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GB-A-1 301 409
GB-A-1 319 670
US-A-3 859 103
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Description

The present invention relates to graded index optical fibres and their production by thermal diffusion using the double crucible drawing technique.

In order to produce optical fibres suitable for use in telecommunications systems it is necessary to ensure that the loss in the optical fibres is 20dB/km or less. This requirement imposes stringent conditions on the quality of the glasses from which the fibres are made. For example it is important that such glasses should have a low concentration of transition metal ions and water, which give rise to absorption bands. It is also important that phase separation and devitrification should not occur in the glasses when the fibre is drawn, because even if present to only a slight extent these effects will result in glasses with high scatter loss.

Up to the present time greatest success has been encountered with pure and doped vitreous silicas. It is possible to produce vitreous silica in an extremely pure state, so that absorption losses due to impurities are as low as 2dB/km. In order to produce a second glass, with a refractive index different from that of pure silica, small quantities of dopants, for example titanium dioxide, are added. In this way optical fibres can be made with a doped silica core and a pure silica cladding. Such optical fibres have an extremely low loss. Because, however, of the higher softening point of vitreous silica, there are difficulties in the preparation of optical fibres from these materials. For example, the usual technique used in the fabrication of dielectric optical waveguides is to prepare a preform consisting of a clad rod and then to draw this down to a suitable diameter to form the dielectric optical waveguide.

From the point of view of convenience of manufacture the double crucible technique for drawing fibres is ideal. This technique involves melting two glasses, one in a first crucible and the other in a second crucible, the first crucible being located within the second crucible. Both crucibles have drawing nozzles. The fibre thus formed is a clad fibre which is capable of acting as a dielectric optical waveguide. Ideally low melting point glasses are required for the double crucible technique. Such glasses are however complex, containing as a rule at least three oxides, and this introduces problems in keeping the glass losses at a sufficiently low level to permit the production of satisfactory optical fibres. US Patent Specification No. 3 957 342 describes and claims a family of sodium borosilicate glasses of low softening point and low absorption and scatter loss which have proved highly satisfactory for the production of stepped index optical fibres.

The double crucible drawing technique is especially well adapted for the production of graded index fibre by thermal diffusion see, for example, USA 4 040 807 and Proceedings of the Second European Conference on Optical Fibre Communications, Paris, September 1976, pages

21—26. In this process, the core and cladding glasses are subjected to a heat treatment which permits inter-diffusion of the mobile oxides in the two glasses, this heat treatment being carried out during the drawing operation by controlling the length of the drawing nozzle in the double crucible. Using the glasses described and claimed in US Patent Specification No 3 957 342, graded index fibre suitable for a wide range of applications can be produced by this process but the quality is not of the very highest.

The present invention is concerned with optical fibres made from a family of glasses related to those defined in US—A 3 957 342, but modified by the addition of alkaline earth metal oxides. These glasses show considerable potential for the production of high quality graded index fibre by the double crucible method. It is believed that the oxide responsible for the gradation of refractive index is the alkaline earth metal oxide. Glass pairs for fibre core and cladding may readily be produced, the two glasses having significantly different refractive indices. If desired, the glasses may be matched so as to have substantially the same coefficient of thermal expansion but this is not essential.

Previously it has been thought that calcium oxide, for example, was not able to diffuse readily at fibre-drawing temperatures. We have, however, demonstrated that this is incorrect and that calcium oxide and other alkaline earth metal oxides can be used in thermal diffusion techniques for the production of graded index fibre. This represents a major advance in the state of the art with regard to the production of graded index fibre using the double crucible technique.

According to a first aspect of the present invention there is provided a graded index optical fibre drawn from a double crucible having a total insertion loss of less than 20 dB/Km and having a core and cladding, the said optical fibre being characterised in that the core is formed from a melt of a first glass containing between 50 and 70 mole per cent of silica, and 13 to 33 mole per cent of sodium oxide and up to 5 mole per cent of one or more other compatible oxides, and boric oxide, its composition being calculated by taking a particular notional sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Figure 1 of the accompanying drawings, and at least partially replacing sodium oxide or sodium oxide and silica by alkaline earth metal oxide in such a proportion that the total content of alkaline earth metal oxide in the glass melt is less than 20 mole per cent and in that the cladding is formed from a melt of a second glass having a refractive index lower than that of the first glass and having a sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Figure 1, and containing up to 5 mole per cent of one or more other compatible oxides, the compositions of the first and second glasses being selected to exclude compositions which undergo phase separation or devitrification during production in the double crucible and the

gradation of refractive index resulting from a composition gradient caused by thermal diffusion in the double crucible of alkaline earth metal oxide from higher concentrations in the core to lower but finite concentrations in the cladding.

The first glass preferably contains only one alkaline earth metal oxide, and that oxide is preferably calcium oxide or barium oxide.

It appears that any soda-boro-silicate glass falling within the region A of Figure 1 of the accompanying drawings can be modified by the addition of an alkaline earth metal oxide to form a glass suitable for use in the production of optical fibre. The upper limit for silica has been set at about 70 mole per cent because above this limit difficulties in homogenisation and in melting in silica crucibles are encountered. The lower limit for silica has been set at 50 mole per cent because of poor glass durability below this value. The lower limit for sodium oxide has been set at 13 mole per cent because of problems due to phase separation of the glass below this limit and the upper limit has been set at 33 mole per cent because of lack of data on glasses with higher soda content.

Advantageously, the thermal expansivities of the two glasses may be matched, i.e., the proportion of alkaline earth metal oxide in the core glass may be such that the thermal expansion coefficient between 0°C and the glass transition temperature of the substituted glass is substantially the same as that of the soda-boro silicate glass.

If the alkaline earth metal oxide is calcium oxide, thermal expansivity matching may be achieved if substitution of sodium oxide and silica is in such a proportion that the total molar percentage ($\text{Na}_2\text{O} + \text{XCaO}$) in the four-component glass is equal to the molar percentage of Na_2O in the three component glass, where $X = 0.34 \pm 0.03$. The basis of this relationship is given in detail in Example 1 below.

The second or cladding glass may also be formed from a similar melt to the first glass with the partial replacement by an alkaline earth metal oxide. In this case the first glass may contain the oxide of a first alkaline earth metal and the second glass the oxide of a second alkaline earth metal, the atomic number of the said first alkaline earth metal being greater than the atomic number of the second alkaline earth metal.

According to another aspect of the invention there is provided a graded index optical fibre drawn from a double crucible having a total insertion loss of less than 20 Db/Km and having a core and cladding characterised in that the core is formed from a melt of a first glass consisting of:

- a) 50—70 mole per cent of silica
- b) Boric oxide
- c) 13-33 mole per cent of one or more alkali metal oxides selected from sodium oxide and potassium oxide and

d) up to 20 mole per cent of one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide, and, optionally,

e) up to 5 mole per cent of one or more other compatible oxides

and in that the cladding is formed from a melt of a second glass having a refractive index less than that of the first glass and consisting of:

a) Silica

b) Boric oxide

c) one or more alkali metal oxides selected from sodium oxide and potassium oxide, and, optionally,

d) one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide, and also optionally,

e) up to 5 mole per cent of one or more other compatible oxides,

the first and second glass compositions being selected to exclude compositions which undergo phase separation or devitrification during production in the double crucible and the gradation of refractive index resulting from a composition gradient caused by thermal diffusion in the double crucible of alkaline earth metal oxide from higher concentrations in the core to lower but finite concentrations in the cladding.

Advantageously the first and second glasses contain different alkaline earth metal oxides, the oxide of the heavier metal normally being in the first glass. For example the first glass may contain barium oxide and the second glass calcium oxide, or the first glass may contain calcium oxide and the second glass magnesium oxide.

If desired, the thermal expansion coefficients of the core and clad glasses may be matched.

Calcium oxide, barium oxide and strontium oxide all behave similarly in glasses and all of these oxides are suitable additives for the core glass of the fibre according to the invention. The dependence of refractive index on alkaline earth metal oxide content is much stronger for barium oxide than for calcium oxide, so that a given molar percentage of barium oxide should give a fibre of higher numerical aperture than could be produced using the same amount of calcium oxide. Magnesium oxide lowers the refractive index slightly and is therefore useful as an additive to cladding glasses. Possible combinations of alkaline earth metal oxides giving the correct refractive index relationships include the following:

	Core	Cladding
	CaO	—
	SrO	—
	BaO	—
	CaO	MgO
	SrO	MgO
	BaO	MgO
	SrO	CaO
	BaO	CaO
	BaO	SrO

Furthermore, the alkali metal oxide present in the first and second glasses may be either sodium oxide or potassium oxide, giving a further area of

choice. The potash-boro-silicate glass system is in many ways similar to the soda-boro-silicate systems except that the region of stable glass formation is smaller. If, for example, sodium oxide is used in the first glass and potassium oxide in the second glass, sodium-potassium exchange can occur in the double crucible in addition to alkaline earth metal oxide diffusion. The provision of several diffusing species enables a better approach to the optimum refractive index profile to be produced.

One glass pair which has been tested and found to be promising (see Example 5 below) is one in which the first glass contains barium oxide, sodium oxide, silica and boric oxide and the second glass contains calcium oxide potassium oxide, silica and boric oxide. During fibre production sodium-potassium exchange occurs with a fast diffusion coefficient and barium oxide-calcium oxide exchange occurs with a slower diffusion coefficient, the diffusion taking place with little change to the glass network.

As previously indicated, other oxides, referred to as compatible oxides, may be included in the glasses according to the invention up to total of about 5 mole per cent, the only limitation on these additives being that they should not cause substantial worsening of the optical properties for example, absorption loss of the glass. For example, arsenic trioxide may be added, as described in US-A 3 957 342, to stabilise the redox state of the glass, or alumina may be added to improve the chemical durability. The use of the latter additive may be advantageous in the case of glasses containing potassium oxide.

The following Examples illustrate the invention. The batch materials used for the preparation of the various glasses described were commercially available materials. The boric oxide, sodium carbonate, potassium carbonate, alumina and silica used in Examples 1 to 4 typically contained from 0.05 to 0.2 ppm by weight of iron, 0.01 to 0.04 ppm by weight of copper, less than 0.05 ppm by weight of chromium and less than 0.01 ppm of other transition elements. The ultra-pure calcium carbonate and barium carbonate used contained less than 100 parts by weight in 10^9 of manganese, less than 20 parts by weight in 10^9 of iron, less than 10 parts by weight in 10^9 of copper, less than 10 parts by weight in 10^9 of nickel, less than 30 parts by weight in 10^9 of chromium and less than 5 parts by weight in 10^9 of cobalt. Less pure materials were used in Examples 5 and 6.

In the Examples reference will be made to the accompanying drawings, in which:

Fig. 1 shows a triaxis plot of the soda-boro-silicate glass system.

Fig. 2 shows a refractive index profile of the optical fibre of the invention described in Example 1,

Fig. 3 shows a plot of total insertion loss against wavelength for the fibre of Example 1.

Fig. 4 shows the pulse width response for the fibre of Example 1,

Fig. 5 shows the refractive index profile of the fibre of Example 2.

Fig. 6 shows the refractive index profile of the fibre of Example 3.

Fig. 7 shows the refractive index profile of the fibre of Example 4,

Fig. 8 shows the refractive index profile of the fibre of Example 5,

Fig. 9 shows the refractive index profile of the fibre of Example 6,

Fig. 10 shows a triaxis plot of thermal expansion coefficient and refractive index data for the soda-lime-silicate glass system based on published data, and

Fig. 11 shows a triaxis plot of thermal expansion coefficient data for the soda-boro-silicate glass system based on published data.

Comparative Example

Referring to Fig. 1 of the accompanying drawings, points representing two soda-borosilicate glasses which have been used to produce graded index optical fibre by thermal diffusion with a double crucible are labelled 1 and 2, 1 being the core glass and 2 the cladding glass. Graded index fibre produced from these glasses had a total optical loss of 9-15 dB/km, a part of which was of unknown origin, ie, due neither to absorption loss nor to Rayleigh scatter loss. The pulse broadening of this fibre was in the range of from 1-5 ns/km. Furthermore, when viewed optically, the core displayed a ring structure of uncertain origin. Finally, the numerical aperture had a typical value of 0.12. While this fibre is of use for certain applications, it is not ideal for telecommunications purposes. The low pulse broadening is probably caused at least in part by inter-mode coupling which would account for the poor total loss. It is suspected that the visible ring may in some way be produced by thermal mismatch between the core and cladding glasses. The diffusing species producing the graded index in this glass pair is of course sodium oxide. Using soda-borosilicate glasses the problem of obtaining a thermal expansion match between core and cladding and at the same time getting a reasonably large numerical aperture by obtaining a significant difference between core and cladding refractive indices is extremely difficult to solve. For this reason it was decided to look into the possibility of modifying the simple soda-boro-silicates by the addition of a further oxide.

Despite the fact that calcium oxide would appear to be an unlikely material to use because it was believed to have a low diffusion coefficient, it was decided to try this material because there was a little ultra-pure calcium carbonate available in the laboratory at a time when no other ultra-pure materials apart from boric oxide, silica and sodium carbonate were available. Much to our surprise we discovered that, contrary to previously held beliefs, calcium

oxide was capable of diffusing at the drawing temperature of the optical fibres with a diffusion coefficient of from 10^{-8} to 10^{-7} cm² sec⁻¹, only very slightly slower than that of sodium oxide. The explanation for this discovery would appear to be that previous measurements of diffusion, coefficient for calcium oxide were made at or below the glass transition temperature where the diffusion coefficient of calcium oxide is at least 100 times lower than that for sodium oxide. Calcium oxide has, however a high activation energy for diffusion. This means that the diffusion coefficient increases with temperature much more rapidly for calcium oxide than for sodium oxide, hence the high diffusion coefficient for calcium oxide at the fibre drawing temperature.

Example 1

A core glass was produced having the following composition: sodium oxide 22.30 mole per cent, boric oxide 15.00 mole per cent, silica 54.70 mole per cent, calcium oxide 8 mole per cent. The glass was prepared by the method described in detail in US-A 3 957 342, ie. appropriate batch material was melted to produce molten glass, and a mixture of carbon monoxide and carbon dioxide was bubbled through the molten glass in order simultaneously to optimise the redox state of the glass and to homogenise and dry it. The glass also contained about 0.1 mole per cent of arsenic trioxide as a redox buffering oxide, as also described in US-A No 3 957 342.

The glass composition was derived from a notional soda-boro-silicate composition of sodium oxide 25.00 mole per cent, boric oxide 15.00 mole per cent and silica 60.00 mole per cent (indicated by point 3 in Fig. 1), the calcium oxide replacing both soda and silica.

A graded index fibre was drawn using the four-component glass described above for the core and, for the cladding, a soda-boro-silicate glass of the composition given in the previous paragraph. The fibre was drawn using a Johnson Mathey platinum double crucible with a 10 cm nozzle. The core diameter of the fibre was 46 microns.

The refractive index profile of the fibre is shown in Fig. 2. This is slightly over-diffused profile, ie, too much diffusion has occurred to give the optimal parabolic refractive index distribution. The extent of diffusion ϕ , which ideally should have a value of from 0.06 to 0.08, was calculated from the measured profile to have a value of 0.20. The quantity ϕ is given by the equation:

$$\phi = \frac{Dt}{A^2} = \frac{DL}{a^2v}$$

where D is the diffusion coefficient (dependent on temperature).

t is the residence time of the glass in the nozzle (also temperature-dependent),

A is the radius of the core stream in the double crucible,

L is the length of the diffusion nozzle of the double crucible.

a is the radius of the fibre, and

v is the pulling speed of the fibre.

It will be seen that the extent of diffusion can be reduced without much difficulty, by, for example, reducing the length of the nozzle, increasing the pulling speed or decreasing the core size. Increasing the amount of diffusion is much more difficult.

Fig. 3 shows a plot of total insertion loss against wavelength for full numerical aperture launch. From this Figure it can be seen that the total insertion loss of the fibre at 850 to 900 nanometres is 8.2 Db/km. The absorption loss at selected wavelengths is indicated on Fig. 3 by a series of crosses, showing the scatter loss to be approximately 2.5 Db/km which approaches the theoretically predicted loss due to Rayleigh scattering. This means that pulse width measurements on this fibre will give meaningful results. The pulse width of a one-nanosecond pulse after transmission through 1.91 km of fibre is shown in Fig. 4. From this it can be shown that the pulse broadening for the fibre is 2.8 ns/km.

The numerical aperture was calculated from the refractive index profile to be 0.18. As will be seen below (Examples 5 and 6) the use of barium oxide instead of calcium oxide in the core glass gives higher numerical aperture values the use of a higher proportion of calcium oxide has a similar but less marked effect.

From the various figures quoted above it will be apparent that this glass pair is an extremely good combination to use for high-bandwidth low-loss graded index fibre. Successive lengths of fibre drawn from this glass pair gave completely reproducible properties, as did fibre from different fibre batches. It will be noted that the composition of the core glass was computed from the clad glass composition in accordance with the equation



mentioned above, ie. the thermal expansivities of the core and clad glasses are matched. The matching was tested by melting samples of the two glasses, one on top of the other, in a crucible, and then cooling, annealing and sectioning the resulting composite. The sample obtained was free from cracks and exhibited only minor stress at the interface when examined in a strain viewer. This indicates that both glasses has substantially the same thermal expansion coefficient.

The matching occurs because the substitution of calcium oxide for sodium oxide and silica has been carried out in such a manner

that glass compositions with increasing calcium oxide lie on a line of constant expansion coefficient. In Fig. 10 lines of equal expansion coefficient for the soda-lime-silicate systems are shown. In Fig. 11 lines of equal expansion coefficient for the soda-boro-silicate system are shown. Figs. 10 and 11 are based on published data originating from different sources. While the data for both Figs. 10 and 11 are reasonably internally consistent, there is disagreement between the absolute values. To overcome this problem, it has been assumed that, in the region of interest, the expansivity of soda-boro-silicate glasses is independent of the ratio of boric oxide to silica this can be clearly seen from Fig. 11. Turning to Fig. 10, in terms of expansivity boric oxide and silica can be regarded as the same material so that only the variation of expansivity with sodium oxide and calcium oxide need be considered. The equation of a line of constant expansivity in the soda-lime-silicate system is therefore determined. For the line marked "B" in Fig. 10 the equation is

$$\text{Na}_2\text{O} \pm 0.34\text{CaO} = \text{Na}_2\text{O}$$

content of the binary soda-silicate glass having a given thermal expansion coefficient. By varying sodium oxide and calcium oxide in accordance with this equation glasses having the same thermal expansion coefficient will be produced. The coefficient of 0.34 appearing in the above equation should not vary appreciably with varying glass compositions in the region A of Fig. 1. since when these are transposed to Fig. 10, the lines of constant expansion coefficient are all substantially parallel.

Example 2

A fibre was prepared from a core glass having a composition as described in Example 1 and a cladding glass having the composition sodium oxide 25.00 mole per cent, boric oxide 12.50 mole per cent and silica 62.50 mole per cent. The clad composition is represented by point 4 on Fig. 1. The glass was prepared as described in Example 1 and the fibre was again drawn using a Johnson Mathey platinum double crucible with a 10 cm nozzle: the core diameter was 53 microns.

The refractive index profile is shown in Fig. 5. The extent of diffusion ϕ was calculated to be 0.05, ie, the fibre is slightly under diffused.

The best loss value on this fibre was found to be 6.5 Db/km at 850 nm, and the pulse broadening was about 2 ns/km. The maximum numerical aperture was 0.197.

This glass pair is clearly suitable for use in the production of high-bandwidth low-loss graded index fibre. Use of barium oxide instead of calcium oxide in the core should result in a higher numerical aperture.

Example 3

Graded-index fibre was produced from a core glass having the composition sodium oxide 17.30 mole per cent, boric oxide 17.50 mole per cent,

calcium oxide 8.00 mole per cent, silica 57.20 mole per cent and a clad glass having the composition sodium oxide 20.00 mole per cent, boric oxide 17.50 mole per cent and silica 62.50 mole per cent. The glasses were prepared as described in Example 1. The clad composition is represented by point 5 on Fig. 1, and the core composition is derived from that composition by substitution of calcium oxide, to an extent of 8.00 mole per cent, for soda and silica.

The fibre was drawn using a Johnson Mathey platinum double crucible with a 10 cm nozzle. The core diameter of the fibre was 46 microns. Its refractive index profile is shown in Fig. 6; this is a slightly under-diffused profile, the ϕ -value being approximately 0.04. The best loss value obtained with this fibre was 6.4 dB/km at 850 nm.

Example 4

A soda-boro-silicate glass having the composition sodium oxide 22.50 mole per cent, boric oxide 17.50 mole per cent and silica 60.00 mole per cent (point 6 on Fig. 1) was chosen as a suitable cladding glass for graded index fibre and this time a core composition was selected by replacing soda only, not soda and silica, by calcium oxide. The core composition was sodium oxide 15.00 mole per cent, boric oxide 17.50 mole per cent, calcium oxide 7.50 mole per cent and silica 60.00 mole per cent. Both glasses were prepared as described in Example 1.

Fibre was drawn from this glass pair using a Johnson Mathey platinum double crucible with a 10 cm nozzle. The core diameter was 40 microns. The refractive index profile is shown in Fig. 7; the ϕ -value was calculated to be 0.06, which is at the lower end of the ideal range. The maximum numerical aperture was 0.150, and the best loss value was 9.0 dB/km at 850 nm.

It will be seen that this glass pair is exceptionally suitable for the production of low-loss graded-index optical fibre.

Example 5

A core glass having the following composition was prepared: sodium oxide 19.27 mole per cent, boric oxide 7.23 mole per cent, barium oxide 12.04 mole per cent, alumina 3.62 mole per cent, silica 57.82 mole per cent. The clad glass chosen had the following composition: potassium oxide 19.27 mole per cent, boric oxide 7.23 mole per cent, calcium oxide 12.04 mole per cent, alumina 3.62 mole per cent, silica 57.82 mole per cent. It will be noted that the percentages of silica and of boric oxide are the same in core and cladding, and the molar percentages of the monovalent diffusing species (Na^+ and K^+) and of the divalent diffusing species (Ba^{2+} and Ca^{2+}) are matched. The alumina was included to improve the chemical durability of the glass. The starting materials used in this Example were not of such high purity as in the previous Examples, and the gas bubbling stage was omitted. Because of this it was not possible to obtain loss and pulse-broadening measurements on the fibre produced in this run, which was

carried out purely in order to obtain a refractive index profile.

Fibre having a core diameter of 55 microns was drawn using a Johnson Mathey platinum double crucible with a 10 cm nozzle. The refractive index profile is shown in Fig. 8. The ϕ -value was 0.08, the best yet obtained with this class of glasses, and the maximum numerical aperture was 0.21. It will be seen that this pair is extremely promising for use in the production of graded-index fibre.

Example 6

This Example illustrates the use of barium oxide in the core and calcium oxide in the clad, all other components of the two glasses being the same. As in Example 5 the starting materials were not sufficiently pure for loss and pulse-broadening measurements to be carried out.

The core composition was sodium oxide 20.00 mole per cent, boric oxide 10.00 mole per cent, barium oxide 10.00 mole per cent and silica 60.00 mole per cent, and the clad composition was identical except that 10.00 mole per cent of calcium oxide replaced the 10.00 mole per cent of barium oxide. Fibre having a core diameter of 80 microns was drawn in an Engelhard platinum double crucible with a 10 cm nozzle.

The refractive index profile is shown in Fig. 9. The ϕ -value was calculated to be about 0.02, ie, the fibre was considerably under-diffused. This is believed to be largely attributable to the fact that it was made in a crucible designed for large-core slightly-graded fibre; the use of the Johnson Mathey crucible used in Examples 1 to 5 would be expected on the basis of previous experiments, to increase significantly the extent of diffusion. The maximum numerical aperture of the fibre was 0.210.

Claims

1. A graded index optical fibre drawn from a double crucible having a total insertion loss of less than 20 Db/Km and having a core and cladding, the said optical fibre being characterised in that the core is formed from a melt of a first glass containing between 50 and 70 mole per cent of silica, and 13 to 33 mole per cent of sodium oxide and up to 5 mole per cent of one or more other compatible oxides, and boric oxide, its composition being calculated by taking a particular notional sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Figure 1 of the accompanying drawings, and at least partially replacing sodium oxide or sodium oxide and silica by alkaline earth metal oxide in such a proportion that the total content of alkaline earth metal oxide in the glass melt is less than 20 mole per cent and in that the cladding is formed from a melt of a second glass having a refractive index lower than that of the first glass and having a sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Figure 1, and containing up to 5 mole per cent of one or more other compatible

oxides, the compositions of the first and second glasses being selected to exclude compositions which undergo phase separation or devitrification during production in the double crucible and the gradation of refractive index resulting from a composition gradient caused by thermal diffusion in the double crucible of alkaline earth metal oxide from higher concentrations in the core to lower but finite concentrations in the cladding.

2. A graded index optical fibre drawn from a double crucible having a total insertion loss of less than 20 dB/Km and having a core and cladding, the said optical fibre being characterised in that the core and cladding are formed respectively from melts of first and second glasses each containing between 50 and 70 mole per cent of silica, and 13 to 33 mole per cent of sodium oxide and up to 5 mole per cent of one or more other compatible oxides, and boric oxide, their compositions being calculated by taking a particular notional sodium oxide-boric oxide-silica composition lying within the range defined by Region A of Figure 1 of the accompanying drawings, and at least partially replacing sodium oxide or sodium oxide and silica by alkaline earth metal oxide in such a proportion that the total content of alkaline earth metal oxide in each glass melt is less than 20 mole per cent and in that the second glass has a refractive index lower than that of the first glass, the compositions of the first and second glasses being selected to exclude compositions which undergo phase separation or devitrification during production in the double crucible and the gradation of refractive index resulting from a composition gradient caused by thermal diffusion in the double crucible of alkaline earth metal oxide from higher concentrations in the core to lower but finite concentrations in the cladding.

3. An optical fibre as claimed in Claim 2 characterised in that the first glass contains the oxide of a first alkaline earth metal and the second glass contains the oxide of a second alkaline earth metal, the atomic number of the said first alkaline earth metal being greater than the atomic number of the said second alkaline earth metal.

4. An optical fibre as claimed in any one of the preceding claims characterised in that the composition of the first and second glasses are based on the same notional sodium oxide-boric oxide-silica composition.

5. A graded index optical fibre drawn from a double crucible having a total insertion loss of less than 20 dB/Km and having a core and cladding characterised in that the core is formed from a melt of a first glass consisting of:

a) 50-70 mole per cent of silica

b) Boric oxide

c) 13-33 mole per cent of one or more alkaline earth metal oxides selected from sodium oxide and potassium oxide and

d) up to 20 mole per cent of one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide, and, optionally,

e) up to 5 mole per cent of one or more other compatible oxides

and in that the cladding is formed from a melt of a second glass having a refractive index less than that of the first glass and consisting of:

a) Silica

b) Boric oxide

c) one or more alkali metal oxides selected from sodium oxide and potassium oxide, and, optionally,

d) one or more alkaline earth metal oxides selected from calcium oxide, strontium oxide and barium oxide, and also optionally,

e) up to 5 mole per cent of one or more other compatible oxides, the first and second glass compositions being selected to exclude compositions which undergo phase separation or devitrification during production in the double crucible and the gradation of refractive index resulting from a composition gradient caused by thermal diffusion in the double crucible of alkaline earth metal oxide from higher concentrations in the core to lower but finite concentrations in the cladding.

Patentansprüche

1. Aus einem Doppeltiegel gezogene optische Faser abgestuften Index' mit einem Gesamteinführungsverlust von weniger als 20 dB/km und einem Kern und einer Hülle, welche optische Faser dadurch gekennzeichnet ist, daß der Kern aus einer Schmelze eines ersten Glases gebildet ist, das zwischen 50 und 70 Mol-% Siliziumoxid und 13 bis 33 Mol-% Natriumoxid und bis zu 5 Mol-% eines oder mehrerer verträglicher Oxide und Boroxid enthält, wobei seine Zusammensetzung berechnet wird, indem man eine besondere, begriffliche, im durch den Bereich A der Fig. 1 der zugehörigen Zeichnungen definierten Bereich liegende Natriumoxid-Boroxid-Siliziumoxid Zusammensetzung nimmt und wenigstens teilweise Natriumoxid oder Natriumoxid und Siliziumoxid durch Erdalkalimetalloxid in einem solchen Anteil ersetzt, daß der gesamte Erdalkalimetalloxidgehalt in der Glasschmelze weniger als 20 Mol-% ist, und daß die Hülle aus der Schmelze eines zweiten Glases mit einem niedrigeren Brechungsindex als dem des ersten Glases und mit einer Natriumoxid-Boroxid-Siliziumoxid-Zusammensetzung gebildet ist, die im durch den Bereich A der Fig. 1 definierten Bereich liegt und bis zu 5 Mol-% eines oder mehrerer verträglicher Oxide enthält, wobei die Zusammensetzungen der ersten und zweiten Gläser gewählt sind, um Zusammensetzungen auszuschließen, die während der Herstellung im Doppeltiegel und der Abstufung des Brechungsindex, aufgrund eines durch thermische Diffusion des Erdalkalimetalloxids im Doppeltiegel von höheren Konzentrationen im Kern zu niedrigeren, jedoch bestimmten Konzentrationen in der Hülle verursachten Zusammensetzungsgradienten eine Phasentrennung oder Entglasung durchmachen.

2. Aus einem Doppeltiegel gezogene optische

Faser abgestuften Index' mit einem Gesamteinführungsverlust von weniger als 20 dB/km und einem Kern und einer Hülle, welche optische Faser dadurch gekennzeichnet ist, daß der Kern und die Hülle aus Schmelzen eines ersten bzw. eines zweiten Glases gebildet sind, deren jedes zwischen 50 und 70 Mol-% Siliziumoxid und 13 bis 33 Mol-% Natriumoxid und bis zu 5 Mol-% eines oder mehrerer verträglicher Oxide und Boroxid enthält, wobei ihre Zusammensetzungen berechnet werden, indem man eine besondere, begriffliche, im durch den Bereich A der Fig. 1 der zugehörigen Zeichnungen definierten Bereich liegende Natriumoxid-Boroxid-Siliziumoxid-Zusammensetzung nimmt und wenigstens teilweise Natriumoxid oder Natriumoxid und Siliziumoxid durch Erdalkalimetalloxid in einem solchen Anteil ersetzt, daß der gesamte Erdalkalimetalloxidgehalt in jeder Glasschmelze weniger als 20 Mol-% ist, und daß das zweite Glas einen niedrigeren Brechungsindex als den des ersten Glases hat, wobei die Zusammensetzungen der ersten und zweiten Gläser gewählt sind, um Zusammensetzungen auszuschließen, die während der Herstellung im Doppeltiegel und der Abstufung des Brechungsindex' aufgrund eines durch thermische Diffusion des Erdalkalimetalloxids im Doppeltiegel von höheren Konzentrationen im Kern zu niedrigeren, jedoch bestimmten Konzentrationen in der Hülle verursachten Zusammensetzungsgradienten eine Phasentrennung oder Entglasung durchmachen.

3. Optische Faser nach Anspruch 2, dadurch gekennzeichnet, daß das erste Glas das Oxid eines ersten Erdalkalimetalls enthält und das zweite Glas das Oxid eines zweiten Erdalkalimetalls enthält, wobei die Ordnungszahl des ersten Erdalkalimetalls größer als die Ordnungszahl des zweiten Erdalkalimetalls ist.

4. Optische Faser nach irgendeinem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Zusammensetzung der ersten und zweiten Gläser auf der gleichen begrifflichen Natriumoxid-Boroxid-Siliziumoxid-Zusammensetzung basieren.

5. Aus einem Doppeltiegel gezogene optische Faser abgestuften Index' mit einem Gesamteinführungsverlust von weniger als 20 dB/km und einem Kern und einer Hülle, dadurch gekennzeichnet,

daß der Kern aus einer Schmelze eines ersten Glases gebildet ist, das besteht aus:

a) 50-70 Mol-% Siliziumoxid

b) Boroxid

c) 13-33 Mol-% eines oder mehrerer aus Natriumoxid und Kaliumoxid gewählten Alkalimetalloxide und

d) bis zu 20 Mol-% eines oder mehrerer aus Kalziumoxid, Strontiumoxid und Bariumoxid gewählten Erdalkalimetalloxide und, wahlweise

e) bis zu 5 Mol-% eines oder mehrerer anderer verträglicher Oxide,

und daß die Hülle aus einer Schmelze eines zweiten Glases gebildet ist, das einen geringeren Brechungsindex als den des ersten Glases hat

und besteht aus:

- a) Siliziumoxid
- b) Boroxid
- c) einem oder mehreren aus Natriumoxid und Kaliumoxid gewählten Alkalimetalloxiden und, wahlweise,
- d) einem oder mehreren aus Kalziumoxid, Strontiumoxid und Bariumoxid gewählten Erdalkalimetalloxiden und, auch wahlweise,
- e) bis zu 5 Mol-% eines oder mehrerer anderer verträglicher Oxide, wobei die ersten und zweiten Glaszusammensetzungen gewählt sind, um Zusammensetzungen auszuschließen, die während der Herstellung im Doppeltiegel und der Abstufung des Brechungsindex, aufgrund eines durch thermische Diffusion des Erdalkalimetall-oxids im Doppeltiegel von höheren Konzentrationen im Kern zu niedrigeren, jedoch bestimmten Konzentrationen in der Hülle verursachten Zusammensetzungsgradienten eine Phasentrennung oder Entglasung durchmachen.

Revendications

1. Fibre optique à indice gradué, étirée à partir d'un double creuset dont la perte totale d'insertion est inférieure à 20 dB/km, et ayant un coeur et une gaine, la fibre optique étant caractérisée en ce que le coeur est formé à partir d'une fusion d'un premier verre contenant entre 50 et 70 moles pour cent de silice, et 13 jusqu'à 33 moles pour cent d'oxyde de sodium et jusqu'à 5 moles pour cent d'un ou de plusieurs autres oxydes compatibles, et d'oxyde borique, sa composition étant calculée en prenant une composition particulière calculée oxyde de sodium-oxyde borique-silice située à l'intérieur de la gamme définie par la région A sur la figure 1 des dessins ci-annexés, et au moins en remplaçant partiellement l'oxyde de sodium ou l'oxyde de sodium et la silice par un oxyde métallique alcalino-terreux dont la proportion est telle que la teneur totale en oxyde métallique alcalino-terreux dans la fusion de verre est inférieure à 20 moles pour cent, et en ce que la gaine est constituée à partir d'une fusion d'un second verre ayant un indice de réfraction inférieur à celui du premier verre et ayant une composition oxyde de sodium-oxyde borique-silice située à l'intérieur de la gamme définie par la région A de la figure 1, et contenant jusqu'à 5 moles pour cent d'un ou de plusieurs autres oxydes compatibles, les compositions des premier et second verres étant choisies de manière à exclure les compositions qui subissent une séparation de phase ou une dévitrification pendant la production dans le double creuset et la graduation de l'indice de réfraction résultant d'un gradient de composition provoqué par une diffusion thermique dans le double creuset d'oxyde métallique alcalino-terreux depuis les concentrations supérieures dans le coeur jusqu'aux concentrations inférieures mais finies dans la gaine.

2. Fibre optique à indice gradué, étirée à partir d'un double creuset ayant une perte totale d'insertion inférieure à 20 dB/km et ayant un coeur et

une gaine, la fibre optique étant caractérisée en ce que le coeur et la gaine sont respectivement constitués à partir de fusions des premier et second verres contenant chacune entre 50 et 70 moles pour cent de silice, et 13 à 33 moles pour cent d'oxyde de sodium et jusqu'à 5 moles pour cent d'un ou de plusieurs autres oxydes compatibles, et d'oxyde borique, leurs compositions étant calculées en prenant une composition particulière calculée oxyde de sodium-oxyde borique-silice située à l'intérieur de la gamme définie par la région A sur la figure 1 des dessins ci-annexés, et au moins en remplaçant partiellement l'oxyde de sodium ou l'oxyde de sodium et la silice, par un oxyde métallique alcalino-terreux dont la proportion est telle que la teneur totale en oxyde métallique alcalino-terreux de chaque fusion de verre est inférieure à 20 moles pour cent, et en ce que le second verre présente un indice de réfraction inférieur à celui du premier verre et les compositions des premier et second verres étant choisies de façon à exclure les compositions qui subissent une séparation de phase ou une dévitrification pendant la production dans le double creuset et la graduation de l'indice de réfraction résultant d'un gradient de composition provoqué par une diffusion thermique et dans le double creuset d'oxyde métallique alcalino-terreux depuis des concentrations supérieures dans le coeur jusqu'à des concentrations inférieures mais finies dans la gaine.

3. Fibre optique selon la revendication 2, caractérisée en ce que le premier verre contient l'oxyde d'un premier métal alcalino-terreux et le second verre contient l'oxyde d'un second métal alcalino-terreux, le nombre atomique du premier métal alcalino-terreux étant supérieur au nombre atomique du second métal alcalino-terreux.

4. Fibre optique selon l'une quelconque des revendications précédentes, caractérisée en ce que la composition des premier et second verres est basée sur le même composition calculée oxyde de sodium-oxyde borique-silice.

5. Fibre de verre optique à indice gradué étirée à partir d'un double creuset ayant une perte d'insertion totale inférieure à 20 dB/km et ayant un coeur et une gaine, caractérisée en ce que le coeur est formé à partir d'une fusion d'un premier verre consistant en:

- a) 50 à 70 moles pour cent de silice,
- b) oxyde borique,
- c) 13 à 33 moles pour cent d'un ou de plusieurs oxydes métalliques alcalins choisis entre l'oxyde de sodium et l'oxyde de potassium et
- d) jusqu'à 20 moles pour cent d'un ou de plusieurs oxydes métalliques alcalino-terreux choisis parmi l'oxyde de calcium, l'oxyde de strontium et l'oxyde de baryum et éventuellement,

e) jusqu'à 5 moles pour cent d'un ou de plusieurs autres oxydes compatibles,

et en ce que la gaine est formée à partir d'une fusion d'un second verre ayant un indice de réfraction inférieur à celui du premier verre et consistant en:

- a) silice,
- b) oxyde borique,
- c) un ou plusieurs oxydes métalliques alcalins choisis entre l'oxyde de sodium et l'oxyde de potassium, et éventuellement,
- d) un ou plusieurs oxydes métalliques alcalino-terreux choisis parmi l'oxyde de calcium, l'oxyde de strontium et l'oxyde de baryum, ainsi qu'éventuellement
- e) jusqu'à 5 moles pour cent d'un ou plusieurs autres oxydes compatibles, les compositions des

premier et second verres étant choisies de manière à exclure des compositions qui subissent une séparation de phase ou une dévitrification pendant la fabrication dans le double creuset et la graduation de l'indice de réfraction résultant d'un gradient de composition provoqué par diffusion thermique dans le double creuset d'oxyde métallique alcalino-terreux depuis des concentrations supérieures dans le coeur jusqu'à des concentrations inférieures mais finies dans la gaine.

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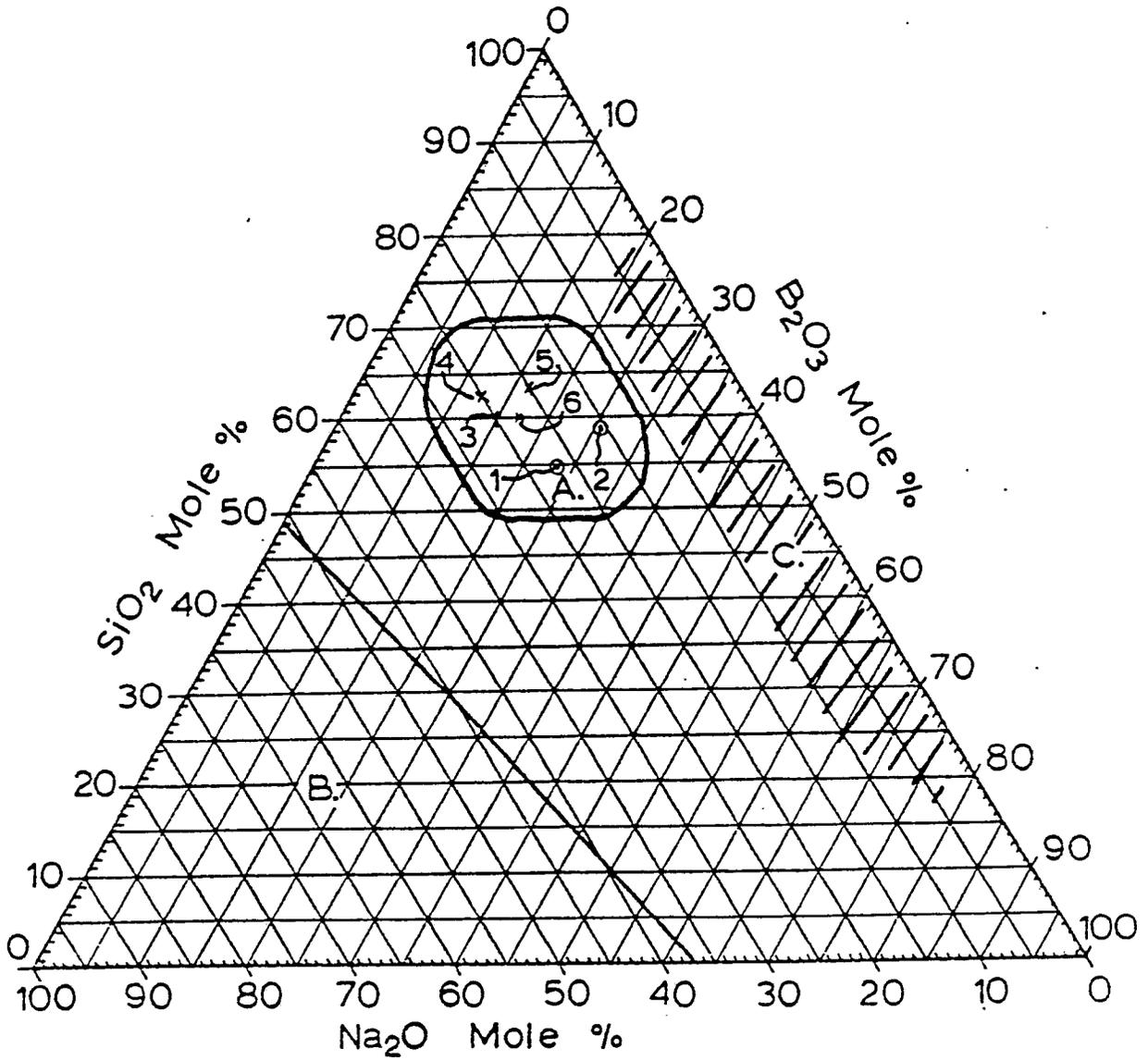


Fig. 1

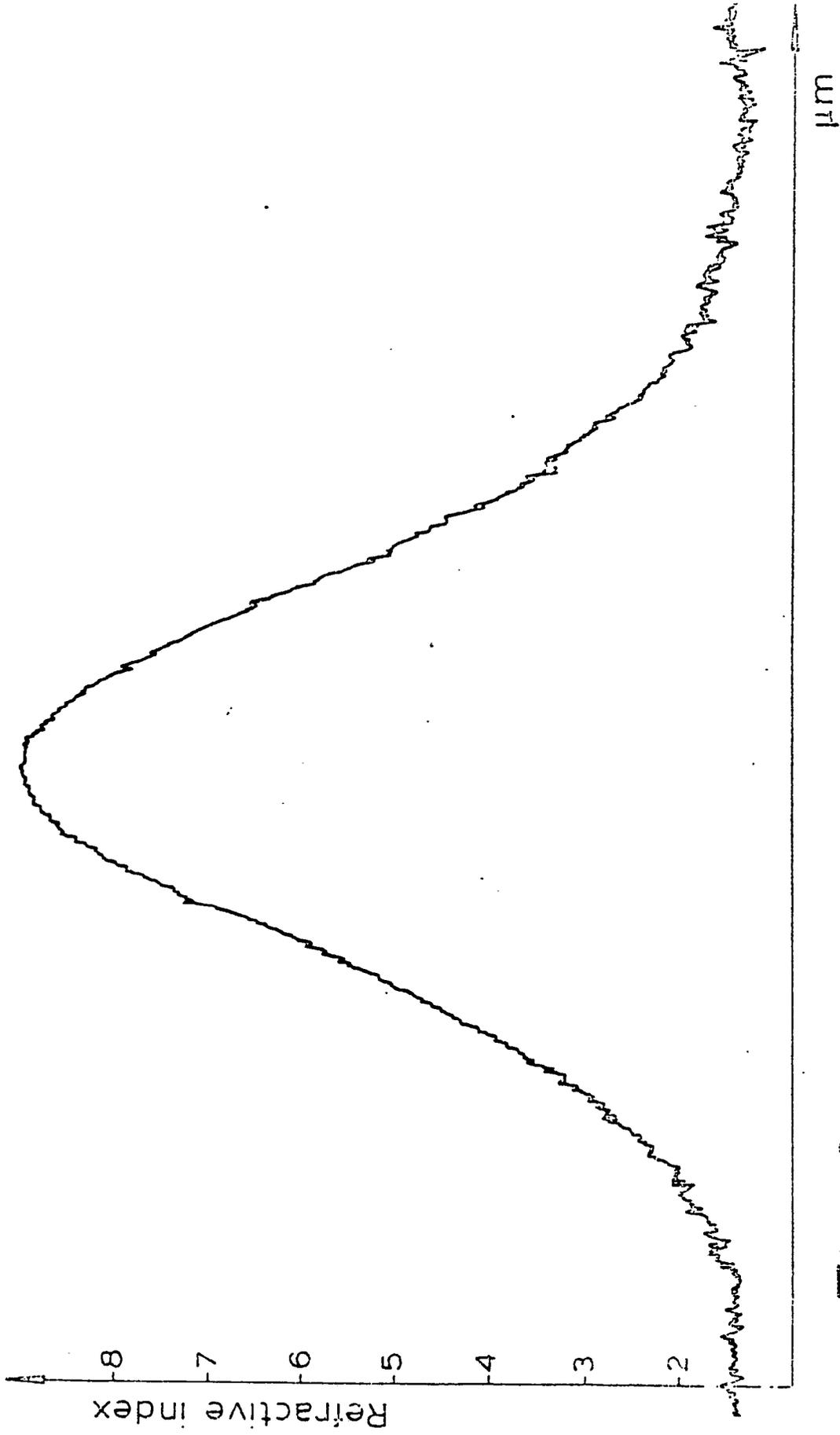


Fig. 2

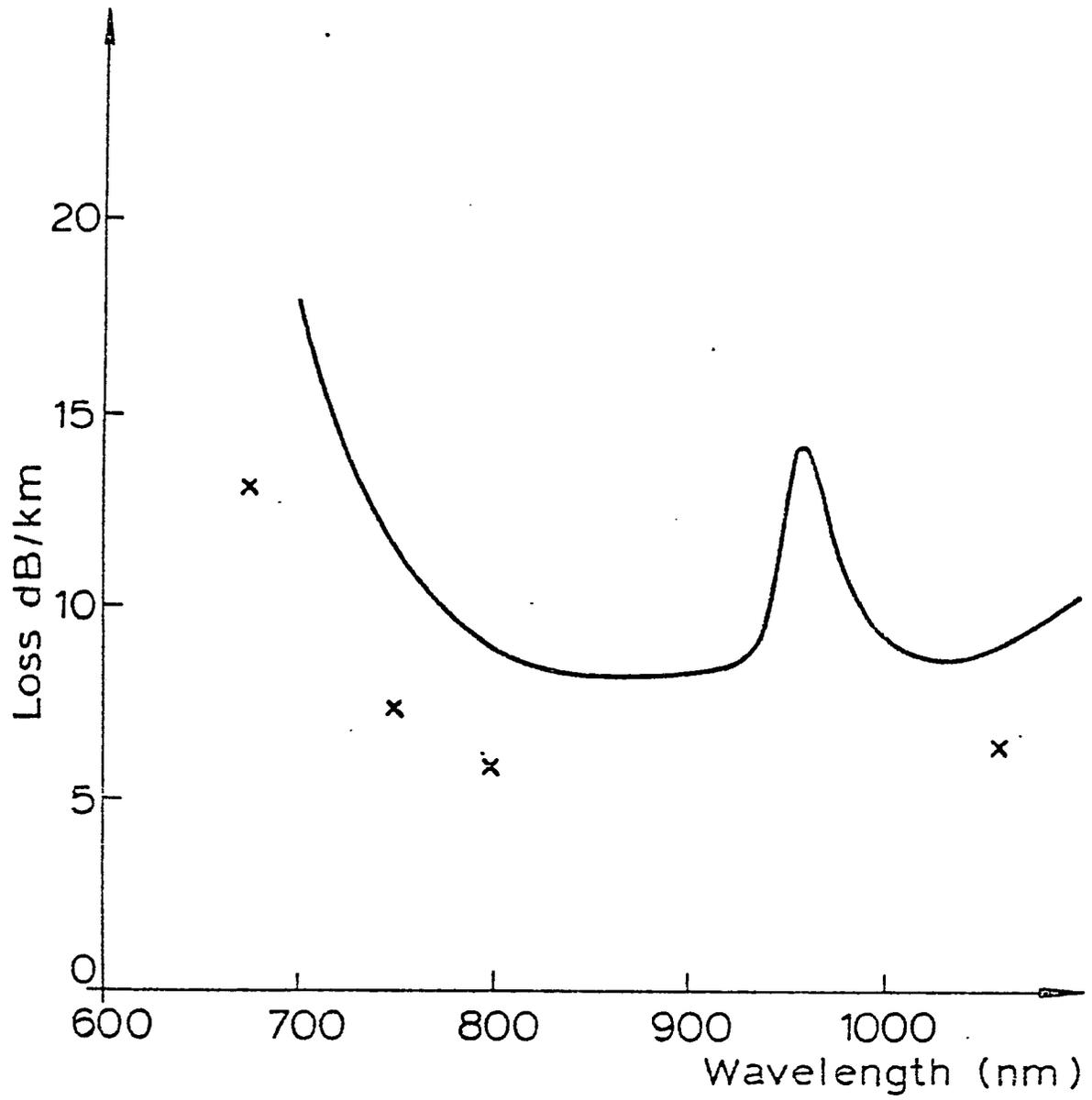


Fig. 3

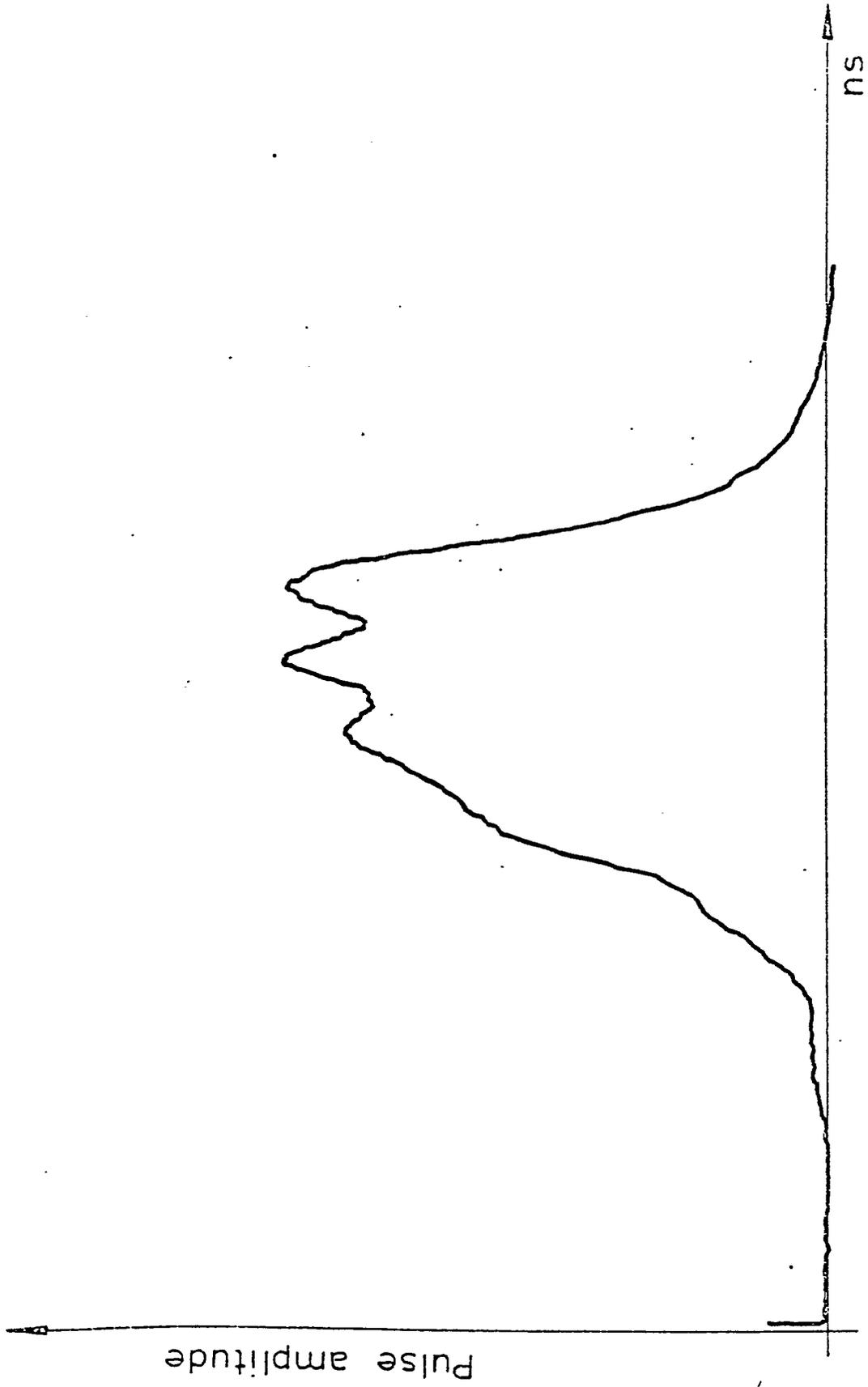


Fig. 4

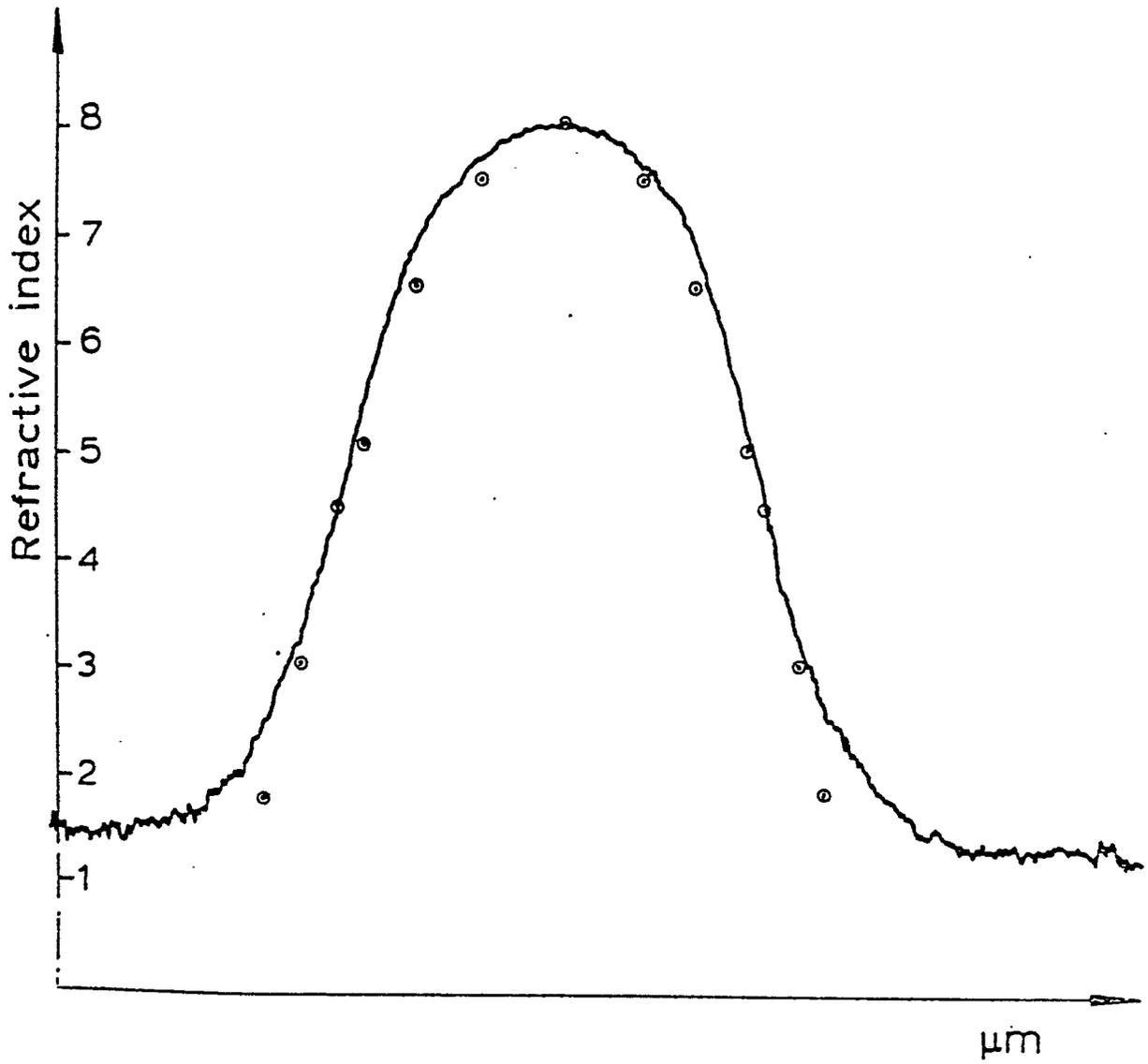


Fig. 5

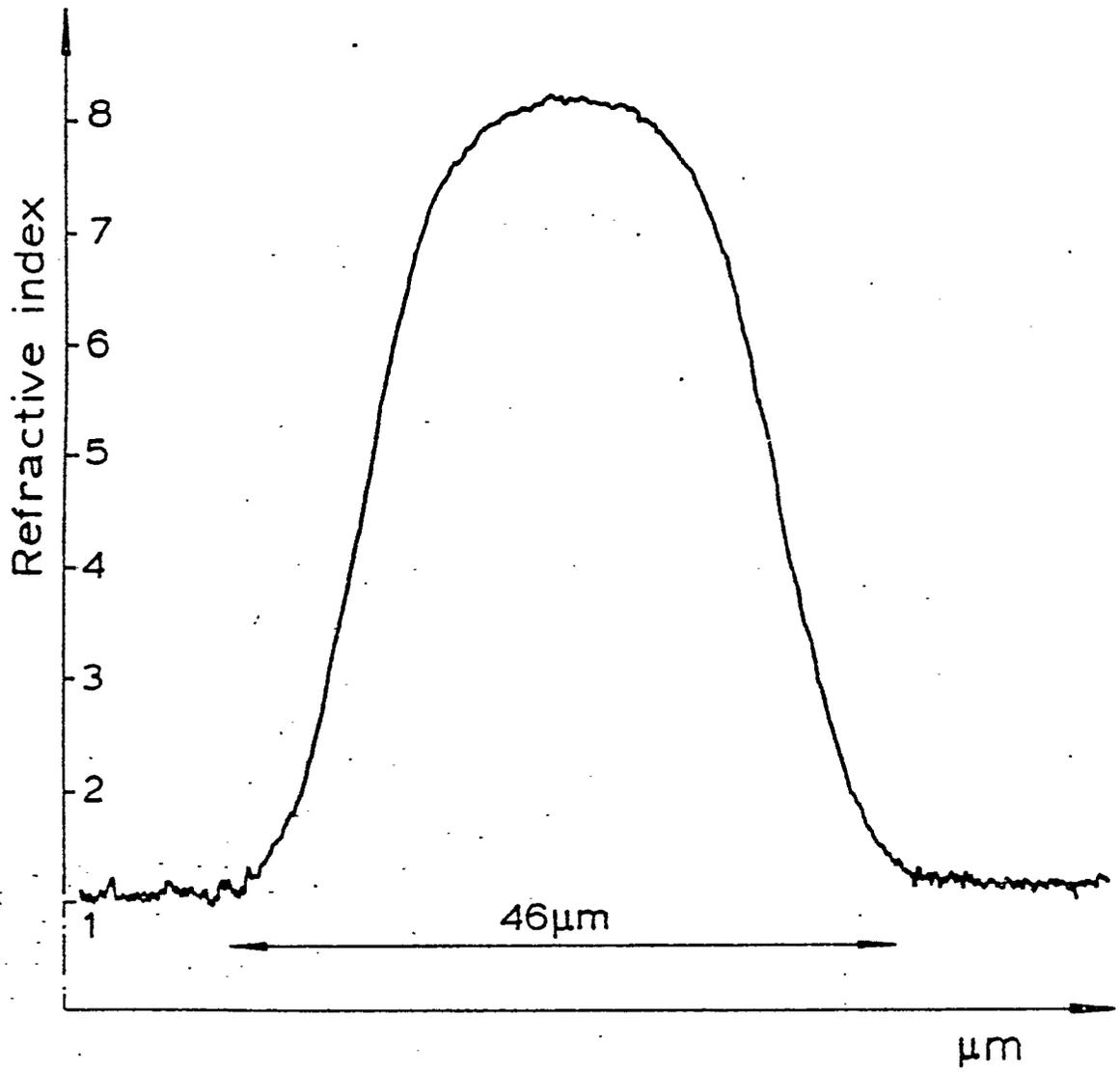


Fig. 6

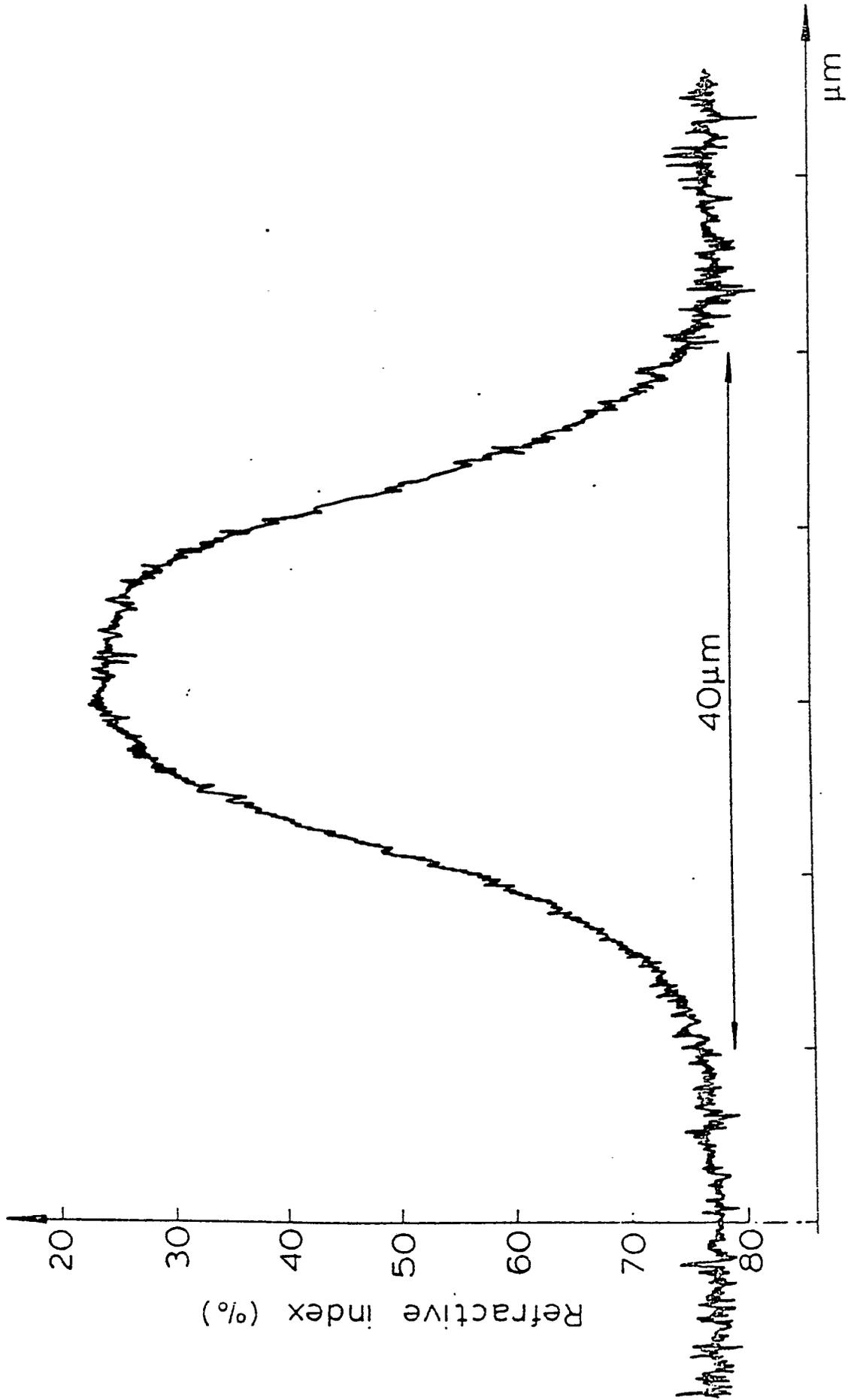


Fig. 7

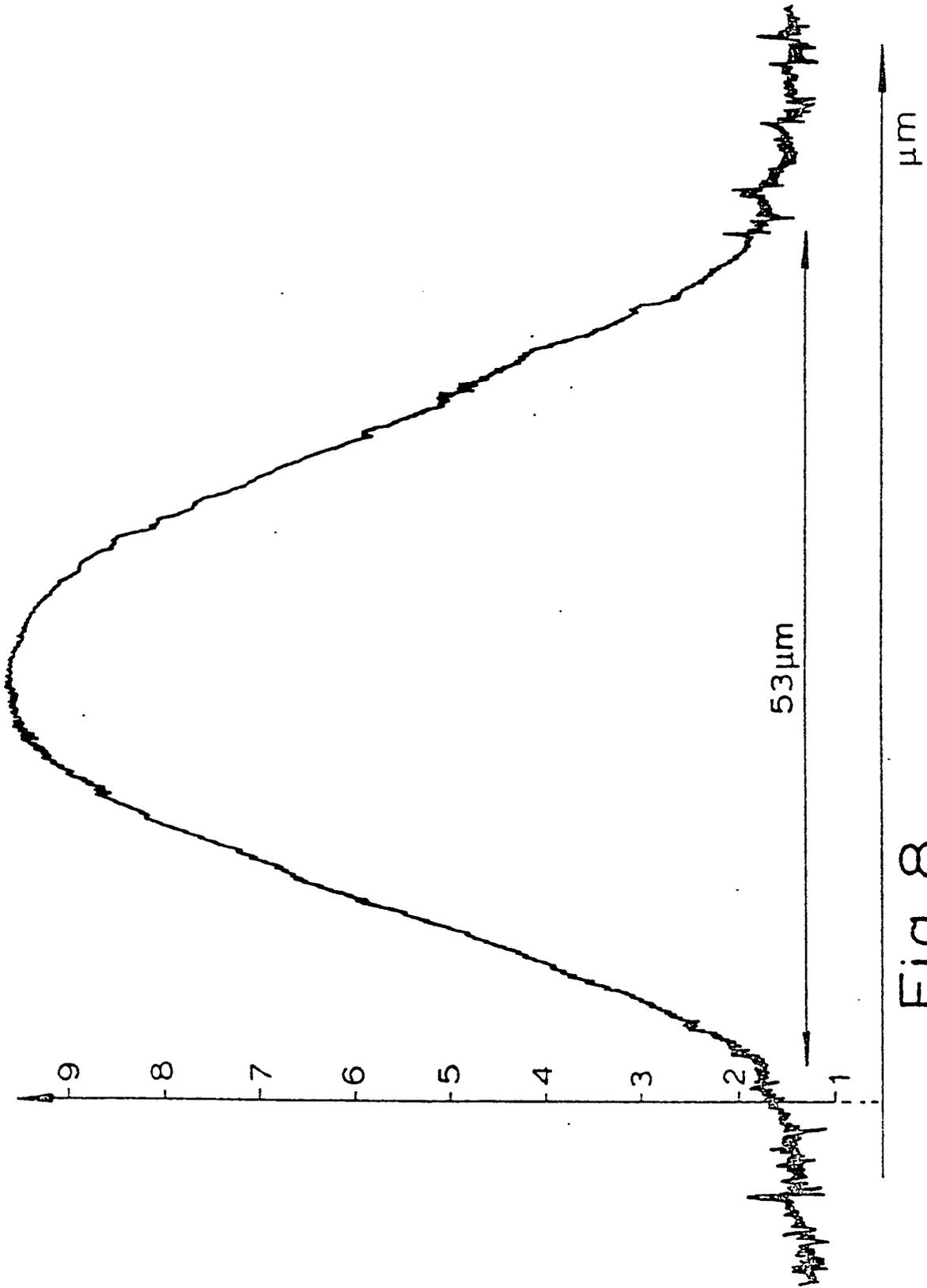


Fig. 8

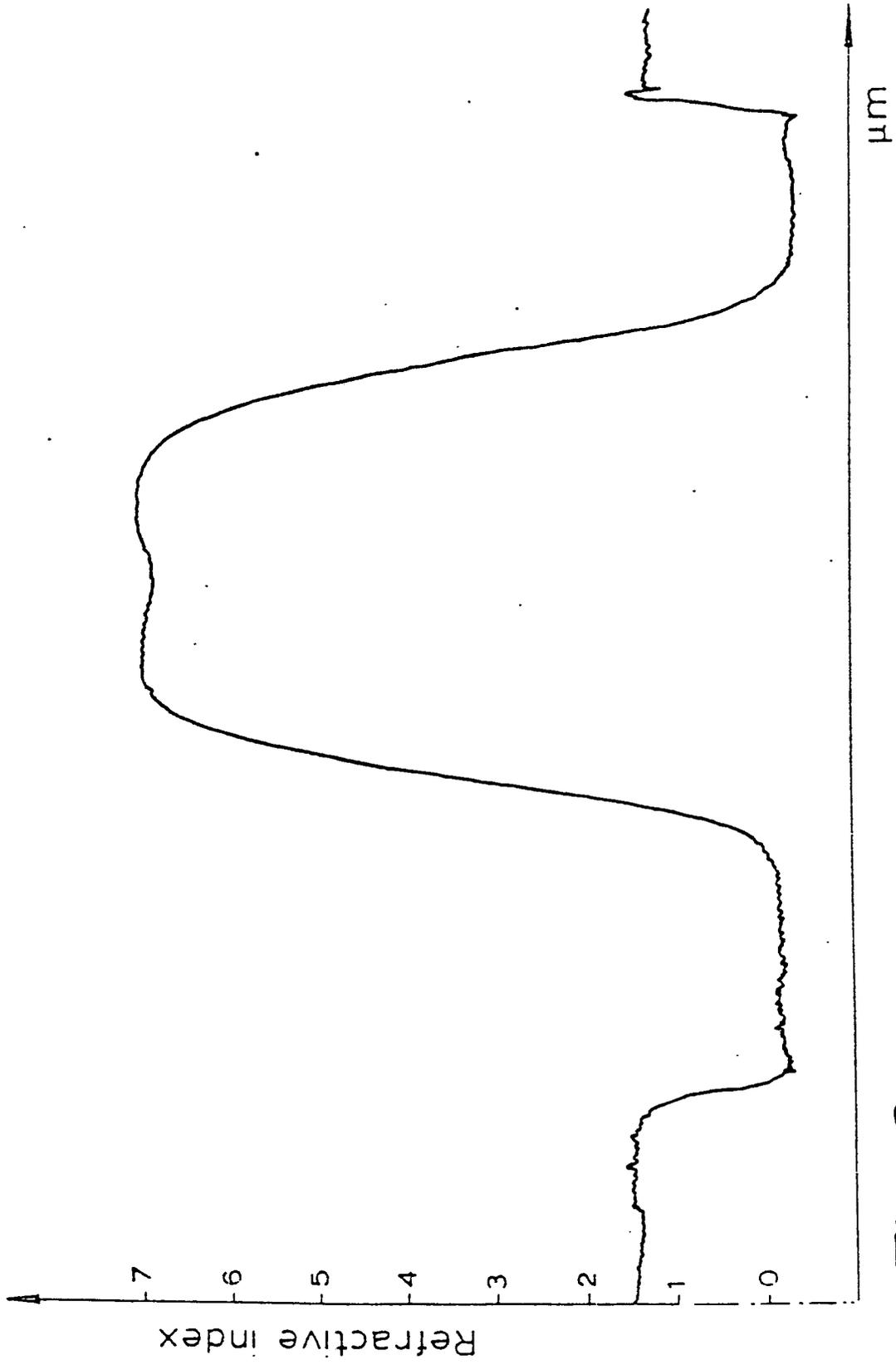
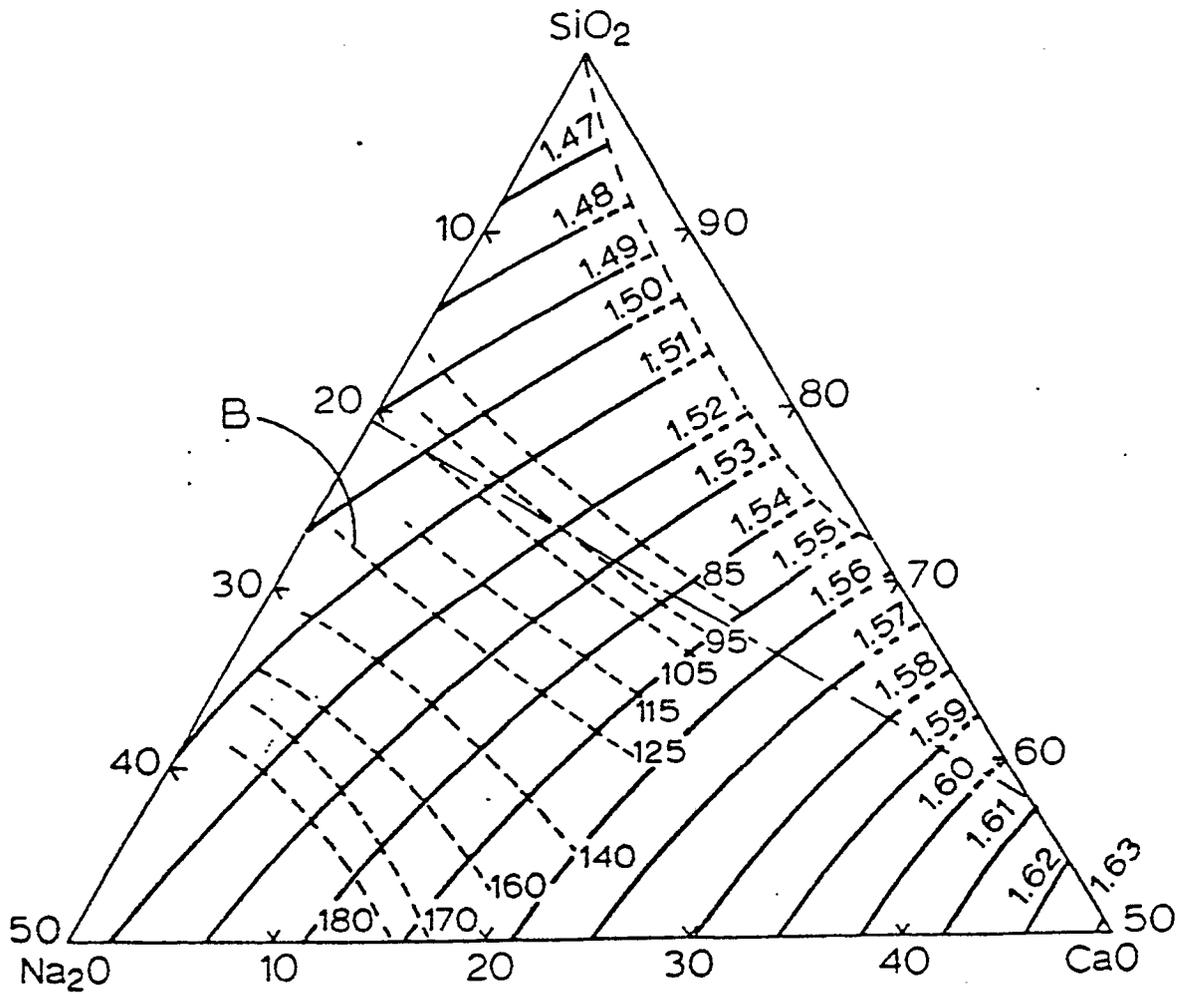


Fig. 9



- Limit of immiscibility region.
- Lines of equal refractive index.
- Lines of equal thermal expansion
25-400°C x 10⁷

Fig.10

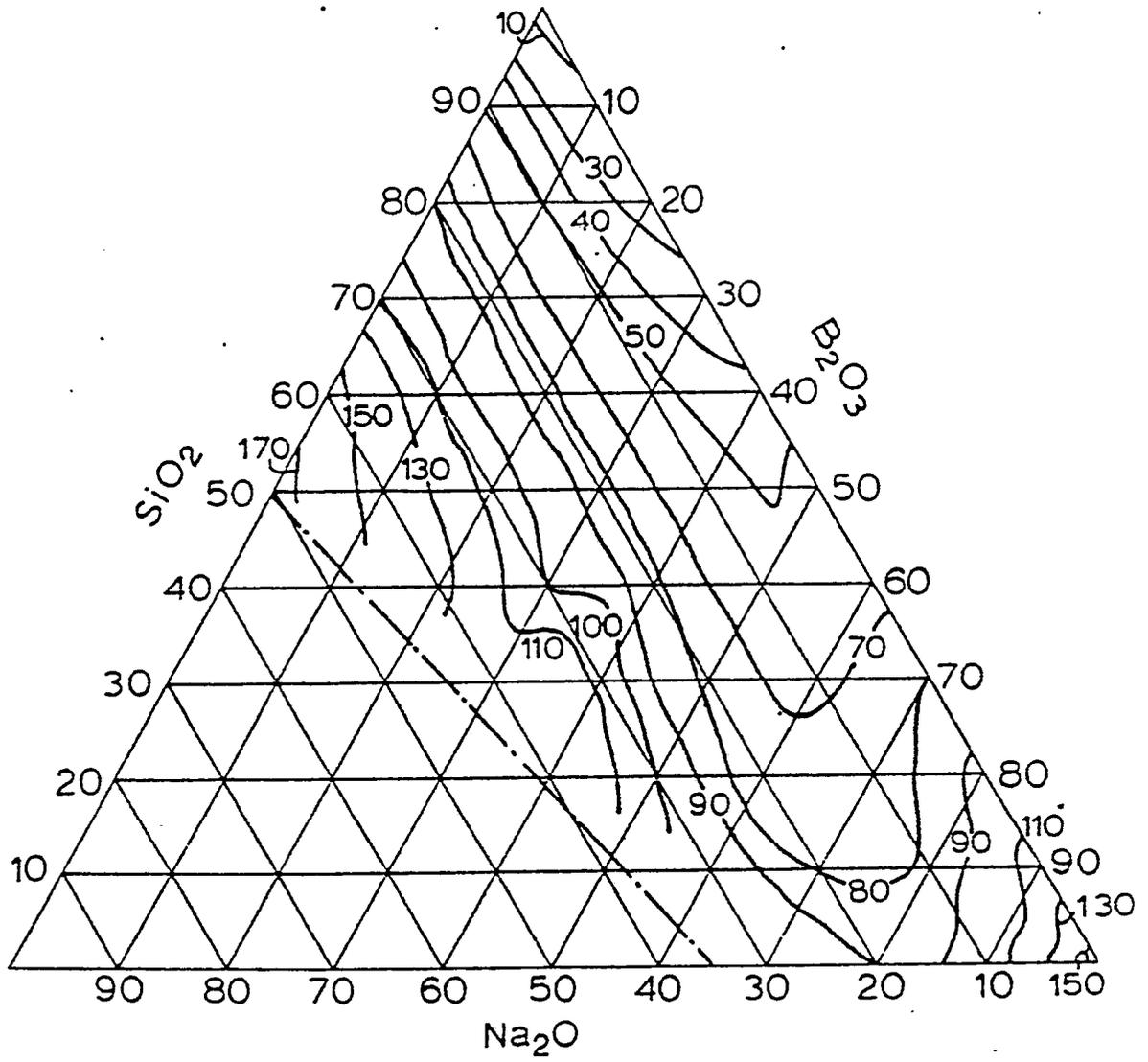


Fig.11