THE OPTICAL ANISOTROPY AND HETEROGENEITY OF VITREOUS SILICA

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1. Introduction

Vitreous silica is a remarkable and most useful material and the investigation of its structure and properties is therefore of much interest. As it is an amorphous solid, one would naturally expect its optical behaviour to be that of an isotropic medium. Actually, however, a polished plate of vitreous silica when interposed in the path of a beam of light between a polariser and an analyser set in the position for extinction always gives rise to an observable restoration of light, as was remarked long ago by Rayleigh (1920). A characteristic feature of the phenomenon is that the restoration of light is not uniform over the surface of the plate. This effect is particularly striking in the case of the disks of the so-called optical silica which are built up by a special process. These exhibit a birefringence pattern of concentric circles, evidently connected with the way in which the material had been fabricated (Fig. 10 in Plate IX).

The present paper describes the results of a re-examination of the behaviour of vitreous silica referred to above, undertaken with a view to elucidate the nature and origin of the phenomenon. The material available for the study included several specimens of the silica glass collected by Dr. L. J. Spencer in the Sand Sea of the Libyan desert in December 1934 and very generously presented to the author during a visit to his London home in 1948. The examination of the specimens of this naturally occurring substance has yielded highly significant results. Numerous examples of the commercially available material have also been examined. These included circular discs of different thicknesses and diameters, two belonging to this Institute and several others very kindly loaned for the study by Prof. R. S. Krishnan. Two silica rods with different forms of cross-section which were presented to the author by Messrs. Adair Dutt of Madras have also been studied.

Large Nicols, such as those used by Rayleigh in his investigation, were not available. But polaroids three inches square in area serve the same purpose admirably. Except in the case of disks having polished faces, it is useful and indeed generally necessary to immerse the specimen under study in a flat-sided trough filled with xylene or carbon tetrachloride. The use of a light source of adequate intensity is essential. Indeed, the most satisfactory way of examining any specimen is to view it when traversed by a direct beam of sunlight with the arrangements described above.

Since the optical anisotropy exhibited by vitreous silica exhibits local variations, it follows that the material is optically heterogeneous. This may be readily demonstrated without the use of polarised light by merely holding a polished disk of vitreous silica in the path of a beam of light diverging from a brilliant source of light of small area. The light which has traversed the disk when received on a screen placed at a suitable distance is found to exhibit a pattern of light and shade bearing a recognisable relationship to the features exhibited by the same specimen between crossed polaroids.

2. OBSERVATIONS WITH NATURAL SILICA GLASS

A remarkable occurrence of vitreous silica scattered over an extensive area in the Libyan desert was reported in a paper by Clayton and Spencer (1934). Further details appeared in a later memoir by Spencer (1939). The material has a pale greenish-yellow colour and some of the specimens are clear and transparent. Chemical analysis shows the mineral to be nearly pure silica, SiO_2 making up 97½% while the rest consists of various metallic oxides. The five specimens gifted to the author by Dr. Spencer from his collection are fully representative of the Libyan occurrence and show the various characters described and illustrated in the paper by Clayton and Spencer. Two of them, though interesting in themselves, contain numerous inclusions and are therefore not suited for the present investigation. The three others when immersed in a trough containing xylene or carbon tetrachloride and placed between crossed polaroids exhibit some striking effects which are illustrated in Figs. 1, 2 and 5 of Plate VIII. Streaks or sheets of luminosity are observed traversing the interior of the glass: there are several such in each specimen, and they run parallel to each other in a direction coinciding more or less exactly with that of the longest dimension of the piece. The luminosity attains its maximum intensity when the specimen is so set that the bright streaks or sheets bisect the angle between the principal planes of the two polaroids. As is to be expected in these circumstances, they disappear when set so as to lie in either of these two planes, the whole of the specimen then appearing more or less perfectly dark.

The photographs reproduced as Figs. 1, 2 and 5 in Plate VIII were recorded with the specimen in each case set so that the luminous streaks or sheets are of maximum intensity: they are seen in the figures running diagonally. The effect was particularly conspicuous with the specimen represented in Fig. 5 which was very clear and transparent: the trough used was unfortunately not large enough to hold the entire piece, otherwise the effects would have shown up much better in the photograph. The specimens illustrated in Figs. 1 and 2 in Plate VIII are distinctly cloudy but nevertheless show the phenomenon clearly enough.

3. OBSERVATIONS WITH TRANSPARENT SILICA RODS

The two rods studied are shown diagrammatically as Figs. 1 and 2 below in the text. The rod illustrated in Fig. 1 has a cylindrical cross-section with a flange added at one end as shown. The second rod has a flattened cross-section and is bent in its own plane into a curve towards the end as shown in Fig. 2.

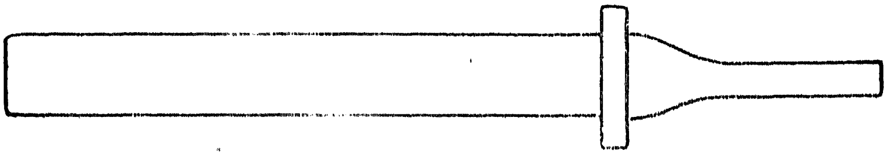


FIG. 1

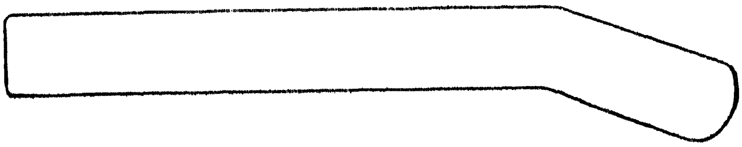


FIG. 2

Examination of the cylindrical rod when immersed in carbon tetrachloride and placed between crossed polaroids shows a birefringence pattern exhibiting a great number of lines or fibres running more or less exactly parallel to the axis of the rod (Fig. 8 in Plate IX). This effect is most conspicuous when the axis of the rod is inclined at 45° to the planes of vibration of the two polaroids and vanishes completely when it is set parallel to either of these planes. In the vicinity of the flange and up to some distance on either side of it, however, a different effect is simultaneously observed. This is of much greater intensity and may be isolated by setting the rod either vertical or horizontal; the fibrous structure then ceases to be visible and the restoration of light shows the continous variation of intensity characteristic of a photoelastic pattern. The second effect thus evidently arises from a distribution of permanent stresses existing in the vicinity of the flange. When, however, the rod is set in an inclined position, both types of birefringence—structual as well as stress-optical—appear simultaneously, and they are superposed on each other. Some very curious features are observed when a fibre-line crosses a dark band of the stress-optical pattern.

The bent rod illustrated in Fig. 2 also exhibits a structural birefringence pattern, consisting of fine fibres running parallel to the axis of the rod and bending round towards the end so as to follow its curvature. There are indications that there exists simultaneously a stress-optical birefringence, as the result of the superposition of which the structural birefringence is seen more weakly at some parts of the cross-section than at others. A similar effect is also apparent in the case of the cylindrical rod (Fig. 8 in Plate IX).

4. OBSERVATIONS WITH TRANSPARENT SILICA DISKS

Reference has already been made above to the behaviour of disks of the so-called "optical silica" built up in a particular manner which show a birefringence pattern consisting of concentric circles. The behaviour of one such disk, 4 centimetres in diameter and 8 millimetres thick, when viewed normally to itself between crossed polaroids, is illustrated in Fig. 10, Plate IX. It will be noticed that the black cross seen in the pattern cutting across the circular rings is somewhat distorted in the vicinity of the centre; when the disk is rotated in its own plane, the cross shifts about a little, showing that the structure giving rise to the observed pattern is not perfectly centro-symmetric. The disk may also be viewed *edgewise* along a diameter, its plane making any desired angle with the principal planes of the polaroids: the restoration of light then observed is very feeble if the plane of the disk is set parallel to either of them, and quite strong if set at an angle of 45° with either of them. We shall return later to the question of the interpretation of the effects observed with this disk, but will here draw attention to a remarkable feature observed in Fig. 10 in Plate IX, namely the sharp definition of the boundaries between the dark and bright areas in the pattern.

Two other disks included in the present study also show a black cross when viewed normally between crossed polaroids, but they are of the so-called " ordinary " silica, and the observed characters of the birefringence are quite different (see Fig. 6 in Plate VIII, and Fig. 12 in Plate IX). In both of these cases, the field of light in the space between the arms of the black cross consists of a criss-cross pattern of streaks intersecting each other: the general directions of the two set of streaks are respectively along the two diagonals making an angle of 45° with the arms of the black cross, as is particularly clear in Fig. 6, Plate VIII, but not so clear in Fig. 12 in Plate IX, the black cross being also a little hazy in that figure.

Figs. 7, 9 and 11 in Plate IX reproduce photographs of still another disk viewed normally to itself between crossed polaroids, the three figures representing three different settings of the disk *in its own plane.* It will be noticed that this disk does not exhibit a black cross, and that its appearance is altogether different in the three settings. In Fig. 7, we see that the streaks seen on the disk run only along one diagonal, in Fig. 9 they run only along the other diagonal, while in Fig. 11 a few patches appear exhibiting a criss-cross pattern with streaks running along both diagonals and intersecting each other. The remarkable difference between the behaviour of this disk and those of the two others—which show a black cross and a criss-cross pattern of streaks all over in every setting—is evidently related to the fact that it is a thin disk, being only 2 millimetres thick, while the other two disks are 13 millimetres and 4 millimetres thick respectively. This explanation is supported by the results of an examination of the thickest of the three disks *viewed edgewise along a diameter.* Such examination immediately reveals in it the presence of a great many birefringent streaks parallel to the surface of the disk (Fig. 4 in Plate VIII): these are equally conspicuous in all settings of the disk in its own plane, and thus effectively form birefringent layers or sheets within the disk parallel to its faces. They appear most brilliantly when the plane of the disk is set at 45° to the principal planes of the polaroids, but continue to be visible over a very considerable range of settings of the disk on either side of this position and disappear only when the disk is parallel to one or other of the two planes. In the latter position, streaks may be seen running in directions inclined to the surface of the disk, but they are much fainter (see Fig. 3 in Plate VIII).

In Fig. 6, Plate VIII, one notices that towards the edge of this disk, the criss-cross structure of the birefringence is apparently replaced by a somewhat brighter continuum. The explanation of this effect has been investigated by immersing the disk in a trough of liquid and viewing it *edgewise* between crossed polaroids. Such an examination revealed that the structure of the disk is effectively modified near the cylindrical edge by the fire-polishing to which the latter had apparently been submitted. A feeble photo-elastic birefringence is also visible near the edges by reason of the disk having been sawn through to form its faces. The other two disks do not show this effect: they have polished faces and ground edges.

5. INTERPRETATION OF THE FACTS

Before we proceed to consider the explanation of the facts brought to light by the present investigation, it may be useful briefly to comment on the opinions expressed by Rayleigh regarding the nature of the effects noticed by him. From certain evidence detailed in his paper, he came to the conclusion that the birefringence pattern of concentric circles shown by the built-up silica disks was a stress-optical phenomenon. On the other hand, the birefringence exhibited by the silica disks of the ordinary variety was ascribed by him to a crystalline granular structure of the vitreous silica which he thought might have been derived from the quartz from which it is obtained by fusion. He believed also that when the silica is fused and drawn out into rods, these same crystalline granules persist but are elongated into fibres.

With regard to the above-mentioned suggestions of Rayleigh, we may remark that theoretical considerations make it extremely difficult to accept them as probable or even possible. As is well known, the formation of vitreous silica from crystalline quartz is attended by a notable diminution in density from 2·65 to 2·20, and is accompanied by a sharp drop of the refractive index to 1·458 for vitreous silica from the much higher values 1·544–1·553 characteristic of quartz. There is simultaneously a fundamental change in structure, as is shown directly by X-ray studies, and is indicated also by the remarkable changes in physical properties, notably the drop in the thermal expansion coefficient from 34×10^{-6} to $1 \cdot 3 \times 10^{-6}$. Moreover, in the range of temperature 1470°–1710° immediately preceding that of fusion, the stable crystalline form of silica is not quartz but high-cristobalite, which is an optically isotropic material. It is also known that when vitreous silica devitrifies, the product is not quartz but cristobalite. In view of all these facts, one could scarcely suppose that any trace either of the crystalline structure or of the birefringence of quartz could survive in the molten liquid obtained by its fusion and be carried over to the glass formed on solidification.

We may also remark that it was the criss-cross structure of the birefringence patterns exhibited by fairly thick disks of the ordinary silica which led Rayleigh to his hypothesis of a granular structure for vitreous silica in the mass. Actually, however, as shown by the present investigation, patterns of this type represent merely the integrated optical effect of the passage of the light through the many birefringent layers present in a thick disk. Figs. 7 and 9 in Plate IX show that even in a disk 2 millimeters thick, the birefringence pattern takes the form of elongated streaks and *not* of a criss-cross pattern. The facts of observation thus lend no support to the postulated existence of crystalline granules having an average dimension of half millimetre in vitreous silica.

We are thus forced to seek for an alternative explanation of the observed phenomena. It is useful to consider the problem in two stages. The first is the purely phenomenological approach to the facts. The various observations described in the present paper make it perfectly clear that in vitreous silica, two kinds of "accidental birefringence" are possible. The first kind is the well-known type of birefringence which is observed in a stressed isotropic solid. If such birefringence is observed in a specimen not subjected externally to any stress, we have necessarily to assume that it arises from an internally compensated system of stresses. How such stresses are set up and persist is a question the answer to which depends on the previous thermal and mechanical history of the specimen. It may be remarked that the thermal expansion coefficient of vitreous silica is extremely small even at high temperatures. From this, it follows, and indeed is actually the case, that the photo-elastic effects arising from an unequal heating of a specimen would be small. One may therefore reasonably assume that though stresses arising from "imperfect annealing" may arise in vitreous silica, as in other types of glass, they would not be so large as to overshadow any other possible kind of effect. This leads us naturally to the recognition of a second kind of "accidental birefringence" in vitreous silca—and presumably therefore also in other amorphous solids—of a "structural birefringence" also arising from the previous thermal and mechanical history of the specimen. The distinction between this and the other is indicated by its name, *viz*., that we are concerned *not* with the elastic deformations of an isotropic medium and the optical consequences thereof, but with changes of the ultimate structure of the substance itself resulting in its becoming birefringent. Accepting such a possibility, we see at once that the phenomena brought to light by the present investigation, both in natural silica glass and in the material prepared artificially, find a natural explanation. Indeed it would be difficult to find any other explanation, since their general character definitely excludes an interpretation of them as stress-optical birefringence of the familiar variety.

6. ORIGIN OF THE STRUCTURAL BIREFRINGENCE IN VITREOUS SILICA

As is well known, viscous liquids when stirred exhibit a temporary birefringence which disappears more or less quickly with time. A theory of this phenomena connecting it with the linear dimensions and optical characters of the molecules of the fluid and with its viscosity was given long ago by the present writer and K. S. Krishnan (1928). The case of vitreous silica is rather different from that of the organic compounds with discrete molecules considered in that paper. We may indeed recognize the presence in vitreous silica of a fundamental building unit, *viz*., a silicon atom surrounded tetrahedrally by four oxygen atoms. But such a unit cannot be regarded as capable of moving or rotating independently of the neighbouring units of the same kind. Indeed, in the solid, the units would be firmly bound to each other at the corners by the sharing of the oxygen atoms. Free mobility of the units in the molten or liquid state would require the breaking and reforming of vast arrays of such bonds. It is this circumstance which distinguishes the behaviour of vitreous silica in the fluid state from that of ordinary liquids composed of discrete molecules bound to each other by comparatively weak forces. Given sufficient time and favourable circumstances, one may expect to find that in the molten silica the building units link themselves in such manner as to become effectively an optically isotropic structure. Such a liquid on solidification would be optically non-birefringent. But that in any actual set of circumstances, and especially when the molten liquid is subject to any type of mechanical disturbance, it is unlikely that such an ideal state would be actually reached or that it would be exhibited in the finally resulting glass. The fashioning of a glass necessarily involves the manipulation of the material in a semi-molten state into the particular form desired. Any such operation would necessarily bring into action the tendency of the bonds connecting the silicon atoms with the oxygen atoms to resist disruption, and for the units to take up new positions by shifting the directions of the bonds rather than by their disruption and reformation. The formation of optically birefringent streaks or sheets in the medium would be a natural consequence.

The foregoing is of course only a general and qualitative picture. But it appears to afford a reasonable explanation of the special type of irregular or accidental birefringence of an obviously structural character exhibited by vitreous silica, and especially of the relationship between the optical characters of the birefringence and the geometric form of the specimen under examination which emerges from the actual facts of observation.

The photographs accompanying this paper were obtained by Mr. J. Padmanabhan, whose efficient assistance I have much pleasure in acknowledging.

SUMMARY

The paper describes the birefringence exhibited by vitreous silica, both in the naturally occurring material found in the Libyan desert and in the commercially available material in the forms of rods and disks. The facts revealed by the investigation are discussed. It is shown that Rayleigh's belief that vitreous silica in the mass has a crystalline granular structure cannot be sustained. It is shown further that, besides the familiar stress-optical birefringence, a second kind of effect, *viz.*, "structural birefringence" is also possible in amorphous solids and that this is particularly prominent in vitreous silica for reasons which are discussed.

12 photographs illustrate the paper.

REFERENCES

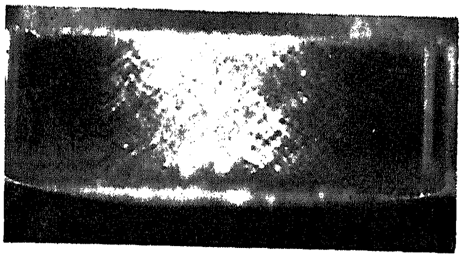
(*In Chronological Order*)

Rayleigh	.. *Proc. Roy. Soc.*, A, 1920, **98**, 284.
Raman and Krishnan	.. *Phil. Mag.*, 1928, **5**, 769.
Clayton and Spencer	.. *Mineral Mag.*, 1934, **23**, 501.
Spencer	.. *Ibid.*, 1939, **25**, 432.

FIG. 1

FIG. 2

FIG. 3



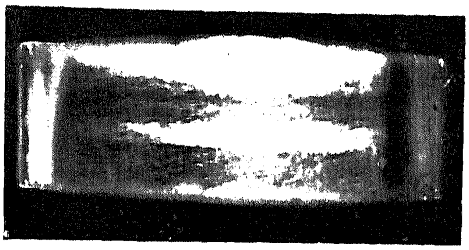


FIG. 4

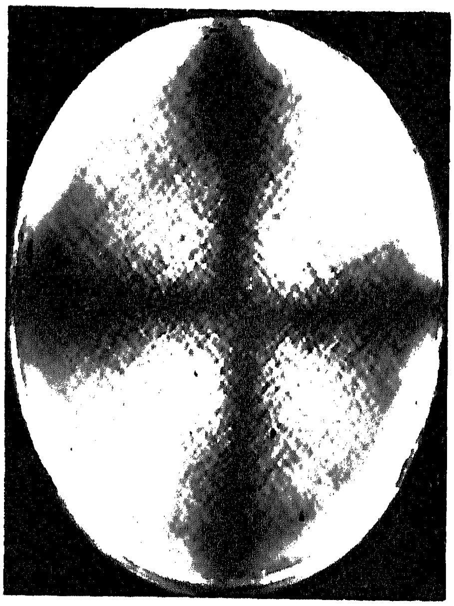


FIG. 7

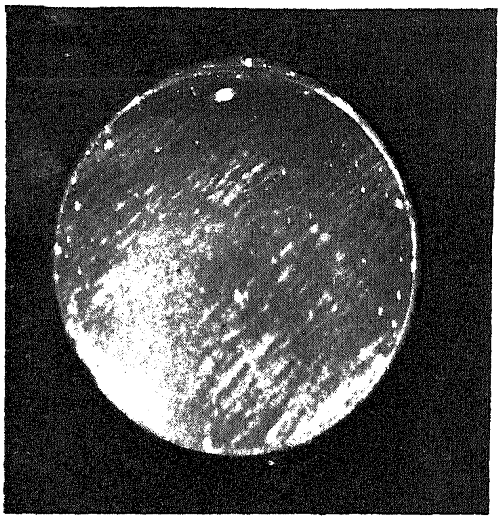


FIG. 8

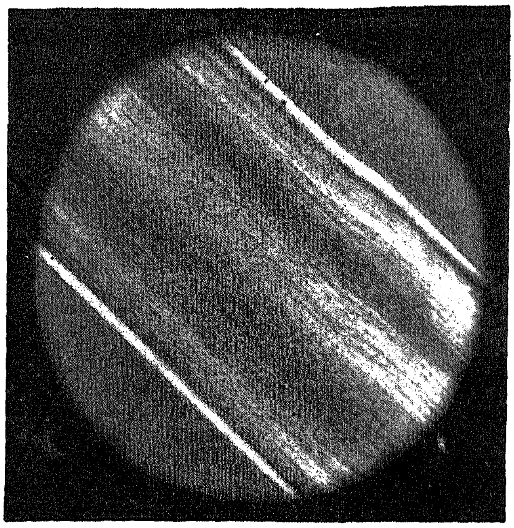


FIG. 9

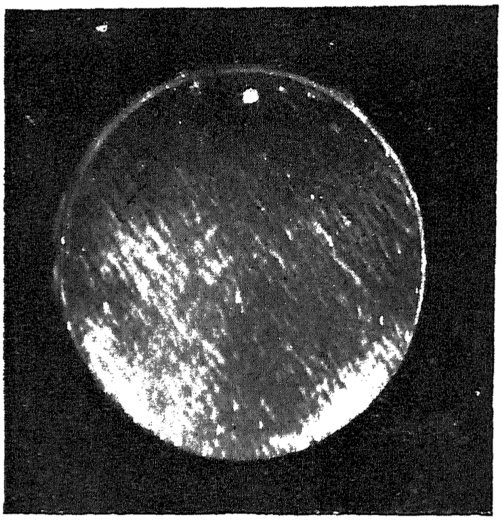


FIG. 10