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X-ray diffraction methods to determine crystallinity and preferred orientation of lithium disilicate in Li–Zn–silicate glass–ceramic fibres

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Three X-ray diffraction methods for the evaluation of the microstructural features shown by glass–ceramic fibres obtained by various heat treatments have been developed and discussed. Fibres made of a Li–Zn–silicate glass of the following chemical composition were investigated (mol %): SiO_2 66.75, Li_2O 23.45, ZnO 8.00, K_2O 1.00, P_2O_5 0.80. The first method is devoted to measure the preferred crystal orientation of lithium disilicate crystals which begin to grow starting from 580° C with the *c*-axis lying preferentially normal to the fibre external surface. This method has employed a four-circle diffractometer by means of which the intensity distribution of the equatorial 002 X-ray reflection could be evaluated. The other two methods regard the crystallinity content determination of lithium disilicate formed at 590° C as well as at 620° C either after a nucleation step at 480° C or at 500° C, or without any nucleation treatment. These two methods, namely the Hermans and Weidinger and the Wakelin, Virgin and Crystal methods, have been transferred for the first time from the organic polymer science to glass–ceramic materials. The results obtained with both methods have been compared together and have been found in good agreement.

1. Introduction

The crystallization of glass fibres has been object of relatively few studies by X-ray diffraction methods (XRD). Booth and Rindone [1], Jones and McMillan [2] published some important contributions on the subject. Interest in microstructure and crystallization kinetics of glass fibres prompted us to examine these phenomena by XRD methods which have not yet been applied in the field of glass–ceramic materials.

Fibres made of Li–Zn–silicate glass of the following chemical composition in mol% were prepared: SiO_2 66.75%, Li_2O 23.45%, ZnO 8.00%, K_2O 1.00%, P_2O_5 0.80%. Methods for glass preparation and fibre drawing will be hereafter described. It is known that lithium disilicate glass–ceramics can be readily obtained from glasses of this approximate composition [3]. In particular, it was shown by DTA, SEM and XRD qualitative investigations that in those glass fibres the crystalline phase, $Li_2Si_2O_5$, could be detected at about 580° C [4]. The phase having an orthorhombic structure [5, 6] exhibited a preferred crystal orientation with the *c*-axis lying normal

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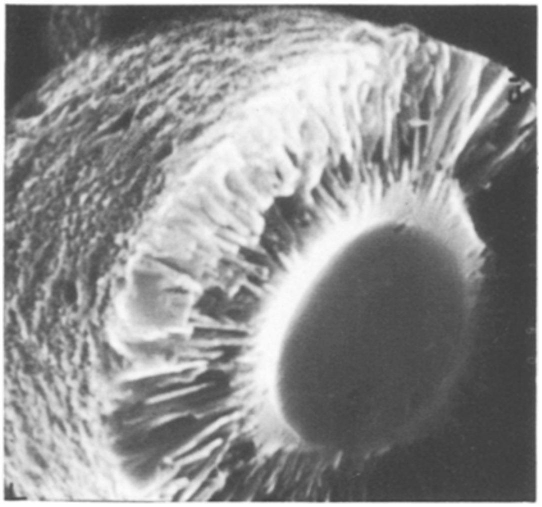

Figure 1 SEM image, X 3000. The oriented crystallization is clearly shown.

to the external surface, and being placed radially on planes perpendicular to the fibre axis.

Fig. 1 shows a fibre with an outer rim of lithium disilicate crystals. X-ray fluorescence microanalysis indicated an increased zinc concentration down into the fibre glassy core [4]. By raising the temperature above 650 to 660° C Li_2ZnSiO_4 could be clearly detected. At higher temperatures the remnant vitreous phase crystallized as cristobalite and quartz (Fig. 2). In the present work a quantitative analysis of both preferred orientation and crystallinity amount has been undertaken for lithium disilicate crystallized at various temperatures and periods of time. The temperature range was controlled to prevent the crystallization of the Li–Zn–silicate phase. The first parameter was calculated from half angular arc length of the equatorial 002 reflection, recorded by means of a four-circle diffractometer. The second one was estimated employing the method of Hermans and Weidinger [7, 8] which was herein compared with the method of Wakelin *et al.* [9]. The method of Hermans and Weidinger has been discussed and modified in order to take into account the compositional variation of the remnant vitreous phase, as the amount of the crystalline $Li_2Si_2O_5$ increased. Among the methods developed for crystallinity determination in the field of organic polymer science, only Field's method [10], which is older and more restrictive than the present ones, has been transferred to the field of glass–ceramic materials [11].

2. Preparation of the glass fibres

Pure chemical compounds, namely the carbonates of lithium, zinc and potassium, were mixed with a fine quartz powder and a proper amount of ammonium phosphate in a platinum alloy crucible; such a mixture was brought up to 1450° C and kept under a stirring action for two days. The fluid glass was poured and quenched to be broken down into small fragments. These latter were used to

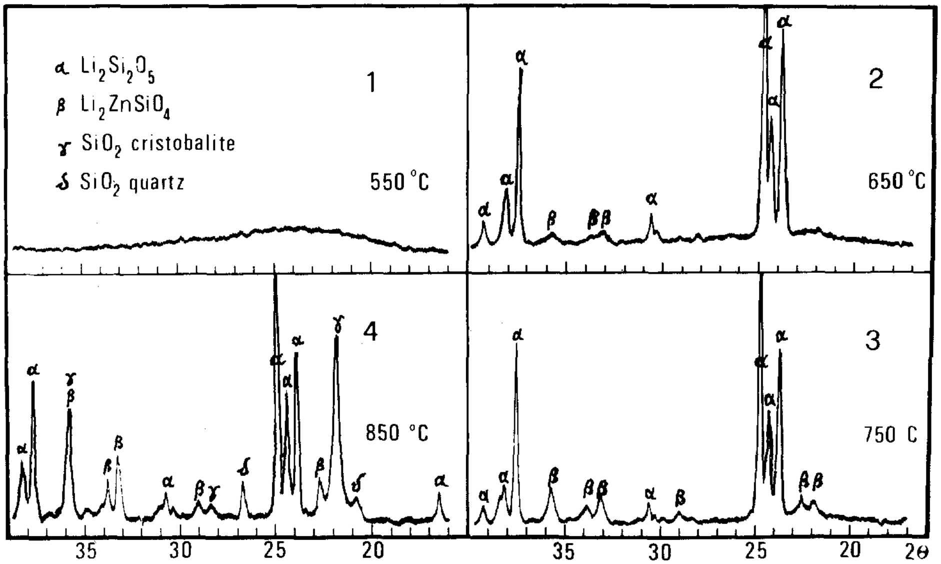

Figure 2 X-ray diffraction patterns of the fibres, after heating and quenching at the temperatures corresponding to the numbers indicated in the DTA curve of Fig. 3.

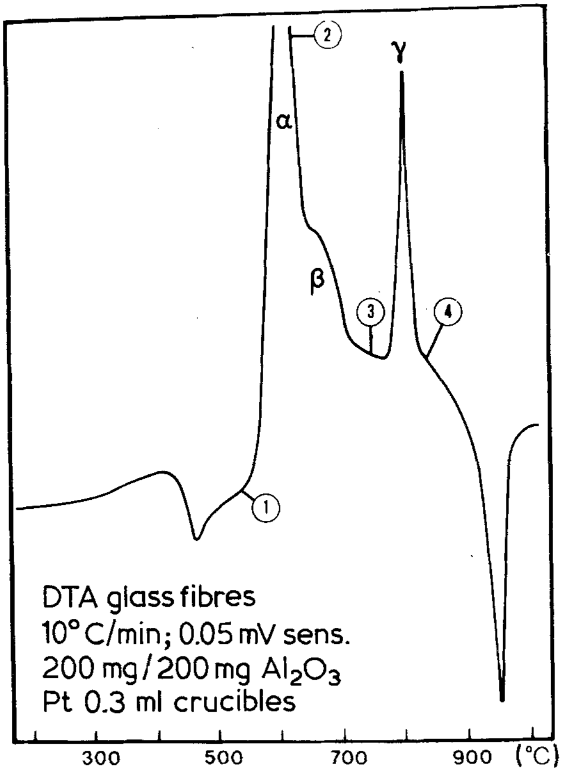

Figure 3 DTA curve of glass fibres. The Greek symbols correspond to the crystalline phases reported in Fig. 2.

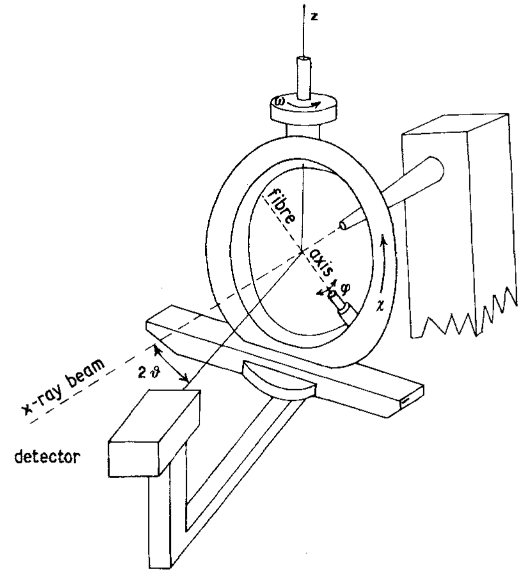

Figure 4 X-ray diffraction geometry of the four-circle diffractometer.

feed the fibre making apparatus. Fibre drawing was carried out from a Pt–Rh crucible provided with one nozzle in its base, and heated electrically by short circuiting the crucible across the secondary windings of a step-down transformer. The fibre was drawn from the nozzle on to a rotating drum of about 15 cm in diameter. The power applied was controlled manually in order to maintain the best flow and a constant temperature at about 1030° C, which was monitored through a thermocouple dipping into the molten glass.

Several tows of fibre with mean cross section of about 15 μm were made. They had been checked under the polarizing microscope and were found to be clear and homogeneous. The thermal treatments of the glass fibres were carried out in a laboratory muffle furnace, automatically controlled within ± 2° C. The temperature for both nucleation and crystallization of $Li_2Si_2O_5$ were established on the basis of a differential thermal analysis (DTA) thermogram (Fig. 3), as well as on the literature data. For example, Hing and McMillan [12] indicated at about 505° C the temperature of the maximum nucleation rate in Li_2O–SiO_2 glasses; they also showed that, at this temperature, a coarse and extensive glass-in-glass separation appeared to be promoted by ZnO addition. This fact is in good agreement with previous results [13] concerning a glass having the molecular percentage composition: SiO_2 72.5%, Li_2O 22.3%, K_2O 1.5%, ZnO 3.0%, P_2O_5 0.7%, in which a distinct two-phase structure appeared at 500° C. On the other hand, various authors [14–17] have reported values in the range between 450 and 485° C for the maximum nucleation rate temperatures in Li_2O–$x SiO_2$ glasses with x ranging between 2 and 3, either pure or containing various other oxides as minor phases.

For the present system, in which the SiO_2/Li_2O molar ratio is 2.85, we have compared two different nucleation treatments: the former at 500° C for 5 min and the latter at 480° C for 1 h. These thermal treatments were followed by isothermal crystallization at 590 or 620° C for times ranging between 10 to 600 min. In addition, direct single-stage crystallization treatments were carried out at 620° C.

3. Determination of the preferred crystal orientation

Bundles of each specimen of glass–ceramic fibres were placed inside capillaries of 0.5 mm diameter which were mounted into the goniometer head of a Philips PW 1100 diffractometer. Fig. 4 shows the diffraction geometry of this instrument and

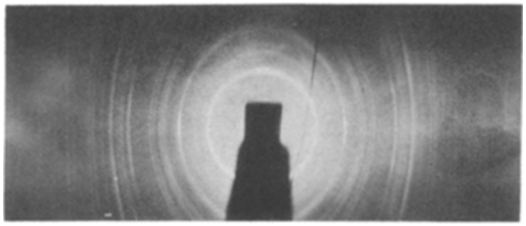

Figure 5 X-ray fibre spectrum for the specimen heated at 620° C for 4 h. The orientation of 0 0 2 reflection is clearly shown.

the definitions of χ, 2θ, ω and ϕ axes can be seen clearly. The X-ray intensity distribution along χ was measured by step scanning at fixed $2\theta_{\max}$ equal to 17.07°, which corresponds to the 2θ Bragg angle for the 0 0 2 reflection of $Li_2Si_2O_5$ (radiation used: Mo$K\alpha$ filtered with zirconium). The angle ω was maintained fixed at zero, whereas the fibre axis rotated through ϕ between 0 and 360° C.

Preliminary fibre spectra were recorded with a cylindrical camera. The spectrum of Fig. 5, derived for a well oriented specimen crystallized directly at 620° C for 4 h, shows an over-intensified equatorial 002 reflection. Bearing in mind that the X-ray beam is perpendicular to the fibre axis, the observed orientation for this reflection just shows that the $(00l)$ planes are preferentially aligned parallel to the fibre external surface.

The $\Delta\chi$ half angular arc length of the 0 0 2 reflection has been measured as the peak width at the half height of the maximum intensity. Using known equations [18] it was possible to calculate, from the $\Delta\chi$ values, the η angles of distribution of the normals to the $(00l)$ planes with respect to the fibre external surface at the corresponding crystallite position. It is evident that a strong orientation is present when η is small, whereas an angle of $\eta = 90°$ indicates an uniform intensity distribution throughout the diffraction ring. X-ray diffraction intensities were collected using a fixed counting time of 100 sec. The correction for background was applied. The results on the preferred orientation in the glass–ceramic fibres of the present system will be reported and discussed in the following paper.

4. Determination of the amount of crystallinity by means of Hermans and Weidinger method

For the application of both methods of Hermans and Weidinger [7] as well as of Wakelin *et al.* [9] a vertical powder Philips diffractometer was used with a highly stabilized molybdenum target-tube (wavelength $\lambda_{\mathrm{Mo}K\bar{\alpha}} = 0.07107\,\mathrm{nm}$). The glass–ceramic fibres were powdered for some minutes in a laboratory vibrating ball mill and sieved through a 400 mesh sieve. We employed the symmetrical transmission mode. The diffracted Zr-filtered radiation was passed through a graphite crystal monochromator before the scintillation detector. A metallic sample-mounting block with a special purpose attachment was built. The apparent specimen thickness was about 1 mm. In order to increase resolution, a very narrow entrance slit of 0.03° and a receiving slit of 0.2 mm were used.

The intensities were graphically recorded at $0.25°\,\mathrm{min}^{-1}$ velocity. Normalization procedures were applied in order to reduce the observed intensities both to equal X-ray optical density of the specimen and to equal relative primary beam intensity, using the completely amorphous sample itself as standard reference of the series. The optical density values of all specimens were in the range of 0.7 to 0.9. The air scattering was subtracted from the integrated intensities according to the procedure indicated by Klug and Alexander [19]. As shown by Hermans and Weidinger, the corrections for Lorentz and polarization factors and thermal scattering contribution are not necessary. The incoherent scattering in the angular range studied was negligible.

The principle of this method is the recording with monochromatic radiation of diffractograms of several samples at different degrees of crystallinity. Integrated intensities, which may be assumed to be proportional to either the unknown amorphous or crystalline fraction were selected and measured as convenient quantities to be compared. It is worth mentioning that the present method can be exactly applied only if the crystalline and amorphous fractions have the same composition. In the present complex glass–ceramic system this condition is not fulfilled. Assuming that each crystalline compound is subsequently originated from a vitreous phase of the same composition, we found that the maximum theoretical wt% of lithium disilicate is 41.7 wt%. Since the $Li_2Si_2O_5$ density ($2.44\,\mathrm{g\,cm^{-3}}$) is close to that of the initial glass ($2.5\,\mathrm{g\,cm^{-3}}$), the wt% crystallinity is close to the vol% one. The glassy phase (A2)

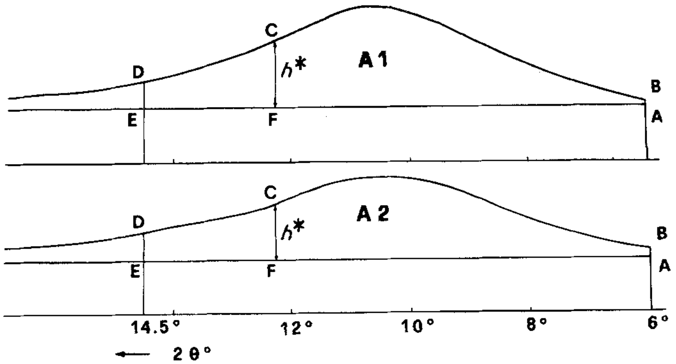

Figure 6 X-ray diffraction normalized curves of the initial glass (A1) and of the final glass (A2) which has a chemical composition corresponding to 41.7% lithium disilicate crystallinity.

which remains in the fibre core at this stage has the following composition (mol%): SiO_2 66.8%, Li_2O 14.9%, ZnO 14.9%, K_2O 1.9%, P_2O_5 1.5%. This latter is rather different from the initial glass (A1) composition.

In order to make an internal check of the method, we prepared a glass of composition A2. The normalized X-ray intensities of both amorphous specimens, A1 and A2, are displayed in Fig. 6. It is possible to see that the two X-ray diffraction curves are similar, the integrated intensity of A2 being slightly smaller than that of A1. As an approximation we propose that the low crystallinity specimens have to be compared with A1, whereas those with high crystallinity have to be compared with A2. Another semi-empirical approach to this problem consists of a simultaneous treatment of the data versus both A1 and A2 taken as reference standards. Differences in scattering power among the phases involved, one of which changes composition as a function of the crystallinity content, would require further theoretical adjustments which are beyond the purpose of the present work†.

The crystalline peaks must be separated from the diffuse background. At first, we have drawn the curves of the amorphous "cap" for each diffractogram congruently with the X-ray diffraction curve of either A1 or A2, according to the procedure used. The three main crystalline peaks of $Li_2Si_2O_5$, indexed 130, 040 and 111, are very close to one other, with the centre of their maxima placed between 2θ values of 10.87 and 11.36°, above the maximum of the amorphous halo. As shown in Fig. 7, where the recording of a highly crystallized sample is reported, the 2θ range of the analysis was 6 to 14.5°; in this way the 002 reflection, whose intensity may be biased by preferred orientation effects, has been on purpose left out.

The surface of the "cap" ABCDEF (see Fig. 7), normalized as indicated and designated by O_{am}, has been taken as a quantity proportional to the amorphous portion. This quantity, together with the corresponding O_{cr} surface pertinent to the crystalline peaks, was measured by paper weight. The pairs of the so obtained O_{am} and O_{cr} values were plotted in relative units, as shown in Fig. 8, where all specimens have been correlated to both A1 and A2. From a statistical analysis of these data a regression straight line was obtained, from which the extrapolated O^*_{am} and O^*_{cr} values, corresponding either to a totally amorphous or crystalline sample, could be calculated. A similar statistical analysis on the samples with high crystallinity (> 30%) was carried out only with respect to A2 as reference amorphous standard. The crystalline fraction (*C*) is given by:

$$C = 1 - \frac{O_{am}}{O^*_{am}} \qquad (1)$$

The *C* percentage values obtained for high crystallinity samples, as referred to A2, are about 2% smaller than the corresponding ones calculated with reference to both A1 and A2. Since some points in these linear correlations were not well aligned, it was interesting to estimate *C* by means of an equation similar to Equation 4 of [8], where the O_{cr} values are also directly involved. For this purpose it was necessary to compute the O^*_{am}/h^*_{am} ratio for the completely glassy sample, h^*_{am} being in this case the height of the amorphous

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†As suggested by Dr C. G. Vonk, it should be possible to taken into account theoretically the difference of composition between crystalline and amorphous phases using Ruland's method of X-ray determination of crystallinity and diffuse disorder scattering [20] (private communication).

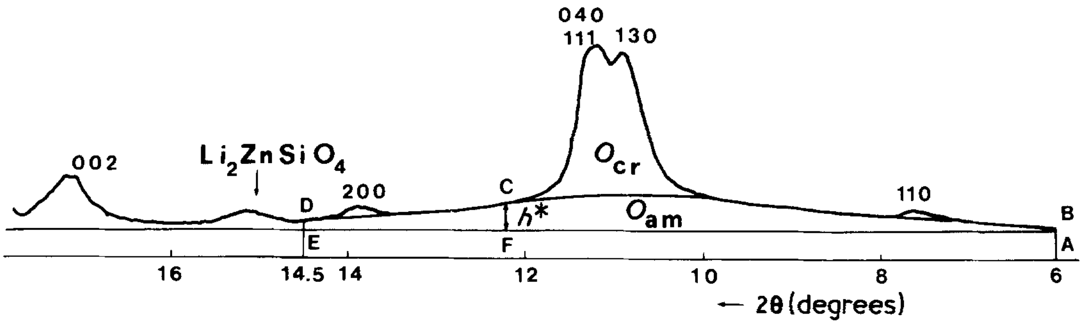

Figure 7 X-ray recording of a highly crystallized specimen (number 7 of Table I). The separation of the crystalline peaks of $Li_2Si_2O_5$ from the amorphous background is indicated.

"cap" at $2\theta = 12.25°$. This angular value was chosen since the crystalline peaks gave no contribution and air scattering was negligible.

Table I reports all C values determined on the basis of the different equations employed. The data, transformed in percentages, approximately agree within ± 3%. The deviations from linearity shown in Fig. 8 are higher than those observed by Hermans and Weidinger in polymeric materials. This may be due to two main causes; the first one is a possible presence in some specimens of systematic errors due to a persistent preferred orientation which, anyhow, has been minimized with the present procedure. The second cause may depend on the variation of composition of the vitreous phase from sample to sample, as previously discussed. It is possible to note from Table I that, for long times of heating, the crystallinity of $Li_2Si_2O_5$ slightly diminishes. This behaviour cannot be explained by errors in the methods employed; it could instead be ascribed to a beginning of phase transformation of $Li_2Si_2O_5$ towards Li_2ZnSiO_4. This is supported by the presence of a weak X-ray line at $2\theta = 15.15°$ which can be attributed to the 3 3 0 and 0 0 4 reflections of lithium–zinc–silicate, the X-ray powder pattern of which was published by Stewart and Buchi [21]. The diffractogram, reported in Fig. 7, of the sample heated at 620° C for 4 h after a nucleation at 500° C for 5 min, clearly shows the presence of Li_2ZnSiO_4.

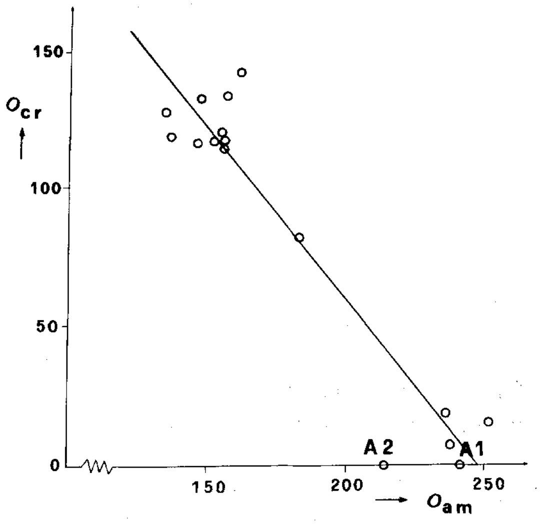

Figure 8 Regression of O_c on O_a for lithium disilicate crystallinity determination, where O_c and O_a are two quantities proportional to the crystalline and the amorphous fraction, respectively.

5. Determination of the crystallinity by means of Wakelin, Virgin and Crystal method

The method of Wakelin *et al.* [9] has the advantage with respect to the foregoing method that it is based only on the measurements of intensity differences at constant 2θ. These quantities are automatically corrected for the incoherent scattering while the correction for Lorentz and polarization factor is unnecessary. They must be corrected for variations in the primary beam intensity and normalized to equivalent X-ray optical density. Since in the present case the specimens have a similar optical density, it was not necessary to make the correction for air scattering.

The disadvantage of the method consists in the relativeness of the measurements which must be referred to the crystallinity content of two reference standards. We have chosen as amorphous standard the initial glass A1 and as the crystalline standard, with respect to lithium disilicate, the sample 6 of Table I. The intensities were collected in symmetrical transmission by step-scanning mode using 0.2° as unit step and a

TABLE I Crystalline fraction of lithium disilicate calculated by Hermans and Weidinger method according to the equations indicated

Sample number	Specimen[*] treatment	From Equation 1 (amorphous samples A1 and A2)[†]	From Equation 1 (amorphous sample A2)[‡]	From Equation 4 of [8] (amorphous sample A1)	From Equation 4 of [8] (amorphous sample A2)	Mean
1	5 min 500° C/20 min 590° C	–	–	0.045	–	0.045
2	5 min 500° C/2 h 590° C	0.453	0.438	0.429	0.408	0.432 ± 0.013
3	5 min 500° C/4 h 590° C	0.363	0.338	0.337	0.315	0.338 ± 0.012
4	5 min 500° C/10 min 620° C	0.236[§]	–	0.246	0.233	0.238 ± 0.005
5	5 min 500° C/20 min 620° C	0.363	0.339	0.371	0.352	0.356 ± 0.011
6	5 min 500° C/2 h 620° C	0.448	0.430	0.420	0.417	0.429 ± 0.010
7	5 min 500° C/4 h 620° C	0.445	0.426	0.391	0.371	0.408 ± 0.027
8	1 h 480° C/20 min 620° C	0.056	–	0.067	–	0.061 ± 0.06
9	1 h 480° C/4 h 620° C	0.400	0.378	0.444	0.422	0.411 ± 0.022
10	1 h 480° C/10 h 620° C	0.403	0.381	0.403	0.382	0.392 ± 0.010
11	1 h 620° C	0.058	–	0.021	–	0.040 ± 0.018
12	2.5 h 620° C	0.338	0.312	0.384	0.363	0.349 ± 0.024
13	4 h 620° C	0.368	0.344	0.393	0.373	0.369 ± 0.014
14	10 h 620° C	0.379	0.356	0.387	0.367	0.372 ± 0.011

[*] The first temperature indicated refers to the nucleation and the second one to the crystallization heating treatment.

[†] The statistical analysis was made on all specimens referred to both A1 and A2 glasses.

[‡] The statistical analysis was made only on the specimens of high crystallinity referred to glass A2.

[§] For this specimen with intermediate crystallinity an iteration procedure, which takes into account both amorphous samples A1 and A2 has been applied.

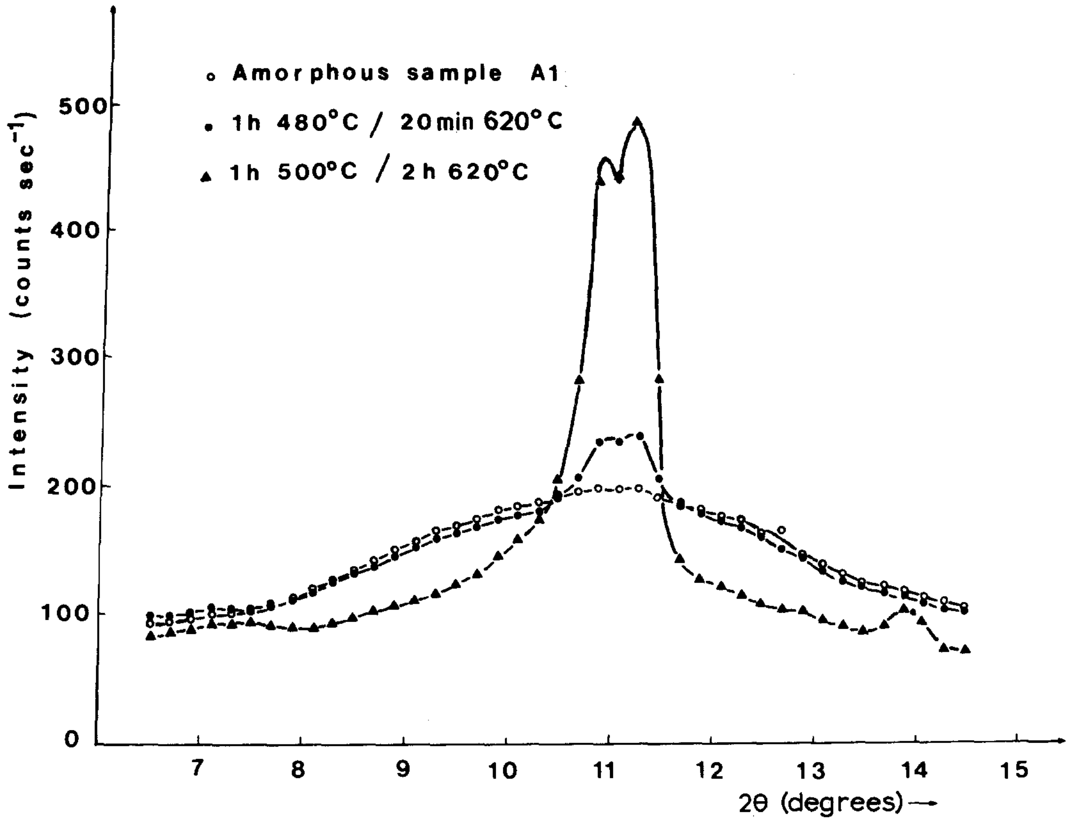

Figure 9 X-ray normalized intensities obtained by step-scanning for the crystalline and amorphous standards as well as for a low crystallinity fibre specimen (number 8 of Table I).

fixed counting of 4×10^4. The angular range was chosen between 6.5 and 14.5°. Fig. 9 shows the X-ray intensity diagrams of the crystalline and the vitreous standards as well as the curve of the partially crystalline sample 8, nucleated at 480° C for 1 h and then heated at 620° C for 20 min.

I_a, I_c, I_u being the numerical values of the normalized intensities of the amorphous standard, the crystalline standard and the specimen of unknown crystallinity, at constant 2θ, respectively, it is possible to obtain a correlation crystallinity index C_c by the best straight line through the plotted points $I_u - I_a$ against $I_c - I_a$:

$$(I_u - I_a) = C_c\,(I_c - I_a) + B \qquad (2)$$

where B should be very small, theoretically zero. C_c is given by the least squares optimization formula:

$$C_c = \frac{\Sigma xy - (1/n)\,\Sigma x\,\Sigma y}{\Sigma x^2 - (1/n)(\Sigma x)^2} \qquad (3)$$

where $x = I_c - I_a$, $y = I_u - I_a$ and n denotes the number of pairs of observations. As an example, Fig. 10 shows the plot of $(I_u - I_a)$ against $(I_c - I_a)$ for the specimen 5 of Table I.

In Table II we report both C and C_c for five specimens for which a comparison between the Hermans and Weidinger [1] and the Wakelin *et al.* [9] methods has beeen carried out. The initial relative C_c values were transformed into absolute values placing the crystallinity amount of the crystalline standard equal to the corresponding value given by Hermans and Weidinger method. Because of the variation of composition of the vitreous phase, the Wakelin *et al.* method is also an approximation of theory, however the similar trend shown by the two X-ray diffraction curves of A1 and A2 justifies the application of this procedure. Furthermore, the final agreement between the two methods employed strengthens the validity of both.

6. Conclusions

A method for the preferred crystal orientation determination of lithium disilicate grown in glass–ceramic fibres has been elucidated. This method employs a four-circle diffractometer by means of which the χ angle of intensity distribution of the 002 X-ray line could be exactly

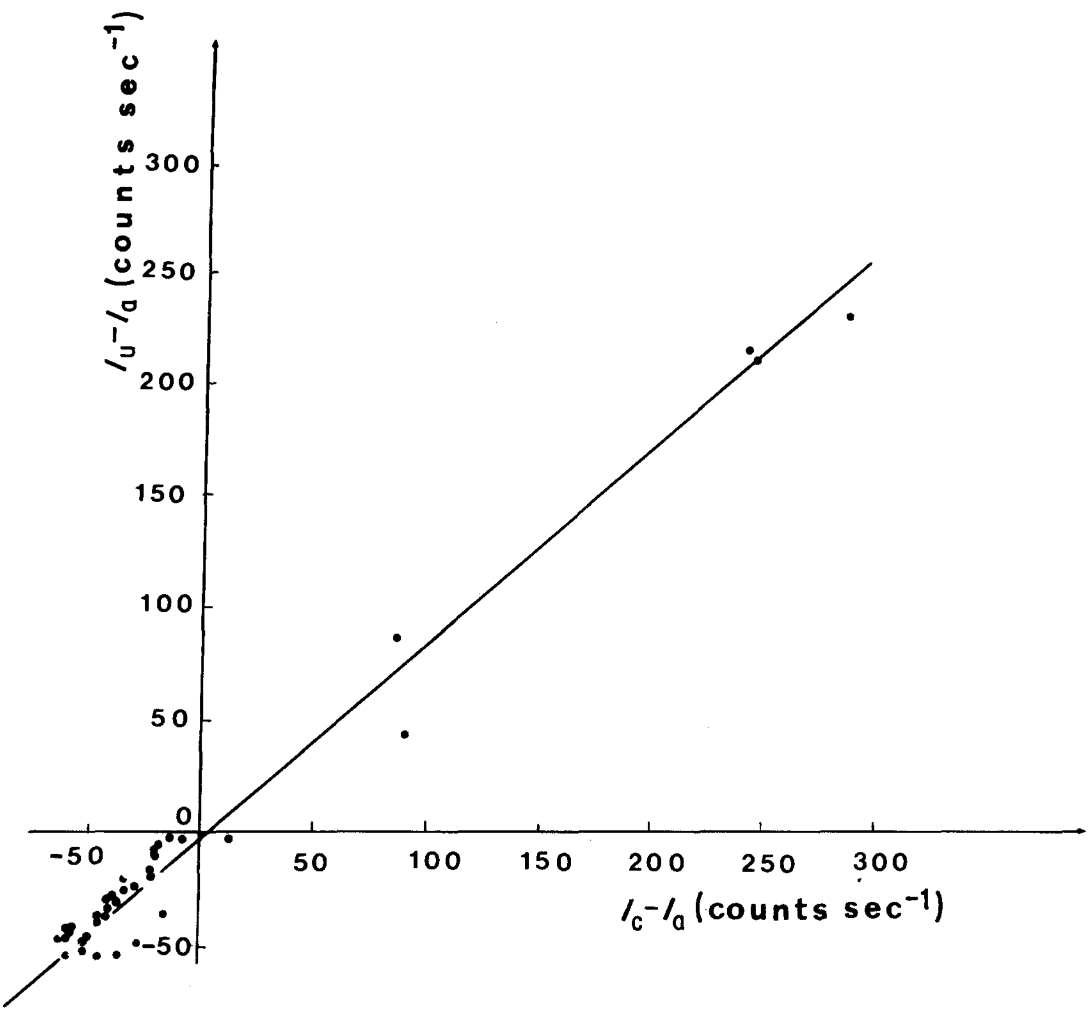

Figure 10 Plot of $I_u - I_a$ against $I_c - I_a$ for a typical lithium disilicate glass–ceramic fibre (number 5 of Table I).

evaluated without any distortion due to the diffraction geometry.

We have shown that the crystallinity amount of $Li_2Si_2O_5$ formed in fibres of a complex glass–ceramic system may be measured with fairly good precision by means of the method of Hermans and Weidinger [7] as well as of the one in Wakelin *et al.* [9]. The first method is simpler, less time consuming and gives absolute information, while the Wakelin *et al.* method, which in principle is more precise, gives only relative values of crystallinity or crystallinity indexes.

TABLE II Comparison between the crystallinity values obtained with Hérmans and Weidinger and with Wakelin *et al.* methods, respectively

Sample number	Specimen	Crystallinity (%)	
		C Hermans and Weidinger method	C_c Wakelin *et al.* method
1	5 min 500° C/20 min 590° C	4.5	4.2
5	5 min 500° C/20 min 620° C	35.6	36.2
7	5 min 500° C/4 h 620° C	40.8	40.2
8	1 h 480° C/20 min 620° C	6.1	6.0
13	4 h 620° C	36.9	42.4

In the present study this latter method has given a positive check of the results obtained by the former one. The Hermans and Weidinger method can be applied when a series of several specimens with different crystallinity is available. However, it is not necessary to have the completely amorphous and the completely crystalline compounds of the series.

Both methods herein described have been transferred from the organic polymer science and we think that they can be extended to many other glass–ceramic systems. As regards the Hermans and Weidinger method, the obstacle presented by the change of composition of the amorphous phase, when crystallinity increases, has been overcome and discussed on a semi-empirical basis.

In some respects the Herman and Weidinger method appears more advantageous than the internal standard ones proposed by various authors (see for example Williams *et al.* [22]). In fact, the diffuse background due to the amorphous phase is neglected in the internal standard procedure while, on the contrary, it is fully estimated in the present method since it is compared with the integrated intensity of the crystalline fraction, in order to give absolute values of crystallinity. Moreoever, in the case of glass–ceramic materials, a 100 wt % crystalline calibration standard must be employed. Sometimes this latter is not available and, furthermore, the calibration samples made by mixing the initial glass with different amounts of the crystalline compound do not represent the true materials under study.

For all the above mentioned reasons the methods herein explained may be of interest for studying series of several glass–ceramic specimens of different crystallinity as it happens when a study of crystallization kinetics has to be undertaken.

Acknowledgements

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