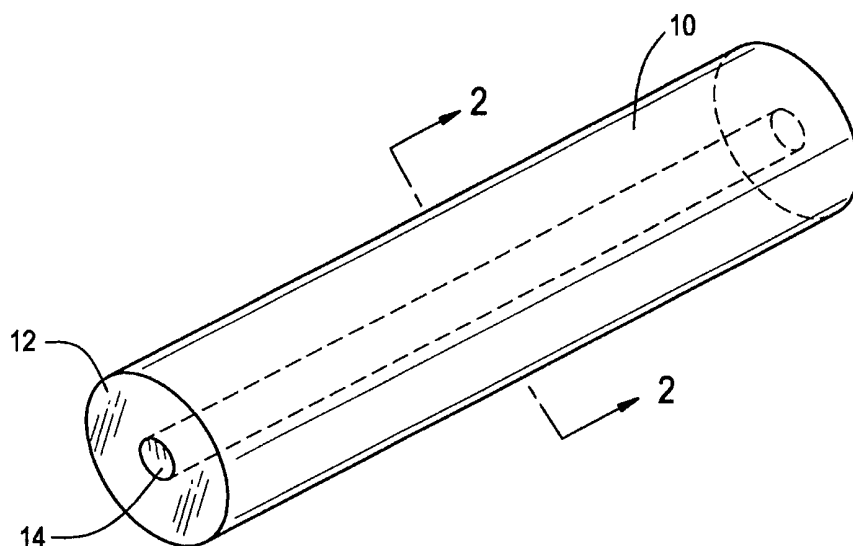




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(21) International Application Number: PCT/US98/22739 (22) International Filing Date: 27 October 1998 (27.10.98) (30) Priority Data: 60/064,273 4 November 1997 (04.11.97) US (71) Applicant (for all designated States except US): CORNING INCORPORATED [US/US]; 1 Riverfront Plaza, Corning, NY 14831 (US). (72) Inventors; and (75) Inventors/Applicants (for US only): AITKEN, Bruce, G. [US/US]; 42B Spencer Hill Road, Corning, NY 14830 (US). CROOKER, David, H. [US/US]; 1223 Riff Road, Corning, NY 14830 (US). POWLEY, Mark, L. [US/US]; 5541 Route 125, Campbell, NY 14821 (US). (74) Agent: PETERSON, Milton, M.; Corning Incorporated, Patent Dept., SP FR 02-12, Corning, NY 14831 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, GM, HR, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>

(54) Title: STABLE CLADDING GLASSES FOR SULPHIDE FIBRES



(57) Abstract

A stable cladding glass (12) for use in optical fibers (10). The invention is based upon the discovery that the addition of silicon or phosphorus in small amounts to GeAs sulfide glasses results in improved thermal stability and a lower refractive index.

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STABLE CLADDING GLASSES FOR SULPHIDE FIBRES

Field of the Invention

This invention relates generally to glasses for use in optical fibers, and more specifically to cladding glasses which exhibit improved thermal stability and a low refractive index.

Background of the Invention

U.S. Patent 5,389,584, "Ga-and/or In-Containing AsGe Sulphide Glasses" describes the addition of either Ga or In to GeAs Sulphide glasses, which when doped with a suitable rare earth metal, can be used for the fabrication of efficient amplifier, laser and/or upconverter devices. In the particular application of 1300 nm optical amplification, such glasses are excellent hosts for Pr, and are characterized by a high quantum efficiency for the desired $^1G_4 > ^3H_5$ emission. These glasses also have sufficient thermal stability to be drawn into fibre, and are therefore suitable for use as the core glass of an optical waveguide to amplify 1300 nm signals.

In order to fabricate such a sulphide glass waveguide, it is necessary to clad the core glass with another chemically and physically compatible glass that has a lower refractive index. In the basic GeGaAsS or GeInAsS systems, lower index glasses can be obtained by reducing the As content, and/or increasing the Ge content, respectively, relative to that of a given core glass. However, such compositional changes typically degrade the thermal stability of these materials, e.g. as measured by the temperature interval $T_x - T_g$, resulting in an increased tendency towards crystallization. It can therefore be seen that there is a need for a method to both lower the refractive index and maintain or improve the thermal stability of such sulphide glasses so as to be able to

fabricate a waveguide with suitable light-guiding properties. The present invention is based on the discovery that the addition of silicon or phosphorus to GeAs sulphide glasses provides a means to achieving the above goals.

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Summary of the Invention

In one embodiment of the present invention, the glass composition consists principally of Ge, As and S, $\pm$ Ga and/or In, with small but necessary additions of Si. Other metals, including Ca, Sr, Ba, Ag, Tl, Cd, Sn, Hg, Pb, Y, La and other rare-earth metals from the lanthanide series and Sb, as well as optional anionic components such as Se, Te and the halogens F, Cl, Br and I, can be added to optimize various other physical properties such as thermal expansion, viscosity, etc., but are not essential constituents. In a second embodiment of the present invention, the addition of phosphorus to GeAs sulphide glasses can be used instead of silicon to accomplish the same objectives. Glasses of these compositions provide for a cladding glass which exhibits improved thermal stability and a lower refractive index relative to that of a GeGaAsS or GeInAsS core.

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Brief Description of the Drawings

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For a fuller understanding of the nature and objects of the invention, reference should be made to the following detailed description of a preferred mode of practicing the invention, read in connection with the accompanying drawings, in which:

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FIG. 1 is a perspective view of a segment of an optical fiber made of a glass composition of the present invention.

FIG. 2 is a cross sectional view of the fiber of Fig. 1 taken along line 2-2.

FIG. 3 is a plot of the refractive index based on the concentration of Si (as expressed in terms of atomic %) in a GeAs sulfide glass.

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FIG. 4 is a plot of the thermal stability of GeAs sulfide glasses with varying concentrations of Si as expressed in atomic %.

FIG. 5 is a plot of the refractive index based on the concentration of P as expressed in terms of atomic % in a GeAs sulfide glass.

Detailed Description of the Invention

Fig. 1 illustrates a segment of an optical fiber 10 suitable for use in an amplifier, laser and/or upconverter device. The fiber comprises an inner glass core 14 which is clad with an outer glass cladding 12 which is a chemically and physically compatible glass that has a lower refractive index than core glass 14 (see Fig. 2).

The present invention, in one embodiment, is based on the discovery that the incorporation of Si in a GeAs sulphide glass results in a progressive decrease of the refractive index, as illustrated in Fig. 3 of the drawings. The data in Fig. 1 show that substitution of 2.5% At% of Si for Ge lowers the refractive index by about 0.025 for glasses with the $(\text{Ge}, \text{Si})_{25}\text{As}_{10}\text{S}_{65}$ stoichiometry. Therefore, if glasses Nos. 7 and 1 were utilized as core and cladding glasses, respectively, the numerical aperture (NA) of the resultant waveguide would be about 0.35, which is sufficiently high for an efficient amplifier fibre.

Tables 1 and 2 report a group of glass compositions expressed in terms of atomic percent (At%) , illustrating the subject inventive glasses. Because the glasses were prepared in the laboratory, the glasses were typically prepared by melting mixtures of the respective elements, although in some cases a given metal was batched as a sulfide. As can be appreciated, however, that practice is not necessary. The actual batch ingredients can be any materials which, upon melting together with the other batch components, are converted into the desired sulfide in the proper proportions.

The batch constituents were weighed, loaded and sealed into silica ampoules which had been evacuated to about 10^{-5} to 10^{-6} Torr. The ampoules were placed into a furnace designed to impart a rocking motion to the batch during melting. After melting the batch for about 1-3 days at 850° - 950° C., the melts were quenched to form homogeneous glass rods having diameters of about 7-10 mm and lengths of about 60-70 mm, which rods were annealed at about 325° - 425° C.

Table 1 also records the glass transition temperature (T_g), the temperature at the onset of crystallization (T_x), and the difference between those measurements ($T_x - T_g$), which quantity is commonly used to gauge the thermal stability of a glass, as well as the refractive index at the sodium D

line (n_D).

It will be appreciated that the above-described procedures represent laboratory practice only. That is, the batches for the inventive glasses can be melted in large commercial glass melting units and the resulting melts formed into desired glass shapes utilizing commercial glass forming techniques and equipment. It is only necessary that the batch materials be heated to a sufficiently high temperature for an adequate period of time to secure a homogeneous melt, and that melt thereafter cooled and simultaneously shaped into a body of a desired configuration at a sufficiently rapid rate to avoid the development of devitrification.

Examples of Si-containing glasses of the present invention that are useful for the purpose of cladding a core consisting of GeGaAsS or GeInAsS glass are tabulated below in Table 1 in At%, along with an example of a representative GeGaAsS core glass (Example 7).

Table 1

Glass	1	2	3	4	5	6	7
Ge	22.5	20	17.5	25.3	22.5	19.7	25.0
Si	2.5	5	7.5	2.8	5.6	8.4	-
As	10	10	10	6.3	6.3	6.3	9.8
S	65	65	65	65.6	65.6	65.6	65.0
Ga	--	--	--	--	--	--	0.2

T_g	312	348	339	364	368	361	-
T_x	> 650	~630	585	~640	~625	~630	-
$T_x - T_g$	> 335	~280	246	~275	~255	~270	-
n_D	2.283	2.265	-	2.264	2.252	2.241	2.308

In order to achieve core/cladding structures with a comparable NA in the basic GeGaAsS or GeInAsS systems, the thermal stability ($T_x - T_g$) of typical cladding glasses is on the order of 230-250°C. However, the $T_x - T_g$ of Si-substituted glasses can be maintained at a value in excess of 250°C over a wide range of compositions, and in some cases can be in excess of that of the base GeAs sulphide glass, as illustrated in Fig. 2 of the drawings.

The composition of the Si containing cladding glasses comprise the following approximate ranges in terms of mole percent on the sulfide basis (see Table 2): 50-95% GeS_2 , 2-40% As_2S_3 , 0.1-30% SiS_2 , 0-20% Ga_2S_3 and /or In_2S_3 , 0-10% MS_x , where M is selected from Ca, Sr, Ba, Ag, Tl, Cd, Hg, Sn, Pb, Y, La and other rare-earth metals of the lanthanide series, or Sb, 0-5% of the corresponding metal selenide and/or telluride, 0-20% of the corresponding metal halide, and wherein the sulfur and/or selenium and/or tellurium content can vary between 85-125% of the stoichiometric value.

Table 2 (Mole %)

Glass	1	2	3	4	5	6	7
GeS_2	75.0	66.7	58.3	81.0	72.0	63.0	83.3
SiS_2	8.3	16.7	25.0	9.0	18.0	27.0	-

Ga_2S_3	-	-	-	-	-	-	0.3
As_2S_3	16.7	16.7	16.7	10.0	10.0	10.0	16.3
Pr_2S_3	-	-	-	-	-	-	0.03

In a second embodiment of the present invention, the glasses consist principally of Ge, As and S, $\pm$ Ga and/or In, with a small but necessary addition of P. Other metals, including Ca, Sr, Ba, Ag, Tl, Cd, Hg, Sn, Pb, Y, La and other rare-earth metals from the lanthanide series and Sb, as well as optional anionic components such as Se, Te and the halogens F, Cl, Br and I, can be added to optimize various other physical properties such as thermal expansion, viscosity, etc., but are not essential constituents. Compositions (in atomic %) of suitable P containing glasses that are useful for the purpose of cladding a core consisting of GeGaAsS or GeInAsS glass are given below in Table 3:

Table 3 (Atomic %)

Glass	8	9	10	11	12	13	14
Ge	24.4	23.8	23.6	23.3	22.2	19.5	16.9
P	2.4	4.8	5.7	7.0	2.5	4.9	7.2
As	7.3	4.8	3.8	2.3	9.9	9.8	9.6
S	65.9	66.7	67.0	67.4	65.4	65.8	66.3

Glass	15	16	17	18	19	20	21
Ge	23.0	22.1	21.3	22.8	21.9	21.1	23.6
P	4.8	4.8	4.8	5.7	5.7	5.7	2.4
As	5.7	6.7	7.7	4.7	5.7	6.7	7.1
S	66.5	66.4	66.2	66.8	66.7	66.5	66.9

In this embodiment, the incorporation of P in a GeAs sulphide glass results in a progressive decrease of refractive index, and a reduced tendency of GeS₂ to crystallize, leading to enhanced thermal stability. Accordingly, when Example 8 is used as cladding for a core glass with the composition of Example 7, the resultant fibre is expected to have a numerical aperture of 0.32 which is more than adequate for a sulphide 1.3 μ m amplifier fibre.

The compositions of these phosphorous containing cladding glasses comprise the following approximate ranges in terms of mole percent on the sulfide basis (see Table 4); 50-95% GeS₂, 2-40% As₂S₃, 0.1-25% P₂S₅, 0-20% Ga₂S₃ and/or In₂S₃, 0-10% MS_x, where M is selected from Ca, Sr, Ba, Ag, Tl, Cd, Hg, Sn, Pb, Y, La and other rare-earth metals of the lanthanide series, or Sb, 0-5% of the corresponding metal selenide and/or telluride, 0-20% of the corresponding metal halide, and wherein the sulfur and/or selenium and/or tellurium content can vary between 85-125% of the stoichiometric value.

Table 4 (Mole %)

Glass	8	9	10	11	12	13	14
GeS ₂	83.3	83.3	83.3	83.3	78.3	72.7	66.7

P_2S_5	4.2	8.3	10.0	12.5	4.4	9.1	14.3
As_2S_3	12.5	8.3	6.7	4.2	17.4	18.2	19.1
T_g	331	337		315	317	280	
T_x	>583	>577		>557	>544	>512	
T_x-T_g	>252	>240		>242	>227	>232	
n_D	2.286	2.259		2.239	2.314	2.316	2.317
Glass	15	16	17	18	19	20	21
GeS_2	81.4	79.3	77.2	81.3	79.3	77.2	83.3
P_2S_5	8.5	8.6	8.8	10.2	10.3	10.5	4.2
As_2S_3	10.2	12.1	14.0	8.5	10.3	12.3	12.5
Excess S	-	-	-	-	-	-	105
n_D	2.280	2.278	2.298	2.275	2.285	2.289	--

Fig. 5 illustrates that the substitution of 2.5 At% P for Ge lowers the

refractive index by about 0.022 for glasses with the $(\text{Ge,P})_{25}\text{As}_{10}\text{S}_{65}$ stoichiometry.

5 While the present invention has been particularly shown and described with reference to the preferred mode as illustrated in the drawing, it will be understood by one skilled in the art that various changes in detail may be effected therein without departing from the spirit and scope of the invention as defined by the claims.

I Claim:

1. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising;

5 (a) a core which is made of a glass selected from the group consisting of GeGaAsS and GeInAsS; and

(b) a glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains Si in an amount sufficient to lower the refractive index of said GeAs sulphide glass and improve its thermal stability.

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2. The optical fiber of claim 1 in which the Si is present in a concentration of from about 0.1 to 30% SiS₂.

15 3. The optical fiber of claim 1 in which the glass cladding comprises the following composition in mole percent:

GeS ₂	50-95%
As ₂ S ₃	2-40%
SiS ₂	0.1-30%

20 4. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising;

(a) an inner core which is made of an AsGe sulfide glass; and
(b) a glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains Si in an amount sufficient to lower the refractive index of said GeAs sulphide glass, and improve its thermal stability.

25

5. The optical fiber of claim 4 in which the Si is present in a concentration of from about 0.1 to 30% SiS₂.

30

6. The optical fiber of claim 4 in which the glass cladding comprises the following composition in mole percent:

GeS ₂	50-95 %
As ₂ S ₃	2-40 %
SiS ₂	0.1-30 %

5 7. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising;

(a) an inner glass core which is doped with a suitable rare earth element and which is made of a glass selected from the group consisting of GeGaAsS and GeInAsS; and

10 (b) a transparent glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains Si in an amount sufficient to lower the refractive index of said GeAs sulphide glass and improve its thermal stability.

15 8. The optical fiber of claim 7 in which the Si is present in a concentration of up to about 30 mole percent SiS₂.

9. The optical fiber of claim 7 in which the glass cladding comprises the following composition in mole percent:

20

GeS	50-95 %
As ₂ S ₃	2-40 %
SiS ₂	0.1-30 %

25 10. The fiber of claim 7 in which the rare earth dopant is Pr.

11. A glass composition which is suitable for use as a stable cladding for an optical fiber which comprises a GeAs sulfide glass which contains Si in an amount sufficient to lower the refractive index of the glass and improve its thermal stability.

30 12. The composition of claim 11 in which the Si is present in a concentration of up to about 30 mole percent of SiS₂ of the total glass

composition.

13. The composition of claim 11 in which the glass composition contains Ga and/or In in a concentration of up to about 20 mole percent of Ga_2S_3 and/or In_2S_3 .

14. A stable glass composition suitable for use in cladding optical fibers comprising in mole percent:

	GeS_2	50-95%
10	As_2S_3	2-40%
	SiS_2	0.1-30%
	Ga_2S_3	0-20%
	In_2S_3	0-20%
	MS_x	0-10%

- 15 where M is selected from Ca, Sr, Ba, Ag, Tl, Cd, Hg, Pb, Y, La and other rare earth metals of the lanthanide series, or Sb.

15. The composition of claim 14 in which any one of the recited sulfides may be replaced with 0-5% of the corresponding metal selenide and/or telluride, and/or 0-20% of the corresponding metal halide, and in which the sulfur and/or selenium and/or tellurium content can vary between 85-125% of the stoichiometric value.

16. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising;

(a) a core which is made of a glass selected from the group consisting of GeGaAsS and GeInAsS ; and

(b) a glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains P in an amount sufficient lower the refractive index of said GeAs sulphide glass and improve its thermal stability.

17. The optical fiber of claim 16 in which the P is present in a concentration of from about 0.1 to 25 mole percent of P_2S_5 .

18. The optical fiber of claim 16 in which the glass cladding comprises the following composition in mole percent:

GeS_2	50-95 %
As_2S_3	2-40 %
P_2S_5	0.1-25 %

19. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising;

- (a) an inner core which is made of an AsGe sulfide glass; and
- (b) a glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains P in an amount sufficient to lower the refractive index of said GeAs sulphide glass, and improve its thermal stability.

20. The optical fiber of claim 19 in which the P is present in a concentration of from about 0.1 to 25 mole percent of P_2S_5 .

21. The optical fiber of claim 19 in which the glass cladding comprises the following composition in mole percent:

GeS_2	50-95 %
As_2S_3	2-40 %
P_2S_5	0.1-25 %

22. An optical fiber which exhibits improved thermal stability and enhanced light guiding properties comprising:

- (a) an inner glass core which is doped with a suitable rare earth element and which is made of a glass selected from the group consisting of GeGAAsS and GeInAsS; and

(b) A transparent glass cladding surrounding said core, said cladding being made of a GeAs sulphide glass which contains P in an amount sufficient to lower the refractive index of said GeAs sulphide glass and improve its thermal stability.

5

23. The optical fiber of claim 22 in which the Si is present in a concentration of up to about 25 mole percent P_2S_5 .

24. The optical fiber of claim 22 in which the glass cladding comprises the following composition in mole percent:

10

GeS_2	50-95 %
As_2S_3	2-40 %
P_2S_5	0.1-25 %

15

25. The fiber of claim 22 in which the core is doped with Pr.

26. A glass composition which is suitable for use as a stable cladding for an optical fiber which comprises a GeAs sulfide glass which contains P in an amount sufficient to lower the refractive index of the glass and improve its thermal stability.

20

27. The composition of claim 26 in which the glass composition contains Ga and/or In in a concentration of up to about 20 mole percent of Ga_2S_3 and/or In_2S_3 .

25

28. The composition of claim 26 in which P is present in a concentration of up to about 25 mole percent of P_2S_5 of the total glass composition.

30

29. A stable glass composition suitable for use in cladding optical fibers comprising in mole percent:

GeS_2	50-95 %
As_2S_3	2-40 %

P_2S_5	0.1-25%
Ga_2S_3	0-20%
In_2S_3	0-20%
MS_x	0-10%

5 where M is selected from Si, Ca, Sr, Ba, Ag, Tl, Cd, Hg, Pb, Y, La and other rare earth metals of the lathanide series, or Sb.

30. The composition of claim 28 in which any one of the recited sulfides may be replaced with 0-5% of the corresponding metal selenide and/or
10 telluride, and/or 0-20% of the corresponding metal halide, and in which the sulfur and/or selenium and/or tellerium content can vary between 85-125% of the stoichiometric value.

31. A glass composition which is suitable for use as a stable cladding
15 for an optical fiber which comprises a GeAs sulfide glass which contains Si and/or P in an amount sufficient to lower the refractive index of the glass and improve its thermal stability.

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FIG. 1

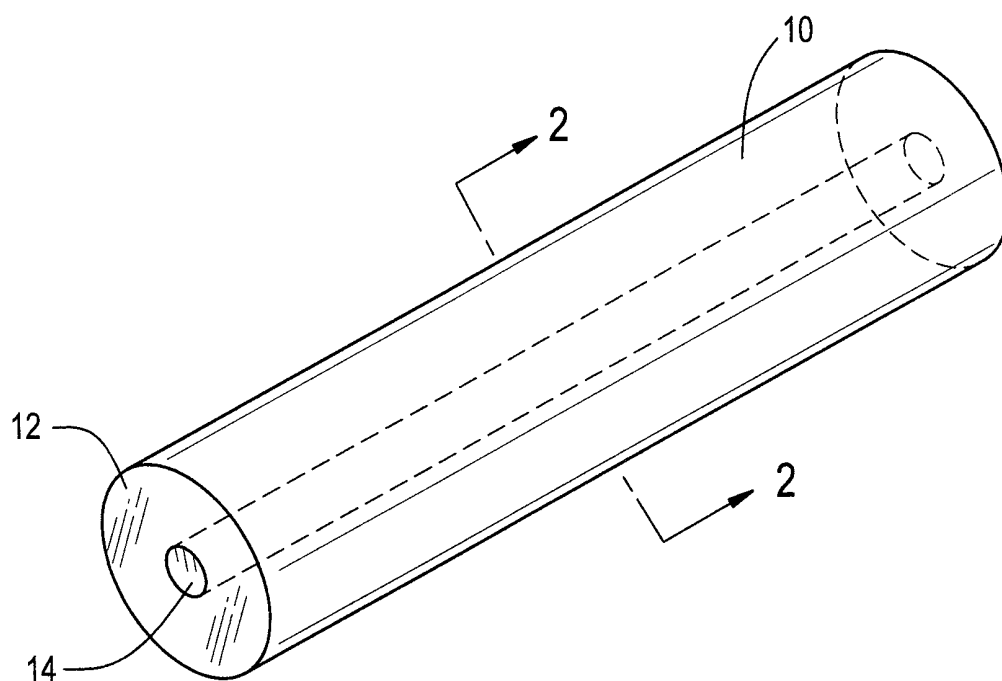
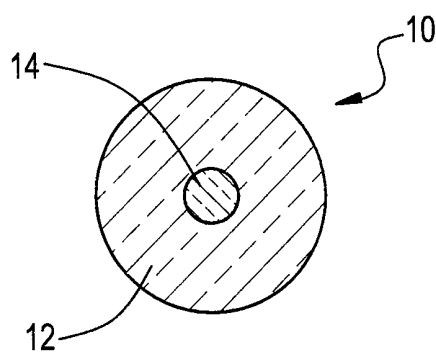


FIG. 2

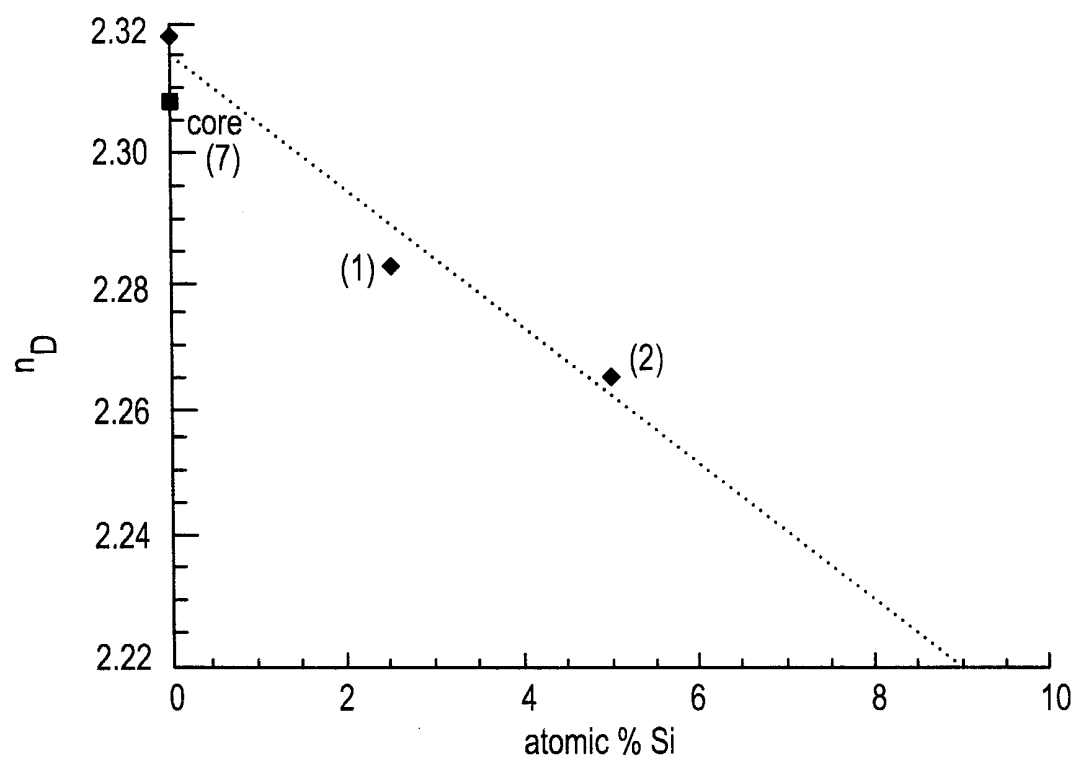


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FIG. 3

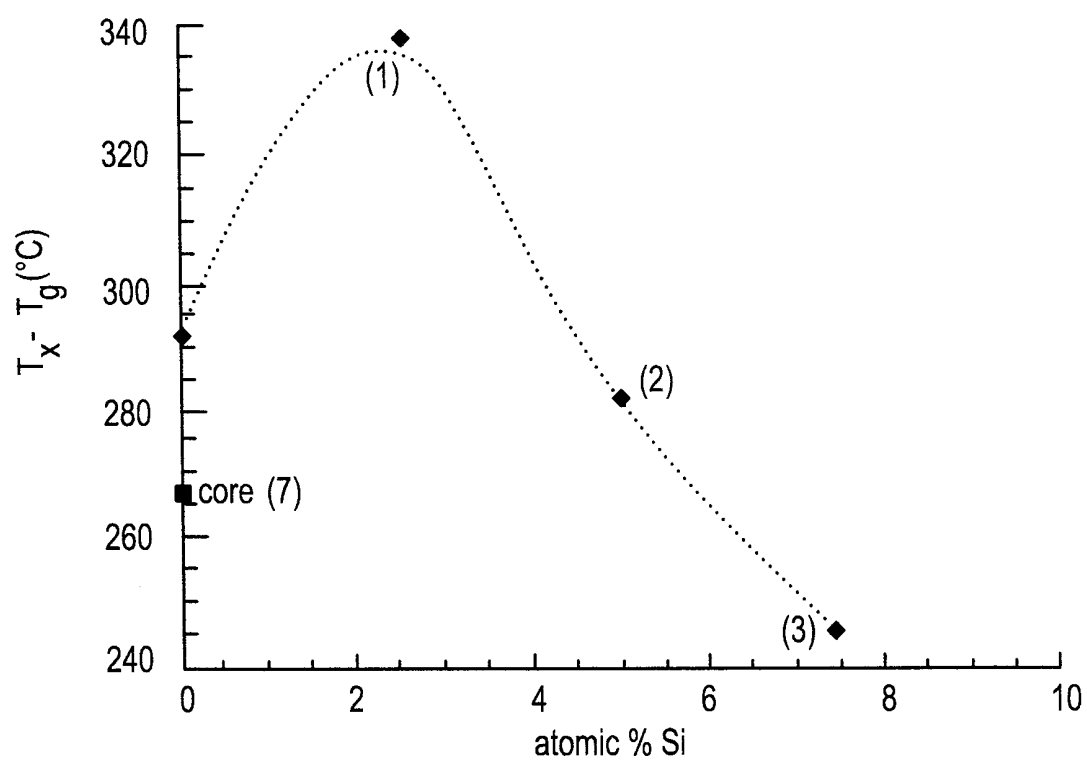
Refractive Index of Cladding Glasses



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FIG. 4

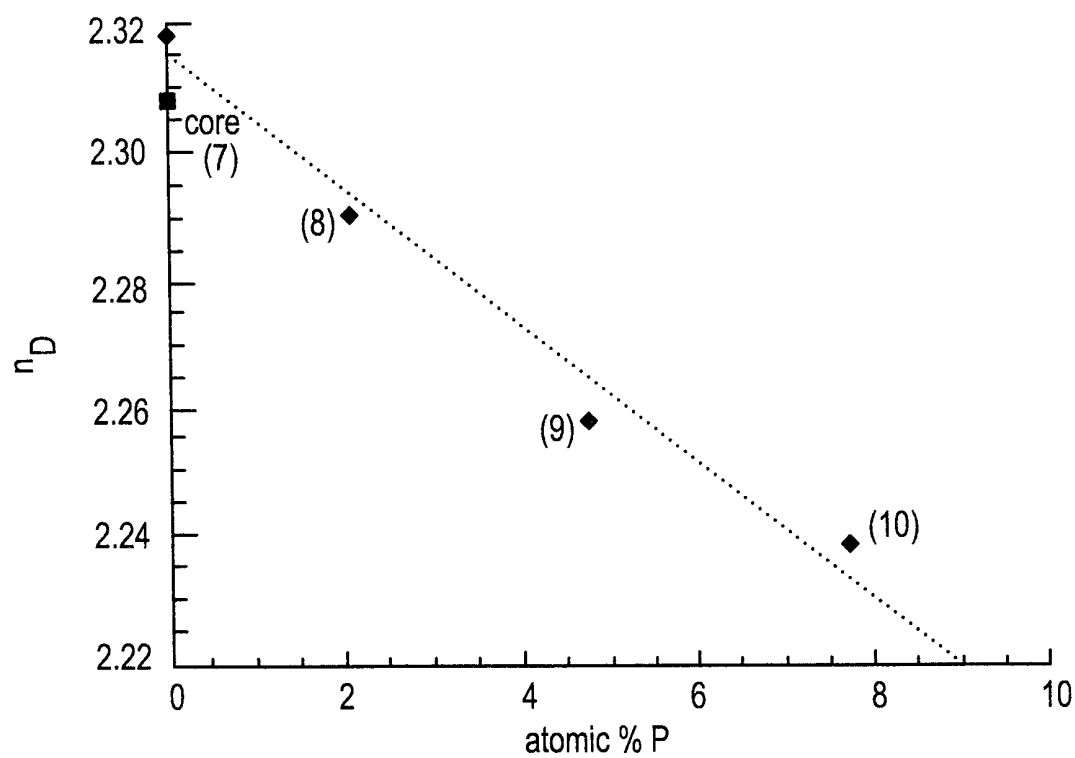
Thermal Stability of Cladding Glasses



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FIG. 5

Refractive Index of Cladding Glasses



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US98/22739

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : G02B 6/00, 6/16; CO3C 3/32; HO1S 3/07

US CL : 385/ 123, 124, 126, 129, 141, 147; 372/ 6; 65/311; 359/341

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 385/ 123, 124, 126, 129, 141, 147; 372/ 6; 65/311; 359/341

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
NONEElectronic data base consulted during the international search (name of data base and, where practicable, search terms used)
APS**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A,P	US 5,764, 661 A (TAWARAYAMA ET AL) 09 June 1998 (09/06/98), see the entire document	1-31
A	US 5,136,677 A (DREXHAGE ET AL) 04 August 1992 (04/08/92), see the entire document	1-31
A	US 4,863,237 A (FRANCE) 05 September 1989 (05/09/89), see the entire document	1-31

☐ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

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Date of the actual completion of the international search

25 JANUARY 1999

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