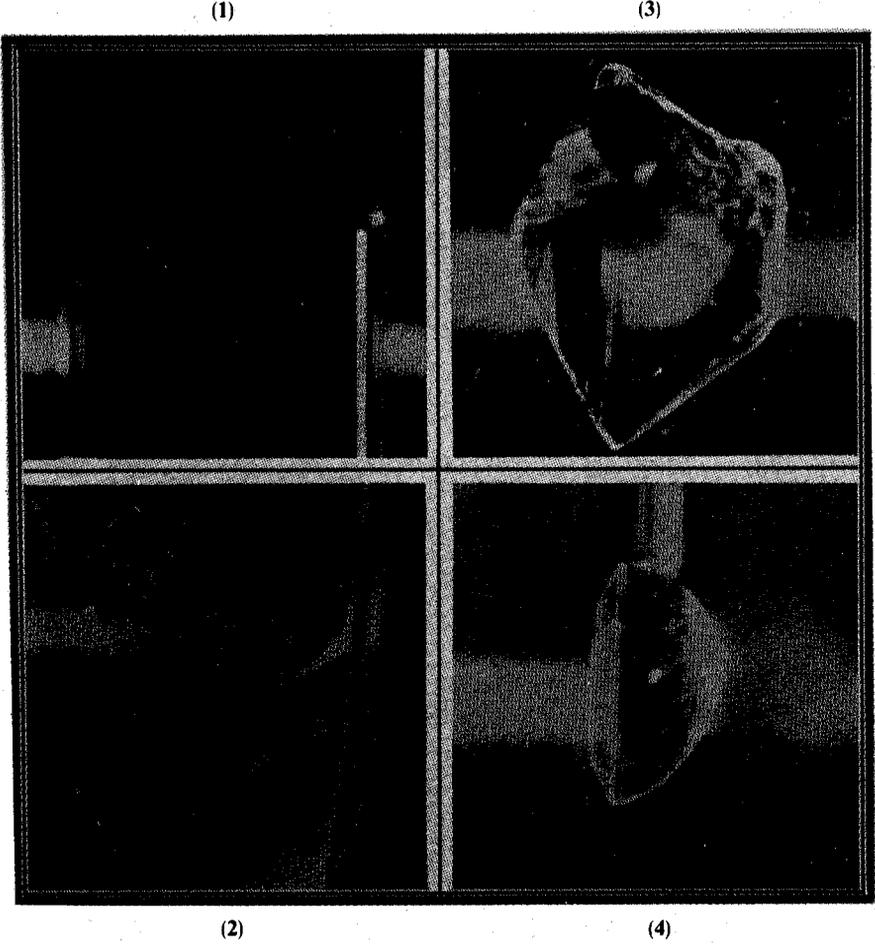


Figure 1. Laue pattern of amethyst section plate.

Plate I



Figures 1-4. Scattering of light in clear quartz, amethyst and smoky quartz.

Plate II