



**GLASS STRANDS CAPABLE OF REINFORCING ORGANIC AND/OR
INORGANIC MATERIALS, PROCESS FOR MANUFACTURING
SAID STRANDS AND COMPOSITION USED**

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The present invention relates to glass strands (or "fibers"), that can be used for reinforcing organic and/or inorganic materials and can be used as textile strands, these strands being able to be obtained by the
10 process which consists in mechanically drawing streams of molten glass flowing out from orifices located at the base of a bushing generally heated by resistance heating.

15 The present invention is aimed more particularly at glass strands of low dielectric constant having a particularly advantageous novel composition for forming fine strands.

20 This is because there is a growing demand for glass strands whose permittivity and dielectric losses are low, these being mainly used to form lightweight fabrics, which are used in order to reinforce printed-circuit substrates. The latter consist mainly
25 of a reinforcement, especially glass strands, and a resin, on which substrates various electrical and/or electronic components are placed.

With, on the one hand, the increase in the speed of
30 processing of electrical and/or electronic signals, which involve signals of ever higher frequency, and, on the other hand, the miniaturization of the components which allows their density on a substrate to be increased, the dielectric properties of this substrate
35 become crucial. If these properties do not have the expected performance, there may be a risk of overheating and/or of signal distortion. Moreover, to help in miniaturization, strands of ever smaller



diameter are sought in order to reduce the thickness of the components and to improve their planarity.

5 The polymers conventionally used for printed-circuit boards consist essentially of epoxy resin. Polymers having superior dielectric properties are known at the present time, especially polyimide resins, cyanate ethers, polyesters or even PTFE, the dielectric properties of which are satisfactory.

10 Any improvement in the dielectric properties of a printed-circuit board must therefore essentially rely on improving the properties of the reinforcement, represented here by the glass strands according to the
15 present invention, which occupy in general about 60% of the volume.

A glass subjected to an AC current converts some of the latter into electrical energy dissipated in the
20 material. This electrical energy is known as dielectric loss. The dielectric losses are proportional to the permittivity and to the loss tangent ($\tan\delta$) which depend on the composition of the glass for a given frequency. The dielectric losses are expressed (see for
25 example J.C. Dubois in "Techniques de l'Ingénieur [Engineering Techniques]", heading: "Electronique [Electronics]", Chapter E 1850: "Propriétés diélectriques des polymères [Dielectric properties of polymers]") by the formula:

30
$$W = kfv^2 \epsilon \tan\delta$$

where: W is the electrical energy dissipated in the glass or the dielectric loss;

k is a constant;

f is the frequency;

35 v is a potential gradient;

ϵ is the permittivity; and

$\tan\delta$ is the dielectric loss tangent or dielectric dissipation factor.

It is usual to denote $\tan\delta$ as ϵ'' , if $\tan\delta < 0.1$.

It is clearly apparent from this formula that the more the frequency increases, or the more ϵ and/or $\tan\delta$ increase, the greater the dielectric losses become.

In the rest of the text, the term "dielectric properties" refers to the pair (ϵ, ϵ'') . To minimize the distortion of a signal, it is desired that both ϵ and ϵ'' be as low as possible.

It is therefore important to obtain glass compositions that can be fiberized, especially under the conditions of the process already mentioned, in order to form continuous reinforcing strands, having dielectric properties and a diameter that are compatible with the requirements of the latest printed circuits.

More specifically, a tendency to increase the operating frequencies of components, with frequency ranges of the order of GHz (gigahertz), especially 0.9 and 1.8 GHz in the case of telephony, should be noted.

It is therefore very important to study the behavior of glass strands in this frequency range and to optimize their composition so as to limit the dielectric losses, especially for this field of application.

It should be noted that the vast majority of prior studies published in this field relate to dielectric properties of glasses in a frequency range of the order of MHz (megahertz).

The objective of the present invention is to provide novel glass compositions for forming reinforcement strands having dielectric properties of the same order of magnitude as those of the known glasses within the MHz range, which glass compositions have at the same time improved dielectric properties in the GHz range

for a smaller strand diameter, while still having satisfactory fiberizing properties in order to obtain reinforcement strands economically.

- 5 Furthermore, it is desirable that the glass strands in question can be fiberized under conditions giving rise to the lowest possible amount of breakage.

10 In the rest of the invention, the following are defined:

^ the dielectric properties there being for the "MHz range", a frequency range in which the characterization of the dielectric properties of the glasses is carried out, especially at 1 MHz and for the
15 "GHz range", a frequency range in which the characterization of the dielectric properties of the glasses is carried out, especially at 9.5 GHz;

^ the fiberizing properties, which are especially determined by:

- 20 - the temperature corresponding to a viscosity of 10^3 poise (decipascal.second or dPa.s), denoted by "T(log η =3)", which gives precious information about the temperature around which the fiberizing is generally carried out, especially from platinum bushings;
25 - the "liquidus temperature", denoted "T_{liq}", which corresponds to the temperature at which the growth rate of the most refractory crystal is zero. The liquidus temperature gives the upper limit of the temperature range in which the glass may have a tendency to
30 devitrify.

It is considered possible to fiberize the glass economically if T(log η =3) is less than or equal to 1350°C and if T_{liq} is more than 100°C, preferably more
35 than 300°C, below T(log η =3). The greater this difference between T(log η =3) and T_{liq}, the more likely the fiberizing will be carried out without any incident, and the more the risks of breakage during fiberizing are minimized.

The glass reinforcement strands most commonly used are thus strands formed from glasses which derive from the 1170°C eutectic of the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-CaO}$ ternary diagram, particularly the strands referred to as E-glass strands, the archetype of which is described in Patents US-A-2 334 981 and US-A-2 571 074. E-glass strands have a composition essentially based on silica, alumina, lime and boric anhydride. The boric anhydride, present in amounts ranging in practice from 5 to 13% by weight in "E-glass"-type glass compositions, replaces some of the silica. E-glass strands are furthermore characterized by a limited content of alkali metal oxides (essentially Na_2O and/or K_2O). Although their fiberizability is good ($T(\log\eta=3)$ of around 1200°C and T_{liq} of around 1080°C), their dielectric properties, however, prove to be insufficient as regards the new requirements for printed-circuit substrates.

Another family of glass strands is known and obtained from compositions very rich in silica and boron. The glasses of this family, known by the name "D-glasses" comprise about 75% of SiO_2 , 20% of B_2O_3 and 3% of alkali metals. Although these glasses are attractive for their dielectric properties, also they are very difficult to fiberize ($T(\log\eta=3) \geq 1400^\circ\text{C}$) particularly when the strands to be obtained are fine (filament diameter $\leq 10\mu\text{m}$). The yield of this type of strand is low (high degree of breakage) and therefore their production is particularly expensive.

Novel families of compositions have recently been proposed which make it possible to obtain useful dielectric properties and achieve relatively economic fiberizing conditions. These compositions are described for example in applications WO-A-96-A-/39363 and WO 99/52833.

These compositions, although having acceptable dielectric losses in the MHz and GHz ranges, are unsatisfactory for forming fine strands since the degree of breakage during fiberizing remains high.

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Another family of compositions already proposed recently is disclosed in FR-A-2 825 084. These compositions are capable of giving reinforcement strands that can be satisfactorily fiberized economically and make it possible to achieve good dielectric properties in the GHz range. It seems that the high performance level is due to the presence of P_2O_5 in the compositions.

15 Although the addition of P_2O_5 proves to be beneficial for the dielectric properties, it also increases the risk of demixing and consequently the formation of a heterogeneous glass which breaks more easily during fiberizing.

20

It has now been found that the addition of zirconium oxide (ZrO_2) into a composition based on the SiO_2 - Al_2O_3 - B_2O_3 combination makes it possible to obtain strands with a small diameter, especially less than or equal to 10 μm , preferably less than or equal to 7 μm or even around 5 μm under good fiberizing conditions with a reduced breakage rate, while still maintaining acceptable dielectric properties in the MHz and GHz ranges.

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Thus the glass strands according to the invention are obtained from a composition essentially comprising the following constituents, within the limits defined below, expressed as percentages by weight:

35	SiO_2	50 to 60%;
	Al_2O_3	10 to 19%;
	B_2O_3	16 to 25%;
	ZrO_2	0.5 to 1.5%;
	Na_2O	less than or equal to 1.5%;

	K ₂ O	less than or equal to 1.5%;
	R ₂ O (Na ₂ O+K ₂ O+Li ₂ O)	less than or equal to 2%;
	CaO	less than or equal to 10%;
	MgO	less than or equal to 10%;
5	RO (CaO + MgO)	4 to 15%;
	F	0 to 2%;
	TiO ₂	0 to 3%; and
	Various	less than or equal to 3%.

10 The compositions according to the invention make it possible to obtain satisfactory and advantageous fiberizing properties, allowing economic fiberizing to be carried out, especially because $T(\log \eta = 3) \leq 1350^{\circ}\text{C}$.

15 The compositions according to the invention have an acceptable liquidus temperature, especially less than or equal to 1150°C , without major risk of devitrification during fiberizing in the cold regions of the fiberizing crucible and in the feeders
20 conducting the glass from the furnace to the fiberizing crucibles.

Silica is one of the oxides which forms the network of the glass compositions according to the invention and
25 plays an essential role in stabilizing them.

The silica (SiO₂) content of the selected compositions is between 50 and 60%, especially greater than 52%, and/or especially less than or equal to 57%.

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The alumina Al₂O₃ also constitutes a network former of the glasses according to the invention and plays a very important role as regards the hydrolytic resistance of these glasses. Within the context of the limits defined
35 according to the invention, reducing the amount of this oxide to below 10% means that the glass is substantially more susceptible to hydrolytic attack, whereas excessively increasing the amount of this oxide

entails the risks of devitrification and an increase in the viscosity.

5 The Al_2O_3 content of the selected compositions is between 10 and 19%, especially greater than or equal to 13%, and/or especially less than or equal to 17%.

10 The lime (CaO) content of the selected compositions is less than or equal to 10%, especially less than or equal to 8%, or even less than or equal to 6%, and/or preferably greater than or equal to 2%, or even greater than or equal to 4%.

15 The magnesia (MgO) content of the selected compositions is less than or equal to 10%, especially less than or equal to 8%, or even less than or equal to 6%, and/or preferably greater than or equal to 2%.

20 The addition of zirconium oxide (ZrO_2) appears to be an essential point of the invention. The ZrO_2 content is between 0.5 and 1.5%, preferably less than or equal to 1%. This oxide appears to play a very important role in the dielectric properties, more particularly in the GHz range as indicated below in the examples. However, the
25 content must be limited to 1.5% in order to prevent an unacceptable increase in the liquidus temperature.

30 The defined limits, in terms of alkaline-earth metal oxides, lime and magnesia, make it possible to adjust the viscosity of the glasses according to the invention. Good fiberizability is obtained by choosing the sum of these alkaline-earth metal oxides to be between 4 and 15%, preferably greater than or equal to 6% and/or preferably less than or equal to 10%.

35 Furthermore, CaO appears to make a beneficial contribution to the hydrolytic resistance.

Alkali metals, especially Na_2O and K_2O , may be introduced into the compositions of the glass strands according to the invention in order to limit devitrification and possibly reduce the viscosity of the glass. However, the content of alkali metal oxides ($\text{Na}_2\text{O} + \text{K}_2\text{O} + \text{Li}_2\text{O}$) must remain less than or equal to 2% in order to avoid any deterioration in the dielectric properties and to avoid a detrimental reduction in the hydrolytic resistance of the glass. The alkali metal content is generally greater than 0.1%, due to the presence of impurities contained in the batch materials bearing other constituents and it is preferably less than or equal to 1%, or 0.5% or even 0.3%. The composition may contain a single alkali metal oxide (from Na_2O , K_2O and Li_2O) or may contain a combination of at least two alkali metal oxides, the content of each alkali metal oxide being less than or equal to 1.5%, preferably less than or equal to 0.8%.

The boron content is between 16 and 25%, preferably greater than or equal to 18% and/or preferably less than or equal to 22%, or even less than or equal to 20%. According to a preferred version of the invention, it is desired to limit this oxide to moderate contents as compared with those of D-glass so as, on the one hand, not to degrade the hydrolytic resistance, and, on the other, since the cost of boron-bearing batch materials is high. Boron may be introduced in a moderate amount by incorporating, as batch material, glass strand scrap comprising boron, for example E-glass strand scrap.

To improve the melting of the glass, fluorine (F) may be added in a small amount, especially from 0.5 to 2%, or it may be present as an impurity, especially from 0.1 to 0.5%.

Titanium oxide (TiO_2) may also be introduced in an amount possibly representing up to 3%, preferably less

than 2% or even less than 1%, of the composition. It allows the viscosity to be lowered without any appreciable degradation in the dielectric losses.

- 5 The possible Fe_2O_3 content is rather to be considered as an impurity content, frequently encountered in this family of compositions.

10 In the rest of the text, any percentage of a constituent of the composition must be understood as a percentage by weight, and the compositions according to the invention may include up to 2 or 3% of compounds to be regarded as unanalyzed impurities (for example SrO , SO_3 , MnO and MnO_2), as is known in this kind of
15 composition.

The invention also relates to composites formed from glass strands and an organic material, in which the reinforcement is provided at least by the glass strands
20 of compositions defined above.

Preferably, such glass strands are used for the manufacture of printed-circuit substrates especially for forming lightweight fabrics composed of strands
25 with a diameter of less than or equal to 10 μm , preferably less than or equal to 7 μm and advantageously around 5 μm .

The subject of the invention is also a process for
30 manufacturing glass strands of compositions defined above, in which a multiplicity of molten glass streams, flowing out of a multiplicity of orifices placed at the base of one or more bushings, is drawn in the form of one or more webs of continuous filaments, and then the
35 filaments are gathered together into one or more strands which are collected on a moving support.

Preferably, the molten glass feeding the orifices of the bushing or bushings has the following composition, expressed as percentages by weight:

5	SiO ₂	50 to 60%, preferably SiO ₂ ≥ 52% and/or SiO ₂ ≤ 57%;
	Al ₂ O ₃	10 to 19%, preferably Al ₂ O ₃ ≥ 13% and/or Al ₂ O ₃ ≤ 17%;
10	B ₂ O ₃	16 to 25%;
	ZrO ₂	0.5 to 1.5%;
	Na ₂ O	≤ 0.8%;
	K ₂ O	≤ 0.8%;
	R ₂ O	≤ 1%;
	CaO	≤ 10%;
15	MgO	≤ 10%;
	F	0 to 2%;
	TiO ₂	0 to 3%;
	RO	4 to 15%, preferably RO ≥ 6% and/or RO ≤ 10%; and
20	Various	≤ 3%,
	where R ₂ O = Na ₂ O + K ₂ O + Li ₂ O, and RO = CaO + MgO.	

It is thus possible to manufacture such glass strands of small diameter under operating conditions similar to those for E-glass and D-glass and thus to obtain, particularly economically, glasses with good dielectric properties.

The invention also relates to glass compositions suitable for producing glass reinforcement strands, comprising the following constituents, within the limits defined below, expressed as percentages by weight:

35	SiO ₂	50 to 60%, preferably SiO ₂ ≥ 52% and/or SiO ₂ ≤ 57%;
	Al ₂ O ₃	10 to 19%, preferably Al ₂ O ₃ ≥ 13% and/or Al ₂ O ₃ ≤ 17%;
	B ₂ O ₃	16 to 25%;
	ZrO ₂	0.5 to 1.5%;
	Na ₂ O	≤ 1.5%, preferably Na ₂ O ≤ 0.8%;

K₂O ≤ 1.5%, preferably K₂O ≤ 0.8%;
R₂O ≤ 2%, preferably R₂O ≤ 1%;
CaO ≤ 10%;
MgO ≤ 10%;
5 F 0 to 2%;
 TiO₂ 0 to 3%;
 RO 4 to 15%, preferably RO ≥ 6% and/or
 RO ≤ 10%; and
 Various ≤ 3%,
10 where R₂O = Na₂O + K₂O + Li₂O, and RO = CaO + MgO.

The advantages afforded by the glass strands according to the invention will be more fully appreciated through the following examples, denoted Ex. 1 and Ex. 2, given
15 in Table 1, illustrating the present invention without however limiting it.

Comparative examples, denoted A and B, are also given in Table 1 and correspond to the following glasses:

20 A: D-glass
 B: glass according to patent application WO 99/52833.

In these examples, strands composed of 7 μm diameter
25 glass filaments (examples 1, 2 and B) and 10 μm glass filaments (example A) were obtained by drawing molten glass; the glass had the composition indicated in Table 1, expressed in percentages by weight.

30 When the total sum of the contents of all of the compounds is slightly less than or greater than 100%, it should be understood that the residual content corresponds to the impurities and to minor components not analyzed (with contents of at most 1 to 2%) and/or
35 is due to the accepted approximation in this field in the analytical methods used.

$T(\log\eta=3)$ denotes the temperature at which the viscosity of the glass is 10^3 poise (decipascal.second or dPa.s).

- 5 T_{liq} denotes the liquidus temperature of the glass, corresponding to the temperature at which the most refractory phase, which may devitrify in the glass, has a zero growth rate and thus corresponds to the melting point of this devitrified phase.

10

The differences in the dielectric properties ($\Delta\epsilon$, $\Delta\epsilon''$) measured both at 1 MHz and at 9.5 GHz are indicated, compared with the control A (D-glass).

- 15 The measurements at 1 MHz were carried out in a conventional manner, known to a person skilled in the art for this type of metrology.

20 The measurements at 9.5 GHz were carried out according to the method described by W.B. Westphal ("Distributed Circuits", in "Dielectric materials and applications", the Technology Press of MIT and John Wiley & Sons, Inc. New York, Chapman & Hall, Ltd., London, 1954; see especially page 69). The principle of this method is
25 based on measuring the dielectric properties of a disk-shaped specimen placed against a waveguide. This method allows accurate results to be obtained at very high frequency. In Table 1 is also shown the number of complete bobbins of strand that are formed per day
30 under the conditions mentioned above. This number provides a measure of assessing the comparable fiberizing yield for the various glasses.

35 It is apparent that the examples according to the invention represent a remarkable compromise between the fiberizing conditions (breakage rate, fiberizing temperature $T(\log\eta=3)$ and T_{liq}) and the dielectric properties.

The fiberizing range is satisfactory, especially with a difference between $T(\log\eta=3)$ and T_{liq} of greater than or equal to 180°C.

- 5 The dielectric properties of the compositions according to the invention are of the same order of magnitude as those of the compositions according to WO 99/52833 for measurements at 1 MHz and at 9.5 GHz.
- 10 Thus, dielectric properties remarkably close to those of D-glass are obtained, while lowering the fiberizing temperature of the glasses according to the invention, compared with that of D-glass.
- 15 The glasses according to the invention are also noteworthy in that they allow small-diameter strands to be formed with a particularly advantageous yield. Thus, the number of complete bobbins of strand is greater with the glasses according to the invention than with
- 20 the glasses according to WO 99/52833 (by 36%) for an identical filament diameter, and considerably higher (by 300%) than with D-glass, and to be so for a much smaller diameter (7 μm instead of 10 μm).
- 25 Advantageously, the glass strands according to the invention are suitable for all the usual applications of conventional E-glass strands and can replace D-glass strands in some applications. In particular, the glass strands according to the invention have the advantage
- 30 of being able to be obtained with a better yield and a lower cost than the known glass strands.

Thanks to their fineness and therefore their low linear density, the glass strands according to the invention

35 are useful for forming lightweight fabrics exhibiting good planarity, particularly desirable in electronic applications.

TABLE 1

	Example 1	Example 2	A	B
SiO ₂	55.7	54.7	75.3	54.7
Al ₂ O ₃	15	15.0	0.7	15.0
B ₂ O ₃	19.4	19.0	19.6	19.9
Na ₂ O			1.8	
K ₂ O			1.2	
R ₂ O	0.3	0.3	3.0	0.3
CaO	4.1	4.0	0.8	4.0
MgO	4.1	4.0	0.4	4.0
TiO ₂		1.6		2.5
ZrO ₂	0.9	0.9		
F	0.5	0.5		0.5
T (log η =3) (°C)	1343	1330	1410	1310
T _{liq} (°C)	1150	1150	<900	1060
$\Delta\epsilon$ at 1 MHz	+0.4	+0.4	-	+0.6
$\Delta\epsilon''$ at 1 MHz ($\times 10^4$)	0	0	-	0
$\Delta\epsilon$ at 9.5 GHz	+0.5	+0.6	-	+0.6
$\Delta\epsilon''$ at 9.5 GHz ($\times 10^4$)	+150	+160	-	+120
Number of complete bobbins	30	30	10	22

CLAIMS

1. A glass reinforcement strand, the composition of
5 which comprises the following constituents, within the
limits defined below, expressed as percentages by
weight:

	SiO ₂	50 to 60%, preferably SiO ₂ ≥ 52% and/or SiO ₂ ≤ 57%;
10	Al ₂ O ₃	10 to 19%, preferably Al ₂ O ₃ ≥ 13% and/or Al ₂ O ₃ ≤ 17%;
	B ₂ O ₃	16 to 25%;
	ZrO ₂	0.5 to 1.5%;
	Na ₂ O	≤ 1.5%, preferably Na ₂ O ≤ 0.8%;
15	K ₂ O	≤ 1.5%, preferably K ₂ O ≤ 0.8%;
	R ₂ O	≤ 2%, preferably R ₂ O ≤ 1%;
	CaO	≤ 10%;
	MgO	≤ 10%;
	F	0 to 2%;
20	TiO ₂	0 to 3%;
	RO	4 to 15%, preferably RO ≥ 6% and/or RO ≤ 10%; and
	Various	≤ 3%, where R ₂ O = Na ₂ O + K ₂ O + Li ₂ O, and RO = CaO + MgO.

25

2. The glass strand as claimed in claim 1,
characterized in that the composition has a ZrO₂
content such that ZrO₂ ≤ 1%.

30 3. The glass strand as claimed in one of the
preceding claims, **characterized in that** the composition
has a lime (CaO) content such that CaO ≤ 8%, or even
CaO ≤ 6% and/or CaO ≥ 2%, or even CaO ≥ 4%.

35 4. The glass strand as claimed in one of the
preceding claims, **characterized in that** the composition
has a magnesia (MgO) content such that MgO ≤ 8%, or
even MgO ≤ 6% and/or MgO ≥ 2%.

5. The glass strand as claimed in one of the preceding claims, **characterized in that** the composition has a boron (B_2O_3) content such that $B_2O_3 \geq 18\%$ and/or $B_2O_3 \leq 22\%$, or even $B_2O_3 \leq 20\%$.

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6. A composite of glass strands and organic and/or inorganic material(s), **characterized in that** it comprises glass strands as defined by one of claims 1 to 5.

10

7. The use of the glass strands defined by one of claims 1 to 5 for the manufacture of printed-circuit substrates.

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8. A process for manufacturing glass strands as defined in one of claims 1 to 5, in which a multiplicity of molten glass streams, flowing out of a multiplicity of orifices located at the base of one or more bushings, is drawn in the form of one or more webs of continuous filaments and then the filaments are gathered together into one or more strands which are collected on a moving support.

20

9. The process as claimed in claim 8, **characterized in that** the molten glass feeding the orifices of the bushing or bushings has the following composition, expressed as percentages by weight:

25

	SiO_2	50 to 60%, preferably $SiO_2 \geq 52\%$ and/or $SiO_2 \leq 57\%$;
30	Al_2O_3	10 to 19%, preferably $Al_2O_3 \geq 13\%$ and/or $Al_2O_3 \leq 17\%$;
	B_2O_3	16 to 25%;
	ZrO_2	0.5 to 1.5%;
	Na_2O	$\leq 1.5\%$, preferably $Na_2O \leq 0.8\%$;
35	K_2O	$\leq 1.5\%$, preferably $K_2O \leq 0.8\%$;
	R_2O	$\leq 2\%$, preferably $R_2O \leq 1\%$;
	CaO	$\leq 10\%$;
	MgO	$\leq 10\%$;
	F	0 to 2%;

TiO₂ 0 to 3%;
RO 4 to 15%, preferably RO ≥ 6% and/or
RO ≤ 10%; and

Various ≤ 3%,

5 where R₂O = Na₂O + K₂O + Li₂O, and RO = CaO + MgO.

10. A glass composition suitable for producing glass reinforcement strands, comprising the following constituents, within the limits defined below, expressed as percentages by weight:

10 SiO₂ 50 to 60%, preferably SiO₂ ≥ 52% and/or
SiO₂ ≤ 57%;
Al₂O₃ 10 to 19%, preferably Al₂O₃ ≥ 13% and/or
Al₂O₃ ≤ 17%;
15 B₂O₃ 16 to 25%;
ZrO₂ 0.5 to 1.5%;
Na₂O ≤ 1.5%, preferably Na₂O ≤ 0.8%;
K₂O ≤ 1.5%, preferably K₂O ≤ 0.8%;
R₂O ≤ 2%, preferably R₂O ≤ 1%;
20 CaO ≤ 10%;
MgO ≤ 10%;
F 0 to 2%;
TiO₂ 0 to 3%;
RO 4 to 15%, preferably RO ≥ 6% and/or
25 RO ≤ 10%; and
Various ≤ 3%,
where R₂O = Na₂O + K₂O + Li₂O, and RO = CaO + MgO.