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Crystal growth of organic materials in glass capillaries

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Three potentially useful electro-optic organic materials have been grown as good optical quality single crystals of up to 30 mm length inside hollow glass fibres of 35 to 50 μm i.d. Capillary attraction was used to fill the fibres and a furnace with small cross-sectional area was designed for the recrystallization of the material inside. The crystallization process is fast and only 0.5 g purified material is needed, thus making the technique attractive for the rapid assessment of the electro-optic properties of many organic materials.

1. Introduction

Following the demonstration that organic crystals may have useful non-linear optical properties [1], the use of such materials crystallized in hollow glass fibres as active elements in a fibre waveguide system has been reported [2]. The technique of forming a single crystal within a fibre has many advantages not only for optical fibre devices, but also as a way of evaluating organic optical materials generally. For instance it is usually necessary to grow large quality crystals which have to be cut, lapped and polished in order to produce test specimens. Furthermore the crystallization of organic materials has not yet reached the stage of development of that for inorganic materials, and a great deal of time consuming effort is needed to find the optimum conditions for the growth of each substance. Hence a method whereby this aspect of the materials preparation is considerably simplified is of great interest.

To form a single crystal suitably oriented within a fibre, Stevenson and Dyott [2] used a controlled progressive freezing process analogous to Bridgeman growth. Whilst this was evidently successful for *m*-nitroaniline that they used in their experiments, we have found that other materials were less easily crystallized and concluded that a greater degree of control over the growth process was desirable. We report here on an improved apparatus which gives better control of crystal orientation and which has been used successfully in the preparation of crystals of materials found to be intractable by conventional methods.

2. Apparatus

2.1. Filling

The first problem in the growth of material in small-bore capillary tubes is in filling them with the liquid material. Two methods have been used which have given satisfactory results; in both cases capillary attraction was the primary driving force. In the preferred method a small quantity of the material (about 0.5 g) was placed at the bottom of a glass test tube and hollow fibres were introduced. The whole tube was heated in a furnace and the temperature carefully raised to the melting point when vertical filling automatically occurred. Alternatively the fibres were cemented into the perforated bottom of a small glass crucible which was filled and heated as in the previous method. In this case gravity assisted filling, although in practice it made little difference.

2.2. Recrystallization

Having filled the fibres it was necessary to recrystallize the material carefully in order to obtain single crystal regions of sufficient length for use in device studies and property measurments. Effectively growth was achieved by the Bridgman technique; that is, the material was first melted and then recrystallized progressively from one end by passing the fibre through a well defined temperature gradient such as that provided by the

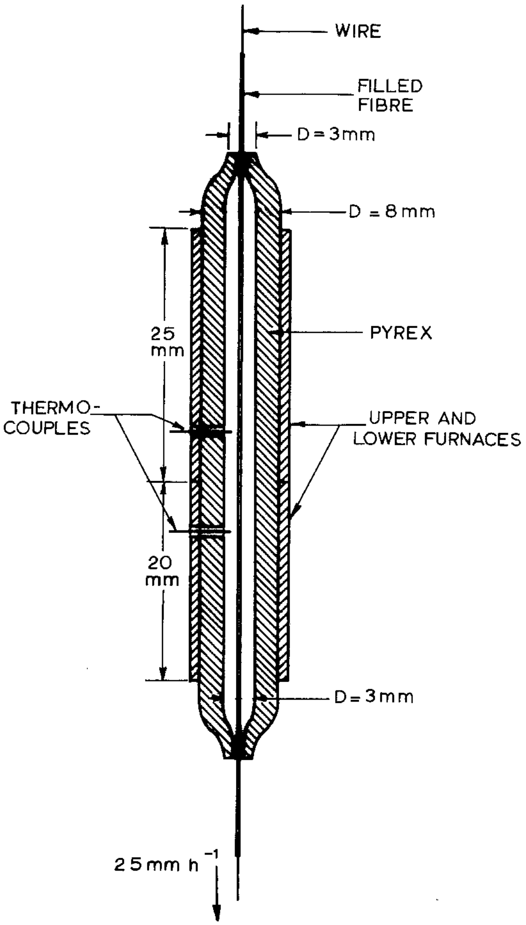

Figure 1 Apparatus for recrystallization of the filled fibres.

furnace shown in Fig. 1. The furnace had a small cross-sectional area and was made from a thick-walled glass tube pulled down at the ends to form a guide for the fibre at the entrance and exit. With symmetrical fibres of circular cross-section (see Fig. 2a) it was possible to produce single crystals about 1 mm long in materials such as *m*-dinitrobenzene. Using fibres of cross-section shown in Fig. 2b it was apparent that due to the variation in thermal capacity of the fibre cladding in various directions, transverse temperature gradients were set up which helped to determine the alignment of the crystal in the cross-sectional plane, and hence the tendency to nucleate in a random manner was decreased. With this modification lengths (up to 30 mm) of single crystal were obtained which were long enough to be useful for experiments. However this technique was still not adequate for controlled growth, and the apparatus was further modified by the introduction of a transverse gradient in the furnace (see Fig. 3). In this way long lengths of single crystals were obtained in fibres with circular cross-section, which are preferred for some applications.

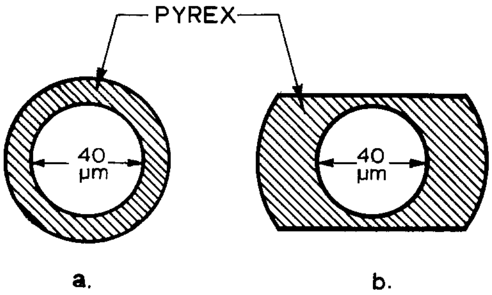

Figure 2 Cross-sectional view of the glass fibres used.

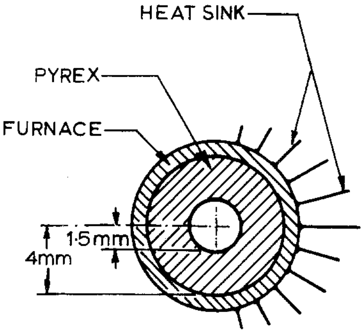

Figure 3 A modification in the furnace cross-section in order to provide a transverse temperature gradient.

It has long been known that for materials which have a marked anisotropy in thermal conductivity, the direction of preferred growth for good quality crystallization is that in which the crystal direction of maximum thermal conductivity aligns with the direction of the steepest thermal gradient. If spontaneous nucleation is used to initiate the growth then the orientation of the crystal formed is usually in this preferred configuration (Fig. 4). It can be easily shown that since both the per-

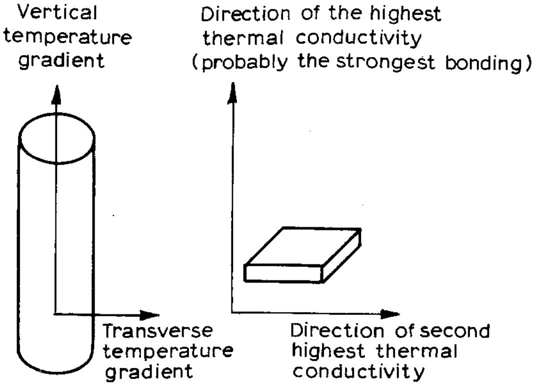

Figure 4 Schematic illustration of the crystal alignment with respect to the temperature gradients.

mitivity and the thermal conductivity can be described by second rank tensors, for crystals of orthorhombic or higher symmetry, one of the principal dielectric axes of the crystal will coincide with the direction of the highest thermal conductivity. Hence the material will crystallize with one of its principal dielectric axes aligned with the fibre axis. This condition has been achieved in the three materials grown to date.

3. Results

The results achieved with this improved furnace have been very encouraging and single crystal lengths up to 30 mm have been obtained for materials which some are known to be difficult to crystallize.

Crystallizations were carried out inside glass fibres of 35 to 50 μm bores and with effective growth rates of 25 to 50 mm h^{-1}. The results are summarized below.

3.1. *m*-Dinitrobenzene (*m*DNB)

This is one of five materials grown by Southgate and Hall [3] for non-linear optical studies on bulk single crystals. The optical quality of the samples of *m*DNB prepared by conventional methods are reported to be the poorest of the five and attempts by the authors to grow it from the melt have confirmed that it is difficult to grow as a good quality single crystal. It was chosen for fibre growth partly in order to obtain crystals of better optical quality by this technique and partly because of its suitability for making electro-optic fibre waveguide components. The material crystallized with the ⟨0 0 1⟩ direction parallel to the axis of the fibre. A section of the crystal-cored fibre is shown in Fig. 5, placed between crossed polarizers with the direction of polarization at 45° to the fibre axis and illuminated with white light. Complete extinction occurs when the light is polarized

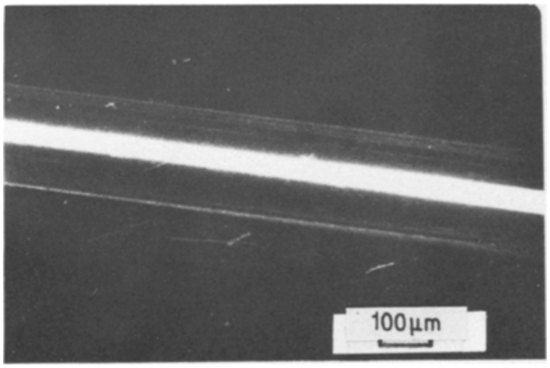

Figure 5 Crystal cored fibre between crossed polarizers, illuminated by white light.

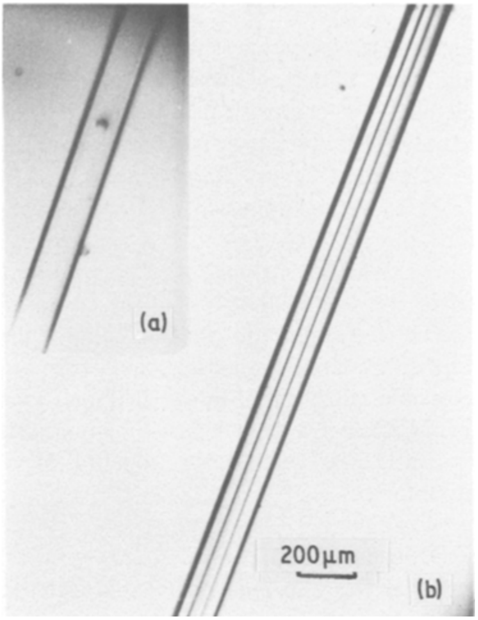

Figure 6 Fibre grown *m*DNB crystal illuminated by polarised light. The direction of polarization is (a) perpendicular to and (b) parallel with the fibre axis. A length of fibre containing a void is photographed in (b) to facilitate detection of the crystal core.

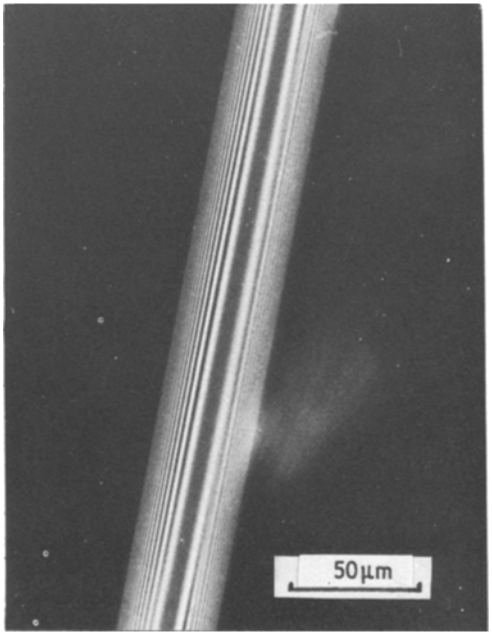

Figure 7 Birefringence of the fibre grown *m*DNB crystal at $\lambda = 589$ nm. The cladding is not visible in the photograph.

in a direction parallel to or perpendicular to the fibre axis. Fig. 6a and b show the crystal and cladding when illuminated by sodium light polarized parallel and perpendicular to the fibre axis, respectively. The principal refractive indices of *m*DNB at the sodium wavelength are: $n_x = 1.74$, $n_y = 1.71$ and $n_z = 1.49$, where as the refractive index of the cladding glass at this wavelength is $n_c = 1.478$. When the direction of polarization is parallel to the $\langle 0\,0\,1\rangle$ direction of the crystal the contrast between core and cladding is lower than with other polarization directions. The birefringence of the crystal is shown in Fig. 7 using sodium light and a higher magnification. This also indicates the good optical quality of the crystals obtained.

3.2. 2-Bromo 4-nitroaniline

This material was also studied by Southgate and Hall [3]. Using the technique described above results similar to those for *m*DNB were obtained. It also crystallized so that one of its principal dielectric axes was aligned with the fibre axis.

3.3. Formyl-nitrophenyl hydrazine (FNPH)

This material has been studied by Owen and White [4], who report that it was difficult to crystallize by conventional methods due to its gradual decomposition either in solution or in the melt. However, crystallization is much faster with the fibre technique, and the material is also totally enclosed so that decomposition is less likely to occur. Although work on FNPH is in its earlier stages, short lengths of crystal of about 1 mm have been obtained. Again one of the principal dielectric orientations lies along the fibre axis.

4. Discussion

The method of preparation of single crystals in fibres has proved to be effective for a number of materials which are otherwise difficult to crystallize. The crystals within the fibres are in a convenient form for X-ray and optical examination, and also for evaluation of their performance in optical devices, e.g. by the determination of their electro-optic coefficients. The method also provides a means of preparing specimens for rapidly assessing new organic materials for optical activity without the need for elaborate and time consuming growth procedures. In addition, only comparatively small quantities of purified materials are needed, which can be an advantage for materials which are expensive or difficult to synthesize.

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