*Proc. Indian Acad. Sci.* **A31** 207–212 (1950)

# Structural birefringence in amorphous solids

SIR C V RAMAN
(Raman Research Institute, Bangalore)

Received April 18, 1950

## 1. Introduction

The birefringence exhibited by optically isotropic solids when deformed by stress is familiar knowledge and forms the theme of the subject of photo-elasticity. There exists, however, a second kind of birefringence which may also be exhibited by amorphous solids and which differs both in its origins and in its observable characters from the photo-elastic effect. To distinguish it from the latter phenomenon, it has been designated as structural birefringence (Raman 1950). The name is intended to convey the idea that such birefringence owes its origin to anisotropy of structure existing even when the material is free from stress. Such anisotropy is, of course, not a normal property of the material as in the case of crystals, but is "accidental" in the sense that it is a consequence of special circumstances existing during the formation of the solid. The recognition of such birefringence as a distinct phenomenon is compelled by a study of the facts observed with vitreous silica and described in the paper cited. Structural birefringence in the case of this substance manifests itself as streaks or sheets of luminosity—inexplicable on the basis of photo-elastic theory—which are clearly the result of flow in the material while in a plastic state before its final solidification.

The present paper describes similar studies made with other materials and especially with the inorganic glasses. The results show unequivocally that structural birefringence is also exhibited by such glasses, either by itself or in conjunction with the photo-elastic effect. As is well known, the process known as "annealing" is an essential part of the technique of glass manufacture. Its purpose is to remove the internal stresses set up in the fabricated material by differential rates of cooling of its parts, and the test applied to determine whether this has been accomplished is the disappearance of birefringence. Except, however, in the case of high-grade optical glass where special techniques are employed to obtain a perfectly homogeneous and isotropic product, the process of annealing never actually succeeds in removing all observable birefringence. Indeed, the commoner commercial varieties of glass exhibit, when critically examined, an easily noticeable birefringence. It is with this phenomenon that we are concerned in the present paper.

As already noted in the paper on vitreous silica, the detection and study of a feeble birefringence needs the use of a light source of adequate intensity. The most satisfactory method is to place the object under examination between two crossed polaroid sheets, and send a beam of sunlight through it. For observation or photography of a large area of the object at one time, it will be necessary to diffuse the incident light beam by a sheet of ground glass. As polaroid sheets are available up to twelve inches square in area, quite large objects can be examined in this way. It is necessary that the surfaces of the object through which the light enters and emerges are flat and parallel. This requirement may be avoided by immersing the object in a flat-sided cell containing a liquid of suitable refractive index. But this naturally restricts the size of the objects which can be examined.

## 2. The birefringence of plate glass

Common glass is produced commercially on a large scale in the form of sheets or plates of any desired thickness. The process of the manufacture and the annealing of the product are both so highly perfected that a sheet of quarter-inch plate glass when held normally between crossed polaroids usually shows no noticeable restoration of light. One might be tempted to infer from such an observation that the material is optically isotropic. Actually however, this is not the case, as becomes apparent when the plate is set and viewed edgewise between crossed polaroids, the light traversing the material in a direction parallel to its surfaces. A strong restoration of light is then noticed; this is a maximum when the plate is inclined at an angle of 45° to the principal planes of the polariser and analyser but, as is to be expected, vanishes when the plate is set parallel to either of these planes. The origin of the birefringence becomes evident when the edge of the plate is viewed through a magnifying lens in the circumstances stated. It is then seen that the entire thickness is made up of a great many laminae parallel to the surfaces of the plate overlying each other (see plate III). To see the laminae clearly, it is necessary that they should be viewed in a direction accurately parallel to the surfaces of the plate; further, as already remarked, the edges through which the light enters and emerges should be flat and parallel. (Alternatively, the observations may be made with the plate immersed in a flat-sided cell containing xylene). The fact that the individual laminae are birefringent and in varying degrees is evident from the varying intensity of the restoration of light that they produce. The same may also be very elegantly exhibited by superimposing a quartz wedge on the edge of the plate; the straight fringes due to the wedge run at right angles to the plate and appear above and below it, while the fringes due to the combination of the wedge and the plate appear in the central strip. The course of the latter fringes then displays the birefringence of the individual laminae very clearly (see plate III).

The foregoing descriptions refer to the phenomena exhibited by a strip of plate glass at a sufficient distance from its free edges. At and near these free edges, however, we observe a restoration of light which is a distinct phenomenon, as is shown by its being most conspicuous when the strip is held in such a position (parallel to the principal plane of either the polariser or the analyser) in which the structural birefringence vanishes; it is evidently a photo-elastic birefringence produced by the stresses set up in the vicinity of the edges of the strip when it is cut. If the strip be inclined so as to restore the visibility of the structural birefringence, we notice a superposition of the two effects in the vicinity of the edges. Such superposition and the special features arising from it are particularly conspicuous when the plate under observation is thick, and its length is also not much greater than its thickness. A characteristic effect noticed is that a lamina which appears as a bright streak on one side of the plate changes over to a dark streak on the other side as it crosses a dark band of the photo-elastic pattern, and *vice versa*. Several examples of this effect are to be seen in the figures reproduced in plate IV.

It should be mentioned here that if the edges of a thick plate of glass are smoothed and polished, its laminated structure may be observed even without the aid of polarised light, by merely viewing the plate in a direction accurately parallel to its surfaces. The individual laminae are then clearly visible, but they disappear if the plate be slightly tilted. If a narrow illuminated slit is observed through the edge of the plate, the laminated structure gives rise to various interesting optical effects ascribable to reflection and diffraction. These vary rapidly when the direction of the light rays traversing the plate is altered with reference to the plane of the laminations. To describe or discuss these effects in any detail would take us far beyond the scope of the present paper.

It seems fairly obvious that the laminated anisotropic structure of plate glass revealed by its optical behaviour is a consequence of the process employed in its manufacture. The molten glass emerges from the container in the furnace and passes between the forming rollers while it is still in a plastic condition and becomes a sheet which moves on continuously until it finally sets and becomes solid. It is scarcely to be supposed that a sheet of glass formed under these dynamic conditions would possess the isotropic structure which is the ideal state of an amorphous solid. It appears much more probable that the movement of the layers of the material with respect to each other would result in the final product having a laminated structure, as is actually observed. The thickness of the laminae would presumably be determined by the plasticity of the material and the speed of its passage through the rollers, as well as by their distance apart.

## 3. The birefringence of moulded glass

The process employed for the mass production of objects of glass having a desired form is to use moulds. The glass is poured into the mould while in the fluid state and removed from it when it has solidified. Examination in polarised light of glass formed in this manner shows that the birefringence pattern which it exhibits bears a readily recognisable relationship to the geometric shape of the object. For instance, a circular disk of glass when viewed normally between crossed polaroids shows a dark cross which remains fixed when the disk is rotated in its own plane, the arms of the cross lying in the principal planes of the polariser and the analyser; the disk also exhibits a strong birefringence when held at an angle of 45° to these planes and viewed edgewise. A cube of moulded glass exhibits cubic symmetry in its birefringence, the pattern observed being the same whichever be the pair of faces through which it is viewed: the black cross seen is parallel to the edges of the cube in one symmetrical setting and to the face-diameters in another symmetrical setting, while in intermediate positions, the dark band seen takes the form of a swastika, the arms of which start at the face-centres and end at the face-corners. An equilateral prism of glass viewed through its end-faces shows trigonal symmetry in its optical behaviour; the birefringence pattern varies with the setting of the prism but repeats itself at regular intervals when the prism is rotated as required by such symmetry. Spheres and spheroids of moulded glass likewise exhibit the symmetry of their respective forms in their behaviour in respect of birefringence.

The foregoing statements, however, require to be qualified in an important respect. In every case, the geometric patterns implied by these descriptions are modified by the superimposition of a "structural birefringence" pattern. This consists of bright streaks traversing the glass block, their form and distribution bearing a recognizable relation to the shape of the block and being strongly suggestive of the shape of the flow lines of a viscous liquid enclosed within the walls of a mould of the concerned geometric shape (see plate I). The structural birefringence in common glass has thus evidently a similar origin to that observed in the case of vitreous silica. The similarity of behaviour is even more vividly indicated by the photograph reproduced as plate II, which shows one of the flat walls of a large glass trough as viewed through a crossed pair of 6″ polaroids placed on either side of it.

The photographs reproduced in plates I, II and III accompanying this paper were obtained by Mr J Padmanabhan, whose excellent assistance in the investigation, I have much pleasure in acknowledging. Plate IV is reproduced from material obtained during an unpublished research by Mr Bawa Kanwal Singh, made at the author's suggestion.

## Summary

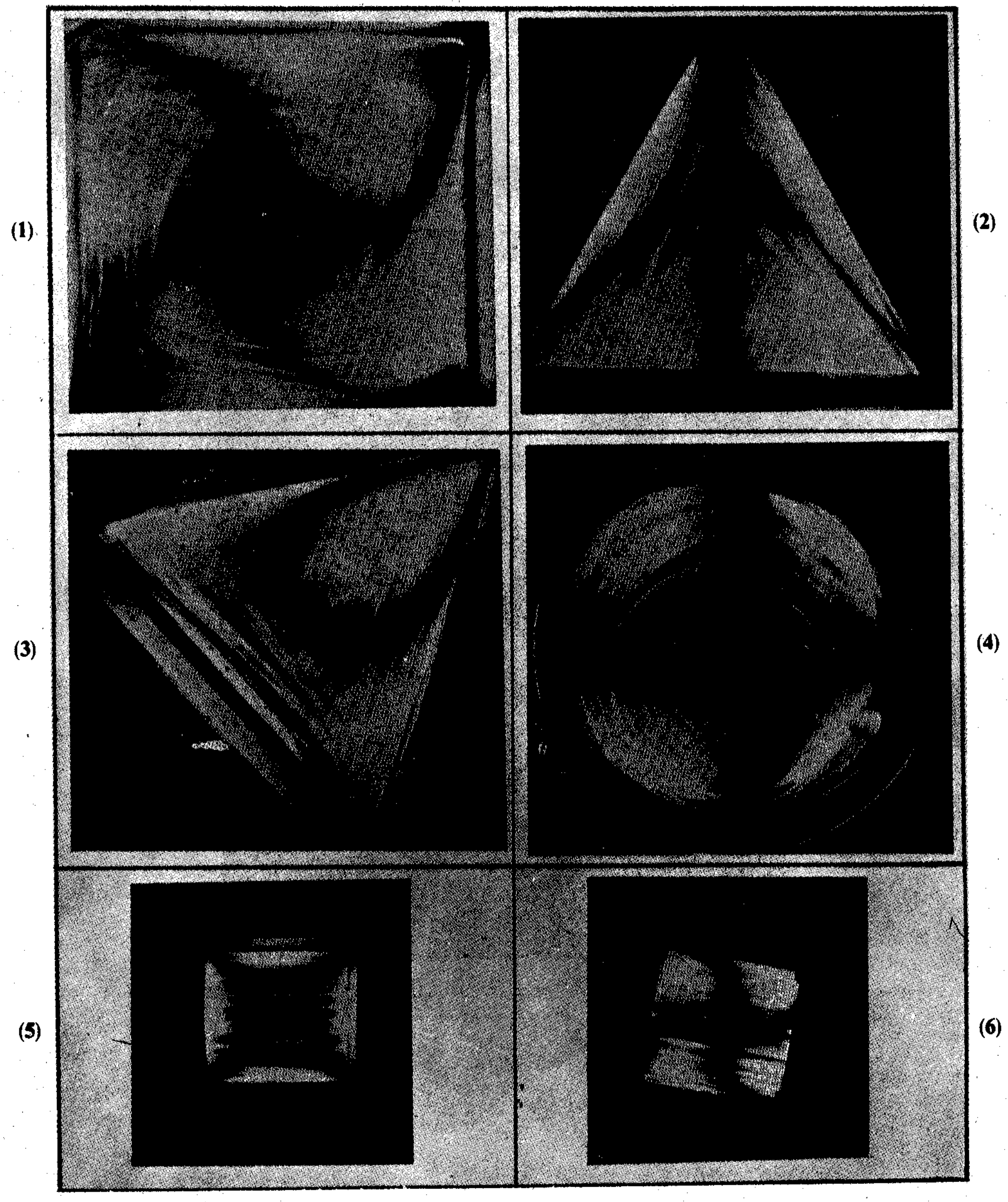
The result reported in an earlier investigation with vitreous silica is now shown to be true also for other amorphous solids, including especially inorganic glasses; besides the well known photo-elastic effect, another kind of birefringence may be

observed differing from the former both in its origins and in its observable characters. This "structural birefringence" arises from anisotropy of structure present in the solid by reason of the circumstances of its formation. It is conspicuously seen with plate glass whose optical behaviour shows it to have a highly laminated structure, while in moulded glass, it exhibits itself as luminous streaks or sheets of variously curved forms.

Numerous photographs illustrate the paper.

## Reference

Raman, C V *Proc. Indian Acad. Sci.* 1950, **A31**, 141.



**Figures 1–6.** Birefringence patterns seen between crossed polaroids. **1.** Cube of canary-yellow glass. **2** and **3.** Equilateral prism of glass in two different settings. **4.** Sphere of canary-yellow glass. **5** and **6.** Cube of glass cut from thick plate in two different settings.

**Plate I**

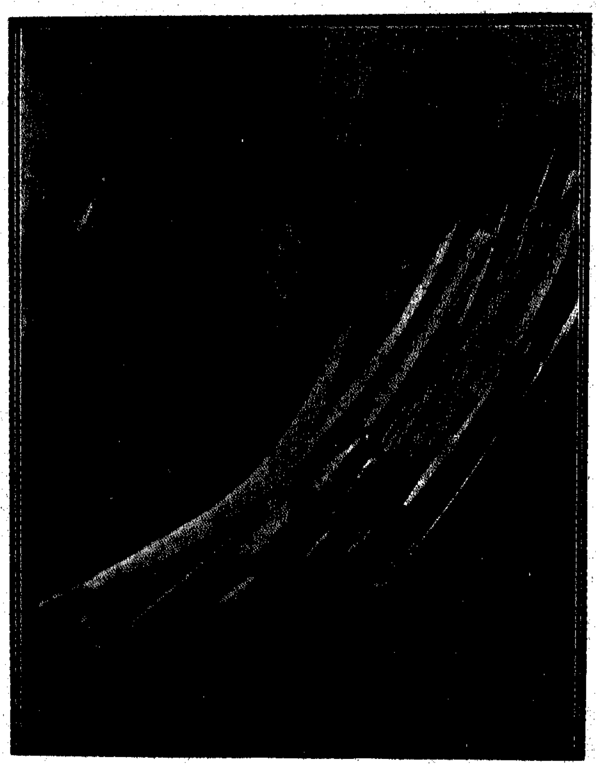
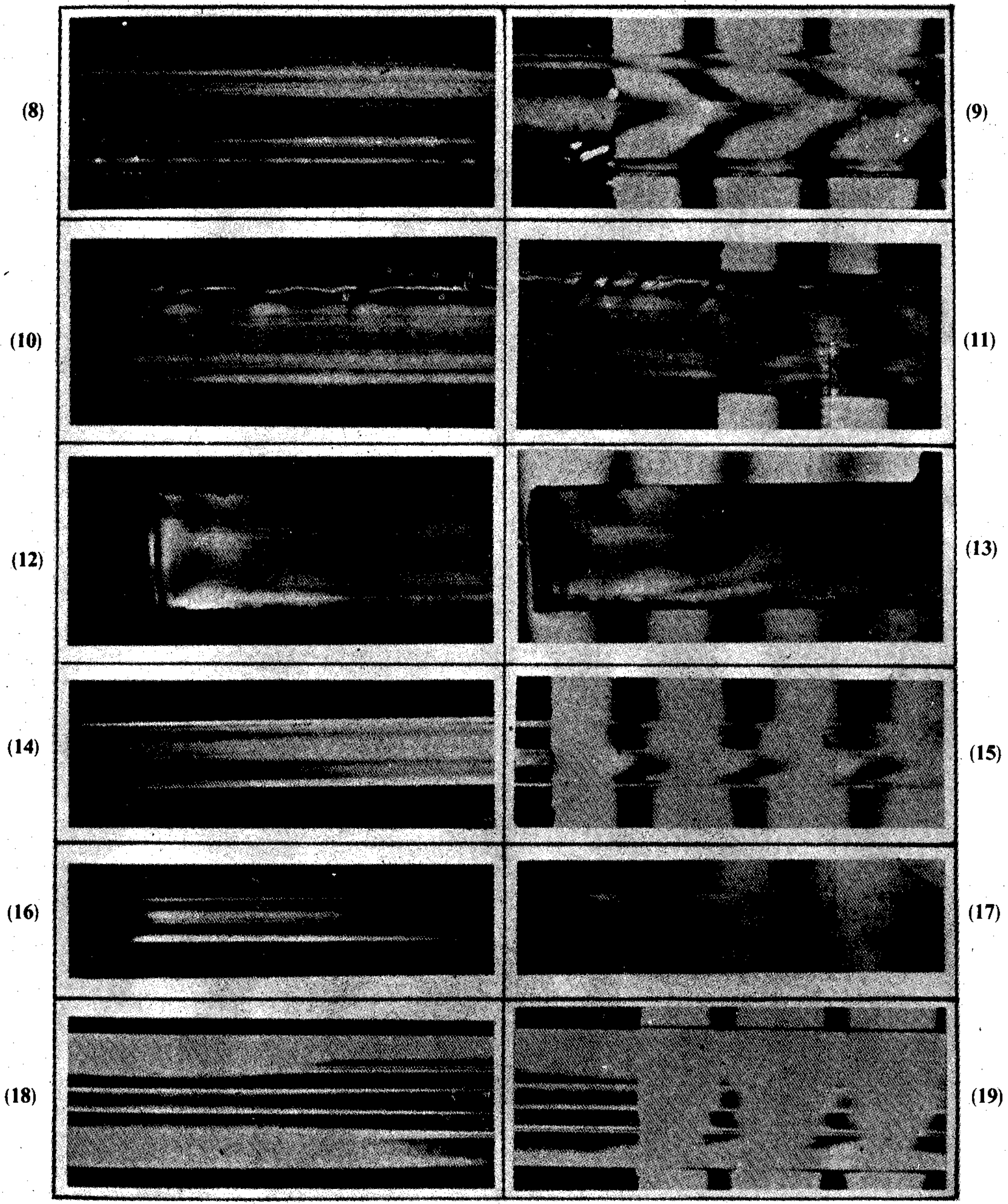


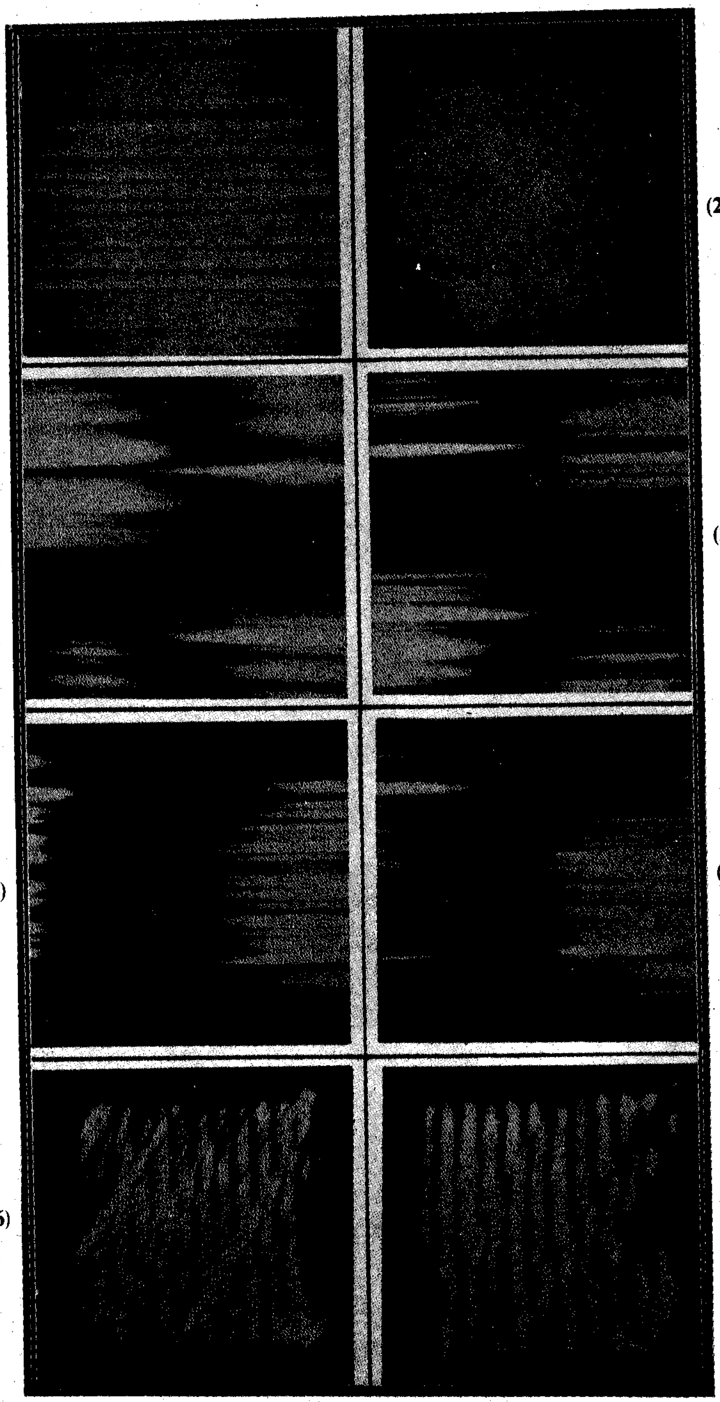
**Figure 7.** Part of one face of a large glass trough, seen through six-inch polaroids sheets crossed, set on either side of it.

**Plate II**



**Figures 8–19.** Plates viewed edgewise, between crossed polaroids. **8.** Quarter-inch thick glass plate, three inches wide. **9.** Same as figure 8 but with the quartz wedge superposed. **10.** Quarter-inch glass plate, $1\frac{1}{4}''$ wide. **11.** Same as figure 10 with quartz wedge superposed. **12** and **13.** Same as figures 8 and 9, but showing free edge. **14.** One-eighth inch glass plate two inches wide. **15.** Same as figure 14 with quartz wedge superposed. **16.** One-sixteenth inch glass plate, $\frac{1}{2}''$ wide. **17.** Same as figure 16 with quartz wedge superposed. **18.** Quarter-inch plastic sheet, $3\frac{1}{2}''$ depth. **19.** Same as figure 18 with quartz wedge superposed.

**Plate III**



**Figures 20–27.** Photographs of glass block cut from thick plate. **20.** Showing the laminated structure of the block viewed in its plane. **21.** Same as figure 20, but with the block tilted slightly. **22–25.** Glass block seen between crossed polaroids, in various settings, showing laminations. **26** and **27.** Glass block with Babinet compensator fringes superposed obliquely, showing effect of the laminations.

**Plate IV**