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(54) Title: IMPROVED MODULUS, LITHIUM FREE GLASS

(57) **Abrégé/Abstract:**

An R-glass composition including SiO₂ in an amount from 59.0 to 64.5% by weight, Al₂O₃ in an amount from 14.5 to 20.5% by weight, CaO in an amount from 11.0 to 16.0% by weight, MgO in an amount from 5.5 to 11.5% by weight, Na₂O in an amount from 0.0 to 4.0% by weight, TiO₂ in an amount from 0.0 to 2.0% by weight, Fe₂O₃ in an amount from 0.0 to 1.0% by weight, B₂O₃ in an amount from 0.0 to about 3.0% by weight, K₂O, Fe₂O₃, ZrO₂, and Fluorine, each of which is present in an amount from 0.0 to about 1.0% by weight, and SrO and ZnO, each of which is present in an amount from 0.0 to about 2.0% by weight. In exemplary embodiments, the glass composition does not contain lithium or boron.

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TITLE OF THE INVENTION**IMPROVED MODULUS, LITHIUM FREE GLASS****CROSS REFERENCE TO RELATED APPLICATIONS**

This application is related to and claims all priority benefits from U.S. Provisional Patent Application Serial No. 61/231,203 entitled "Improved Modulus, Lithium Free Glass" filed August 4, 2009 and U.S. Provisional Patent Application Serial No. 61/231,482 entitled "Improved Modulus, Lithium Free Glass" filed August 5, 2009.

TECHNICAL FIELD AND INDUSTRIAL**APPLICABILITY OF THE INVENTION**

The present disclosure relates generally to a glass composition, and more particularly, to a high performance glass composition that achieves acceptable forming and mechanical properties without the addition or inclusion of lithium and whose components are melted in a refractory melter.

BACKGROUND OF THE INVENTION

Glass fibers are manufactured from various raw materials combined in specific proportions to yield a desired chemical composition. This collection of materials is commonly termed a "glass batch." To form glass fibers, typically the glass batch is melted in a melter or melting apparatus, the molten glass is drawn into filaments through a bushing or orifice plate, and an aqueous sizing composition containing lubricants, coupling agents, and film-forming binder resins is applied to the filaments. After the sizing is applied, the fibers may be gathered into one or more strands and wound into a package or, alternatively, the fibers may be chopped while wet and collected. The collected chopped strands may then be dried and cured to form dry chopped fibers or they can be packaged in their wet condition as wet chopped fibers.

The composition of the glass batch and the glass manufactured from it are typically expressed in terms of percentages of the components, which are mainly expressed as oxides. SiO₂, Al₂O₃, CaO, MgO, B₂O₃, Na₂O, K₂O, Fe₂O₃, and minor amounts of other compounds such as TiO₂, Li₂O, BaO, SrO, ZnO, ZrO₂, P₂O₅, fluorine, and SO₃ are common components of a glass batch. Numerous types of glasses may be produced from

varying the amounts of these oxides, or eliminating some of the oxides in the glass batch. Examples of such glasses that may be produced include R-glass, E-glass, S-glass, A-glass, C-glass, and ECR-glass. The glass composition controls the forming and product properties of the glass. Other characteristics of glass compositions include the raw
5 material cost and environmental impact.

Conventionally, lithium is added to glass fiber compositions in the form of spodumene (a lithium aluminosilicate raw material) to facilitate melting and obtain desirable mechanical and forming properties. For example, lithium is very effective in reducing the viscosity of the glass formulation. Although lithium-containing glass
10 compositions may possess desirable properties with respect to mechanical and forming properties, the presence of lithium in the glass composition raises the cost of glass fiber manufacturing. This cost could be offset if the inclusion of lithium lowered the viscosity sufficiently to enable a high-performance glass such as R-glass to be melted in a refractory tank rather than in a platinum melter. R-glass is commonly melted in platinum melters.

15 There is a unique combination of forming properties that permit a glass to be melted and distributed in a conventional refractory tank and glass distribution system. First, the temperature at which the glass is held must be low enough so that it does not aggressively attack the refractory. An attack on a refractory can take place, for example, by exceeding the maximum use temperature of the refractory or by increasing the rate at
20 which the glass corrodes and erodes the refractory to an unacceptably high level. Refractory corrosion rate is strongly increased as the glass becomes more fluid by a decrease in the glass viscosity. Therefore, in order for a glass to be melted in a refractory tank, the temperature of the refractory tank must be kept below a certain temperature and the viscosity (*for example*, resistance to flow) must be maintained above a certain
25 viscosity. Also, the temperature of the glass in the melting unit, as well as throughout the entire distribution and fiberizing process, must be high enough to prevent crystallization of the glass (*that is*, it must be kept at a temperature above the liquidus temperature).

At the fiberizer, it is common to require a minimum temperature differential between the temperature selected for fiberizing (*that is*, forming temperature) and the
30 liquidus temperature of the glass. This temperature differential, ΔT , is a measurement of how easily continuous fibers can be formed without production of the fibers being

interrupted by breaks caused from devitrification. Accordingly, it is desirable to have as large a ΔT as possible to achieve continuous and uninterrupted glass fiber formation.

In the quest for glass fibers having a higher end performance, ΔT has, at times, been sacrificed to achieve desired end properties. The consequence of this sacrifice is a requirement that the glass be melted in a platinum or platinum-alloy lined furnace, either because the temperature exceeded the maximum end use temperature of the conventional refractory materials or because the viscosity of the glass was such that the temperature of the glass body could not be held above the liquidus temperature while producing a glass viscosity high enough to keep the refractory corrosion at an acceptable level. S-glass is a good example where both of these phenomena take place. The melting temperature of S-glass is too high for common refractory materials and the ΔT is very small (or negative), thus causing the glass to be very fluid and very corrosive to conventional refractories. Conventional R-glass also has a very small ΔT , and is therefore melted in platinum or platinum-alloy lined melters. The addition of lithium to the formulation sufficiently expands the ΔT of the R-glass to permit it to be melted in a standard refractory melter. However, lithium raw materials are very expensive and greatly increase the manufacturing costs for the glass fibers.

Thus, there is a need in the art for high-performance, lithium-free glass compositions that retain favorable mechanical and physical properties (*for example*, specific modulus and tensile strength) and forming properties (*for example*, liquidus temperature and forming temperature) where the forming temperature is sufficiently low and the difference between the forming and liquidus temperatures is large enough to enable the components of the glass composition to be melted in a conventional refractory tank.

SUMMARY OF THE INVENTION

In an aspect, there is provided a composition for preparing R-glass fibers comprising: SiO₂ in an amount from 59.0 to 60.93% by weight of the total composition; Al₂O₃ in an amount from 15.6 to 20.5% by weight of the total composition; CaO in an amount from 11.0 to 13.2% by weight of the total composition; B₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition; MgO in an amount from 5.5 to 11.5% by weight of the total composition; Na₂O in an amount from 0.0 to 4.0% by weight of the total composition; and TiO₂ in an amount from 0.0

to 2.0% by weight of the total composition, wherein the composition has a ΔT of at least 60 °C, a fiberizing temperature from 1,285 °C to 1,320 °C, and is free of Li_2O .

In another aspect, there is provided a continuous R-glass fiber produced from a composition comprising: SiO_2 in an amount from 59.0 to 64.5% by weight of the total composition; Al_2O_3 in an amount from 15.6 to 20.5% by weight of the total composition; CaO in an amount from 11.0 to 13.2% by weight of the total composition; MgO in an amount from 9.4 to 10.9% by weight of the total composition; Na_2O in an amount from 0.0 to 4.0% by weight of the total composition; and TiO_2 in an amount from 0.0 to 2.0% by weight of the total composition, wherein the composition has a ΔT of at least 60 °C and is free of Li_2O , and wherein the composition has a density of at least 2.606 and 2.638 g/cm^3 .

In a further aspect, there is provided a method of forming an R-glass fiber comprising: providing a molten glass composition including: SiO_2 in an amount from 59.0 to 60.93 % by weight of the total composition; Al_2O_3 in an amount from 15.6 to 20.5% by weight of the total composition; CaO in an amount from 11.0 to 13.2% by weight of the total composition; MgO in an amount from 5.5 to 11.5% by weight of the total composition; B_2O_3 in an amount from 0.0 to 1.0% by weight of the total composition; Na_2O in an amount from 0.0 to 4.0% by weight of the total composition; and TiO_2 in an amount from 0.0 to 2.0% by weight of the total composition, wherein the composition has a ΔT of at least 60 °C, a fiberizing temperature from 1,285 °C to 1,320 °C, and is free of Li_2O ; and drawing the molten glass composition through orifices in a bushing to form an R-glass fiber.

In an embodiment disclosed herein, an R-glass composition that includes SiO_2 in an amount from 59.0 to 64.5% by weight, Al_2O_3 in an amount from 14.5 to 20.5% by weight, CaO in an amount from 11.0 to 16.0% by weight, MgO in an amount from 5.5 to 11.5% by weight, Na_2O in an amount from 0.0 to 4.0% by weight, TiO_2 in an amount from 0.0 to 2.0% by weight, B_2O_3 in an amount from 0.0 to about 3.0% by weight, K_2O , Fe_2O_3 , ZrO_2 , and Fluorine, each of which is present in an amount from 0.0 to about 1.0% by weight, and SrO and ZnO , each of which is present in an amount from 0.0 to about 2.0% by weight is provided. The phrase “% by weight”, as used herein, is intended to be defined as the percent by weight of the total composition. Additionally, the composition may optionally contain trace quantities of other components or impurities. In exemplary embodiments, the glass composition is free or

substantially free of lithium and boron. Further, the glass composition possesses a forming viscosity that is low enough to utilize low cost refractory melters instead of conventional high cost platinum-alloy lined melters in the formation of the glass fibers.

In another embodiment, a continuous R-glass fiber formed of the composition described above is produced using a refractory tank melter. By utilizing a refractory tank formed of refractory blocks, manufacturing costs associated with the production of glass fibers produced by the composition may be reduced. The R-glass compositions may be used to form continuous glass strands for use in textiles and as reinforcements for use in forming wind blades and aerospace structures.

In yet another embodiment, a method of forming an R-glass fiber is provided. The fibers may be formed by obtaining the raw ingredients and mixing the components in the appropriate quantities to give the desired weight percentages of the final composition. The mixed batch is then melted in a traditional refractory melter and drawn through orifices of platinum-alloy based bushings to form glass fibers. Strands of glass fibers are formed by gathering the individual filaments together. The strands may be wound and further processed in a conventional manner suitable for the intended application.

In another embodiment, glass fibers formed from the compositions have a liquidus temperature no greater than about 1330°C, a log 3 temperature less than about 1405°C, a ΔT up to about 135°C, and a specific modulus of at least 3.24×10^6 meters.

In yet another embodiment, glass fibers formed from the compositions have a strength from about 4187 Mpa to about 4357 Mpa.

In a further embodiment, the glass composition possesses a forming viscosity that is low enough, and a ΔT large enough, to utilize low cost refractory melters instead of conventional high cost platinum-alloy lined melters in the formation of the glass fibers.

In another embodiment, fibers formed from the R-glass composition are formed at a lower cost due to the lower energy input needed to melt the glass composition.

In yet another embodiment, the glass has a specific modulus strength and ΔT similar to traditional R-glass compositions that contain lithium. Thus, the composition of the present invention retains the ability to make a commercially acceptable R-glass fiber and fiber product produced from the R-glass fibers.

In a further embodiment, the glass composition reduces production cost by excluding lithium from the composition and utilizing a conventional refractory melting operation to melt the components of the composition.

The foregoing and other objects, features, and advantages of the invention will appear more fully hereinafter from a consideration of the detailed description that follows.

DETAILED DESCRIPTION AND PREFERRED EMBODIMENTS OF THE INVENTION

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which the invention belongs. Although any methods and materials similar or equivalent to those described herein can be used in the practice or testing of the present invention, the preferred methods and materials are described herein. The terms “composition” and “formulation” may be used interchangeably herein. Additionally, the phrase “inventive glass composition” and “glass composition” may be interchangeably used.

The present invention relates to a high performance R-glass composition that does not contain lithium and which possesses a specific modulus, tensile strength, and density that are equivalent or substantially equivalent to R-glass compositions. The glass composition possesses a lower forming temperature and larger ΔT than conventional R-glasses, thereby permitting the utilization of low-cost refractory tank melters for the formation of the glass fibers instead of conventional high-cost paramelters formed of platinum. By utilizing a refractory tank formed of refractory blocks, manufacturing costs

associated with the production of glass fibers produced by the inventive composition are reduced. Additionally, the exclusion of expensive lithium raw materials from the composition reduces the manufacturing costs of the glass fibers. Further, the energy necessary to melt the components of the glass composition is less than the energy
5 necessary to melt commercially available R-glass formulations. Such lower energy requirements may also lower the overall manufacturing costs associated with the inventive glass. It has been discovered that the composition of the present invention retains the ability to make a commercially acceptable high performance glass fiber and fiber product produced from the glass fibers.

10 In at least one exemplary embodiment, the inventive glass composition includes the following components in the weight percent ranges given in Table 1. As used herein, the terms "weight percent" and "percent by weight" may be used interchangeably and are meant to denote the weight percent (or percent by weight) based on the total composition. In exemplary embodiments, the inventive glass composition is free or substantially free of
15 lithium, and in some exemplary embodiments, the glass composition is substantially free of lithium and boron. As used herein, the phrase "substantially free" is meant to denote that the composition is free or nearly free of that component(s). For instance, it is to be appreciated that if lithium is present in the glass composition, it is present in only in trace amounts, such as, for example, several hundredths of a percent. Similarly, glass
20 compositions intended to exclude boron may contain trace amounts of boron such as in the range of several hundredths of a percent. Compositions containing such amounts are considered to be "free of lithium" and "free of boron".

TABLE 1

Chemical	% by weight
SiO ₂	59.0 – 64.5
TiO ₂	0.0 – 2.0
Al ₂ O ₃	14.5 – 20.5
CaO	11.0 – 16.0
MgO	5.5 – 11.5
Na ₂ O	0.0 – 4.0
K ₂ O	0 – 1.0
Fe ₂ O ₃	0 – 1.0
SrO	0 – 2.0
ZnO	0 – 2.0
ZrO ₂	0 – 1.0
Fluorine	0 – 1.0
B ₂ O ₃	0.0 - 3.0

In another embodiment of the invention, the glass composition includes the components set forth in Table 2.

TABLE 2

Chemical	% by weight
SiO ₂	60.0 – 64.5
Al ₂ O ₃	14.6 – 20.4
TiO ₂	0.0 – 2.0
CaO	11.0 – 15.8
MgO	5.7 – 11.2
Na ₂ O+ K ₂ O	< 2
B ₂ O ₃	0 – 1.0
Fe ₂ O ₃	0 – 1.0
SrO	0 – 1.0
ZnO	0 – 1.0
Fluorine	0 – 1.0

In yet further embodiments, the glass compositions include the components set forth in Tables 3 and 4.

TABLE 3

Chemical	% by weight
SiO ₂	60.0 – 61.6
TiO ₂	0 – 2.0
Al ₂ O ₃	15.6 – 17.2
CaO	11.7 – 13.2
MgO	9.4 – 10.9
Na ₂ O+ K ₂ O	< 2
B ₂ O ₃	0.0 – 0.5
Fe ₂ O ₃	0 – 1.0
SrO	0 – 1.0
ZnO	0 – 1.0
Fluorine	0 – 1.0

TABLE 4

Chemical	% by weight
SiO ₂	60.0 – 61.6
TiO ₂	0 – 2.0
Al ₂ O ₃	15.6 – 17.2
CaO	11.7 – 13.2
MgO	9.4 – 10.9
Na ₂ O+ K ₂ O	< 2
B ₂ O ₃	0.0 – 0.2
Fe ₂ O ₃	0 – 1.0
SrO	0 – 1.0
ZnO	0 – 1.0
Fluorine	0 – 1.0

Further, impurities or tramp materials may be present in the glass composition without adversely affecting the glasses or the fibers. These impurities may enter the glass as raw material impurities or may be products formed by the chemical reaction of the molten glass with furnace components. Non-limiting examples of tramp materials include potassium, iron, zinc, strontium, and barium, all of which are present in their oxide forms, and fluorine and chlorine.

The forming viscosity of a glass composition is commonly defined by its log 3 temperature. The log 3 temperature is the temperature at which the molten glass composition has a viscosity of 1,000 poise (*that is*, roughly the fiberizing viscosity), where the viscosity is determined by measuring the torque needed to rotate a cylinder immersed in the molten glass material according to ASTM C965. Lowering the fiberizing

temperature may reduce the production cost of the glass fibers because it allows for a longer bushing life, increased throughput, and reduced energy usage. By lowering the log 3 temperature, a bushing operates at a cooler temperature and does not quickly “sag”. Sag occurs in bushings held at an elevated temperature for extended periods of time. Lowering the log 3 temperature reduces the sag rate, and, as a result, the bushing life may be increased. Thus, the cost of producing the fibers may be reduced. In the present invention, the glass composition has a log 3 temperature less than about 1405 °C. In exemplary embodiments, the log 3 temperature is from about 1285 °C to about 1405 °C, or from about 1285 °C to about 1320 °C.

10 The liquidus temperature of the glass composition is the temperature below which the first crystal appears in the molten glass material when it is held at that temperature for 16 hours, according to ASTM C829. Additionally, the liquidus temperature is the greatest temperature at which devitrification can occur upon cooling the glass melt. At all temperatures above the liquidus temperature, the glass is completely molten. The liquidus temperature of the inventive composition is desirably no greater than about 1330 °C, and may range from about 1190 °C to about 1330 °C or from 1190 °C to about 1235 °C.

 The difference between the log 3 temperature and the liquidus temperature is termed “ ΔT ”. If the ΔT is too small, the molten glass may crystallize within the fiberizing apparatus and cause a break in the manufacturing process. Desirably, the ΔT is as large as possible for a given forming viscosity. A larger ΔT offers a greater degree of flexibility during fiberizing and helps to avoid devitrification both in the glass distribution system and in the fiberizing apparatus. Additionally, a large ΔT reduces the production cost of the glass fibers by allowing for a greater bushing life and a less sensitive forming process. The inventive composition may have a ΔT up to about 135 °C, and in exemplary embodiments, from about 60 °C to about 135 °C or from about 75 °C to 105 °C. In some exemplary embodiments, the ΔT is greater than about 60 °C.

 Another property of importance is the specific modulus. Is it desirable to have a specific modulus as high as possible to achieve a lightweight composite material that adds stiffness to the final article. Specific modulus is important in applications where stiffness of the product is an important parameter, such as in wind energy and aerospace applications. In the inventive composition, the glass has a specific modulus of at least 3.24×10^6 meters, or from about 3.24×10^6 meters to about 3.43×10^6 meters. In

exemplary embodiments, the glass has a specific modulus from about 3.39×10^6 meters to about 3.43×10^6 meters.

The inventive glass has a specific modulus, strength, and ΔT similar to traditional R-glass compositions that contain lithium. Thus, the composition of the present invention
5 retains the ability to make a commercially acceptable R-glass fiber and fiber product produced from the R-glass fibers and is able to reduce the cost of production by excluding high cost lithium from the composition and utilizing a conventional refractory to melt the components of the composition.

In general, fibers according to the present invention may be formed by obtaining
10 the raw ingredients and mixing or blending the components in a conventional manner in the appropriate quantities to give the desired weight percentages of the final composition. For example, the components may be obtained from suitable ingredients or raw materials including, but not limited to, sand or pyrophyllite for SiO_2 , limestone, burnt lime, wollastonite, or dolomite for CaO , kaolin, alumina or pyrophyllite for Al_2O_3 , and
15 dolomite, dolomitic quicklime, brucite, enstatite, talc, burnt magnesite, or magnesite for MgO . Glass cullet can also be used to supply one or more of the needed oxides. The mixed batch is then melted in a traditional refractory furnace or melter, and the resulting molten glass is passed along a forehearth and into bushings (*for example*, platinum-alloy based bushings) located along the bottom of the forehearth. The operating temperatures of
20 the glass in the furnace, forehearth, and bushing are selected to appropriately adjust the viscosity of the glass, and may be maintained using suitable methods such as control devices. Preferably, the temperature at the front end of the melter is automatically controlled to reduce or eliminate devitrification. The molten glass is then pulled (drawn) through holes or orifices in the bottom or tip plate of the bushing to form glass fibers. The
25 streams of molten glass flowing through the bushing orifices are attenuated to filaments by winding a strand formed of a plurality of individual filaments on a forming tube mounted on a rotatable collet of a winding machine.

The fibers may be further processed in a conventional manner suitable for the intended application. For instance, the glass fibers may be sized with a sizing composition
30 known to those of skill in the art. The sizing composition is in no way restricted, and may be any sizing composition suitable for application to glass fibers. The sized fibers may be used for reinforcing substrates such as a variety of plastics where the product's end use

requires strength and stiffness equal to or superior to traditional R-glass products. Such applications include, but are not limited to, woven fabrics for use in forming wind blades, armor plating, and aerospace structures.

Having generally described this invention, a further understanding can be obtained
5 by reference to certain specific examples illustrated below which are provided for purposes of illustration only and are not intended to be all inclusive or limiting unless otherwise specified.

EXAMPLES

Example 1: Lithium Free Glass Compositions

10 Glass compositions according to the present invention were made by mixing reagent grade chemicals in proportioned amounts to achieve a final glass composition with the oxide weight percentages set forth in Tables 5-8. The raw materials were melted in a platinum crucible in an electrically heated furnace at a temperature of 1620 °C for 3 hours. The forming viscosity (*that is*, log 3 temperature) was measured using a rotating cylinder
15 method (ASTM C965). The liquidus temperature was measured by exposing glass to a temperature gradient in a platinum-alloy boat for 16 hours (ASTM C829). ΔT was calculated as the difference between the temperature at which the viscosity of the glass was 1000 poise and the liquidus temperature. The speed of sound was measured using the sonic fiber method whereby a sound wave is propagated down the length of a fiber. The
20 modulus was calculated based on the relationship between the speed of sound, density, and Young's modulus. Density was measured by the Archimedes method. Finally, the specific modulus was calculated from the Young's modulus and measured density.

Example 1 set forth in Table 5 is a conventional lithium-containing R-glass. The composition and properties for this lithium-containing R-glass were included for
25 comparison purposes.

TABLE 5

Chemical	Ex. 1 (% by wt.)	Ex. 2 (% by wt.)	Ex. 3 (% by wt.)	Ex. 4 (% by wt.)	Ex. 5 (% by wt.)	Ex. 6 (% by wt.)	Ex. 7 (% by wt.)	Ex. 8 (% by wt.)
SiO ₂	60.15	60.57	60.18	60.18	60.18	60.18	60.18	60.18
TiO ₂	0.30	0.4	1.00	0.00	0.50	0.50	0.50	0.00
Al ₂ O ₃	16.27	16.34	17.15	17.15	17.15	17.15	17.15	17.15
CaO	13.61	12.65	12.24	12.24	12.24	12.24	12.24	12.24
MgO	8.10	9.95	9.43	9.43	9.43	9.43	9.43	9.43
Na ₂ O	0.31	0.03	0.00	0.00	0.50	0.00	0.00	0.00
Li ₂ O	0.75	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.20	0.00	0.00	1.00	0.00	0.50	0.00	0.50
Fe ₂ O ₃	0.29	0.06	0.00	0.00	0.00	0.00	0.50	0.50
B ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Property								
Log 3 Temp (°C)	1269	1299	1304	1318	1304	1312	1308	1317
Liquidus Temp (°C)	1187	1196	1229	1235	1223	1233	1221	1234
ΔT (°C)	82	103	75	84	81	79	88	83
Modulus (GPa)	87.5	87.7	87.5	86.3	87.4	87.0	87.5	86.9
Density (g/cm ³)	2.610	2.621	2.619	2.603	2.615	2.612	2.620	2.611
Specific Modulus (MetersX10 ⁶)	3.42	3.41	3.41	3.38	3.41	3.39	3.41	3.39
Strength (Mpa)								

TABLE 6

Chemical	Ex. 9 (% by wt.)	Ex. 10 (% by wt.)	Ex. 11 (% by wt.)	Ex. 12 (% by wt.)	Ex. 13 (% by wt.)	Ex. 14 (% by wt.)	Ex. 15 (% by wt.)	Ex. 16 (% by wt.)
SiO ₂	60.93	60.93	60.93	60.93	60.93	60.93	60.93	60.93
TiO ₂	0.25	1.00	0.00	0.00	0.50	0.50	0.50	0.00
Al ₂ O ₃	15.65	15.65	15.65	15.65	15.65	15.65	15.65	15.65
CaO	12.24	12.24	12.24	12.24	12.24	12.24	12.24	12.24
MgO	10.18	10.18	10.18	10.18	10.18	10.18	10.18	10.18
Na ₂ O	0.25	0.00	1.00	0.00	0.50	0.00	0.00	0.00
Li ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.25	0.00	0.00	1.00	0.00	0.50	0.00	0.50
Fe ₂ O ₃	0.25	0.00	0.00	0.00	0.00	0.00	0.50	0.50
B ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Property								
Log 3 Temp (°C)	1301	1298	1294	1308	1299	1306	1299	1306
Liquidus Temp (°C)	1224	1209	1223	1232	1216	1229	1220	1216
ΔT (°C)	77	89	72	76	83	77	79	90
Modulus (GPa)	87.0	87.1	86.7	85.8	87.1	86.6	87.4	86.7
Density (g/cm ³)	2.615	2.619	2.61	2.603	2.615	2.612	2.612	2.622
Specific Modulus (MetersX10 ⁶)	3.39	3.39	3.39	3.36	3.40	3.38	3.40	3.38
Strength (Mpa)								

TABLE 7

Chemical	Ex. 17 (% by wt.)	Ex. 18 (% by wt.)	Ex. 19 (% by wt.)	Ex. 20 (% by wt.)	Ex. 21 (% by wt.)	Ex. 22 (% by wt.)	Ex. 23 (% by wt.)	Ex. 24 (% by wt.)
SiO ₂	60.01	60.01	60.01	60.01	60.01	60.61	60.53	60.57
TiO ₂	0.25	1.00	0.00	0.00	0.00	0.42	0.33	0.40
Al ₂ O ₃	16.02	16.02	16.02	16.02	16.02	16.32	16.26	16.34
CaO	12.96	12.96	12.96	12.96	12.96	11.36	11.09	12.65
MgO	10.01	10.01	10.01	10.01	10.01	11.18	11.18	9.95
Na ₂ O	0.25	0.00	1.00	0.00	0.00	0.03	0.05	0.03
Li ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.25	0.00	0.00	1.00	0.00	0.00	0.23	0.00
Fe ₂ O ₃	0.25	0.00	0.00	0.00	1.00	0.06	0.32	0.06
B ₂ O ₃	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Property								
Log 3 Temp (°C)	1290	1289	1287	1298	1291	1300	1301	1308
Liquidus Temp (°C)	1216	1213	1199	1219	1212	1233	1235	1220
ΔT (°C)	88	88	88	86	87	88	87	87
Modulus (GPa)	87.1	87.6	87.1	85.6	87.5	88.2	88.1	87.3
Density (g/cm ³)	2.628	2.632	2.624	2.619	2.638	2.619	2.618	2.606
Specific Modulus (MetersX10 ⁶)	3.38	3.39	3.38	3.33	3.38	3.43	3.43	3.42
Strength (Mpa)						4187	4331	4237

TABLE 8

Chemical	Ex. 25	Ex. 26	Ex. 27	Ex. 28	Ex. 29	Ex. 30	Ex. 31	Ex. 32	Ex. 33
	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)	(% by wt.)
SiO ₂	60.57	60.57	60.57	60.57	60.57	59.57	60.57	60.57	59.57
TiO ₂	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Al ₂ O ₃	16.34	16.34	16.34	16.34	16.34	16.34	16.34	16.34	16.34
CaO	12.2	11.75	12.65	12.2	11.75	12.65	11.65	11.65	12.65
MgO	10.4	10.85	9.95	10.4	10.85	9.95	9.95	9.95	9.95
Na ₂ O	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03	0.03
Li ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
K ₂ O	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe ₂ O ₃	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.06
B ₂ O ₃	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00	0.00
SrO	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00	0.00
ZnO	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00	0.00
Fluorine	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.00
Log 3 Temp (°C)	1303	1301	1299	1300	1298	1288	1307	1307	1284
Property									
Liquidus Temp (°C)	1226	1229	1196	1220	1232	1211	1218	1220	1210
ΔT (°C)	77	72	104	80	66	77	89	86	75
Modulus (GPa)	88.1	88.0	87.7	88.1	88.0	86.4	86.8	87.4	87.1
Density (g/cm ³)	2.620	2.618	2.621	2.62	2.618	2.617	2.624	2.627	2.623
Specific Modulus (MetersX10 ⁶)	3.43	3.43	3.41	3.43	3.43	3.36	3.37	3.39	3.38
Strength (Mpa)			4220			4316	4282	4357	4233

Looking at Tables 5-8, it can be concluded that the glass compositions of Examples 2-33 have forming viscosities and liquidus temperatures that permit them to be produced in a refractory melter without including lithium in the composition. In addition, the exclusion of lithium from the glass composition greatly reduces the production cost of the glass since spodumene and lithium carbonate, which are very expensive, are not required as materials for the batch formulations. Also, many of the compositions listed in Tables 5-8 met or exceeded the specific modulus of commercially available R-glass that included

lithium in the composition (*for example*, Example 1). The inventive glass has strength that is equal to or improved over conventional lithium-containing R-glass compositions.

Example 2: Glass Formulations Containing Lithium

Glasses which included lithium were also investigated for comparison to the
 5 inventive glass compositions. Tables 9 and 10 set forth the data obtained regarding the log 3 temperature, the liquidus temperature, the ΔT , the modulus, the density, and the specific modulus for each of the lithium-containing glass compositions.

TABLE 9

Chemical	Ex. 34 (% by wt.)	Ex. 35 (% by wt.)	Ex. 36 (% by wt.)	Ex. 37 (% by wt.)	Ex. 38 (% by wt.)	Ex. 39 (% by wt.)	Ex. 40 (% by wt.)	Ex. 41 (% by wt.)	Ex. 42 (% by wt.)	Ex. 43 (% by wt.)
SiO ₂	60.51	58.50	58.57	61.32	58.67	58.61	58.75	58.77	58.65	59.29
TiO ₂	0.16	1.69	0.03	0.03	1.57	1.57	1.57	0.48	0.49	0.95
Al ₂ O ₃	16.28	14.75	17.55	18.18	17.09	15.96	17.42	17.35	17.40	16.45
CaO	14.10	12.18	12.16	12.66	13.43	13.48	13.50	14.24	13.43	14.08
MgO	7.73	9.93	8.55	5.82	6.34	7.70	7.51	6.36	7.73	6.90
Na ₂ O	0.77	0.11	0.13	0.32	2.44	0.82	0.80	0.76	0.85	1.27
Li ₂ O	0.45	2.85	3.01	1.67	0.46	1.85	0.44	2.04	1.44	1.06
Property										
Log 3 Temp (°C)	1283	1143	1185	1286	1275	1203	1269	1217	1236	1251
Liquidus Temp (°C)	1233	1190	1165	1225	1223	1184	1245	1197	1253	1198
ΔT (°C)	50	-47	20	61	52	19	24	20	-17	53
Modulus (GPa)	87	91	91	88	86					
Density (g/cm ³)	2.610	2.640	2.613	2.578	2.611	2.630	2.626	2.617	2.620	2.619
Specific Modulus (MetersX10 ⁶)	3.40	3.53	3.53	3.47	3.36					

TABLE 10

Chemical	Ex. 44 (% by wt.)	Ex. 45 (% by wt.)	Ex. 46 (% by wt.)	Ex. 47 (% by wt.)	Ex. 48 (% by wt.)	Ex. 49 (% by wt.)	Ex. 50 (% by wt.)	Ex. 51 (% by wt.)	Ex. 52 (% by wt.)	Ex. 53 (% by wt.)
SiO ₂	59.61	61.40	60.19	58.25	57.42	62.29	60.55	61.52	60.32	61.33
TiO ₂	0.28	0.02	1.36	1.06	0.62	0.51	0.62	0.66	0.62	0.63
Al ₂ O ₃	16.90	16.86	15.96	15.34	15.25	14.58	15.61	15.98	16.29	16.36
CaO	14.45	12.71	13.55	16.08	15.92	12.76	13.32	12.57	13.46	12.45
MgO	7.16	5.82	7.70	6.85	7.42	8.71	9.12	8.57	8.34	8.25
Na ₂ O	0.85	0.31	0.82	1.46	0.94	0.16	0.18	0.16	0.28	0.38
Li ₂ O	0.75	2.89	0.40	0.95	2.43	1.01	0.60	0.54	0.69	0.59
Property										
Log 3 Temp (°C)	1262	1203	1281	1203	1182	1254	1240	1277	1259	1279
Liquidus Temp (°C)	1219	1146	1196	1211	1192	1191	1198	1186	1208	1208
ΔT (°C)	43	56	86	-8	-10	63	42	90	51	71
Modulus (GPa)		88		88		88	89	88	89	87
Density (g/cm ³)	2.619	2.579	2.618	2.649	2.647	2.601	2.619	2.601	2.615	2.585
Specific Modulus (Meters X 10 ⁶)		3.48		3.41		3.44	3.45	3.45	3.46	3.43

It can be concluded from Tables 9 and 10 that levels of Li₂O greater than 1 percent generally resulted in ΔT levels that were less than desirable for melting in a conventional refractory melter. It was noted that a few glasses having a Li₂O content near 0.5% did possess acceptable forming and product properties; however, production costs for those glasses would be far greater than production costs for the inventive lithium-free glass compositions due to the need for expensive lithium raw materials.

The invention of this application has been described above both generically and with regard to specific embodiments. Although the invention has been set forth in what is believed to be the preferred embodiments, a wide variety of alternatives known to those of skill in the art can be selected within the generic disclosure. The invention is not otherwise limited, except for the recitation of the claims set forth below.

WHAT IS CLAIMED IS:

1. A composition for preparing R-glass fibers comprising:
SiO₂ in an amount from 59.0 to 60.93% by weight of the total composition;
Al₂O₃ in an amount from 15.6 to 20.5% by weight of the total composition;
CaO in an amount from 11.0 to 13.2% by weight of the total composition;
B₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition;
MgO in an amount from 5.5 to 11.5% by weight of the total composition;
Na₂O in an amount from 0.0 to 4.0% by weight of the total composition; and
TiO₂ in an amount from 0.0 to 2.0% by weight of the total composition,
wherein said composition has a ΔT of at least 60 °C, a fiberizing temperature from 1,285 °C to 1,320 °C, and is free of Li₂O.
2. The composition of claim 1, further comprising Fe₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition.
3. The composition of claim 2, further comprising:
K₂O in an amount from 0.0 to 1.0% by weight of the total composition;
SrO in an amount from 0.0 to 2.0% by weight of the total composition;
ZnO in an amount from 0.0 to 2.0% by weight of the total composition;
ZrO₂ in an amount from 0.0 to 1.0% by weight of the total composition; and
Fluorine in an amount from 0.0 to 1.0% by weight of the total composition.
4. The composition of claim 1, wherein said composition has a ΔT up to 135 °C.
5. The composition of claim 4, wherein said composition has a ΔT from 75 °C to 105 °C.
6. The composition of claim 1, wherein said composition has a liquidus temperature no greater than 1235°C.
7. The composition of claim 1, wherein components of said composition are melted in a refractory tank melter.

8. The composition of claim 1, wherein said composition has a specific modulus of at least 3.24×10^6 meters.
9. The composition of claim 8, wherein said composition has a specific modulus from 3.24×10^6 meters to 3.43×10^6 meters.
10. A continuous R-glass fiber produced from a composition comprising:
SiO₂ in an amount from 59.0 to 64.5% by weight of the total composition;
Al₂O₃ in an amount from 15.6 to 20.5% by weight of the total composition;
CaO in an amount from 11.0 to 13.2% by weight of the total composition;
MgO in an amount from 9.4 to 10.9% by weight of the total composition;
Na₂O in an amount from 0.0 to 4.0% by weight of the total composition; and
TiO₂ in an amount from 0.0 to 2.0% by weight of the total composition,
wherein said composition has a ΔT of at least 60 °C and is free of Li₂O, and wherein said composition has a density of at least 2.606 and 2.638 g/cm³.
11. The glass fiber of claim 10, further comprising at least one of:
Fe₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition;
B₂O₃ in an amount from 0.0 to 3.0% by weight of the total composition;
K₂O in an amount from 0.0 to 1.0% by weight of the total composition;
SrO in an amount from 0.0 to 2.0% by weight of the total composition;
ZnO in an amount from 0.0 to 2.0% by weight of the total composition;
ZrO₂ in an amount from 0.0 to 1.0% by weight of the total composition; and
Fluorine in an amount from 0.0 to 1.0% by weight of the total composition.
12. A method of forming an R-glass fiber comprising:
providing a molten glass composition including:
SiO₂ in an amount from 59.0 to 60.93 % by weight of the total composition;
Al₂O₃ in an amount from 15.6 to 20.5% by weight of the total composition;
CaO in an amount from 11.0 to 13.2% by weight of the total composition;

MgO in an amount from 5.5 to 11.5% by weight of the total composition;
B₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition;
Na₂O in an amount from 0.0 to 4.0% by weight of the total composition; and
TiO₂ in an amount from 0.0 to 2.0% by weight of the total composition,
wherein said composition has a ΔT of at least 60 °C, a fiberizing temperature from 1,285 °C to 1,320 °C, and is free of Li₂O; and
drawing said molten glass composition through orifices in a bushing to form an R-glass fiber.

13. The method of claim 12, further comprising Fe₂O₃ in an amount from 0.0 to 1.0% by weight of the total composition.
14. The method of claim 12, further comprising:
K₂O in an amount from 0.0 to 1.0% by weight of the total composition;
SrO in an amount from 0.0 to 1.0% by weight of the total composition;
ZnO in an amount from 0.0 to 1.0% by weight of the total composition;
ZrO₂ in an amount from 0.0 to 1.0% by weight of the total composition; and
Fluorine in an amount from 0.0 to 1.0% by weight of the total composition.
15. The method of claim 12, wherein said composition has a ΔT up to 135 °C.
16. The method of claim 12, wherein said composition has a specific modulus of at least 3.24 X 10⁶ meters.
17. The method of claim 12, further comprising:
melting components of said glass composition in a refractory melter.