



(86) Date de dépôt PCT/PCT Filing Date: 2020/07/16
(87) Date publication PCT/PCT Publication Date: 2022/01/10
(45) Date de délivrance/Issue Date: 2023/03/21
(85) Entrée phase nationale/National Entry: 2021/05/26
(86) N° demande PCT/PCT Application No.: CN 2020/102349
(87) N° publication PCT/PCT Publication No.: 2022/006947
(30) Priorité/Priority: 2020/07/10 (CN202010664254.9)

(51) Cl.Int./Int.Cl. *C03C 13/02* (2006.01)
(72) Inventeurs/Inventors:
ZHANG, LIN, CN;
XING, WENZHONG, CN;
CAO, GUORONG, CN;
YAO, ZHONGHUA, CN
(73) Propriétaire/Owner:
JUSHI GROUP CO., LTD., CN
(74) Agent: BORDEN LADNER GERVAIS LLP

(54) Titre : COMPOSITION DE FIBRE DE VERRE A MODULE ELEVE, FIBRE DE VERRE ET MATERIAU COMPOSITE CONNEXE
(54) Title: HIGH-MODULUS GLASS FIBER COMPOSITION, GLASS FIBER AND COMPOSITE MATERIAL THEREOF

(57) Abrégé/Abstract:

The present invention provides a high-modulus glass fiber composition, a glass fiber and composite material thereof. The high-modulus glass fiber composition comprises the following components expressed as percentage by weight: 42-56.8% of SiO₂, 15.8-24% of Al₂O₃, 9.2-18% of MgO, 0.1-6.5% of CaO, greater than 8% but less than or equal to 20% of Y₂O₃, 0.01-4% of TiO₂, 0.01-1.5% of Fe₂O₃, 0.01-1.5% of Na₂O, 0-1.5% of K₂O, 0-0.7% of Li₂O, 0-3% of SrO, and 0-2.9% of La₂O₃; wherein, the total weight percentage of the above components is greater than or equal to 98%, and the range of the weight percentage ratio Cl=Y₂O₃/CaO is greater than 2.1. The composition can significantly increase the modulus of glass fiber, significantly reduce the refining temperature and bubbles content in molten glass; it can also remarkably improve the cooling performance of glass fiber and effectively reduce the crystallization rate. The composition is suitable for large-scale production of high-modulus glass fiber.



ABSTRACT

The present invention provides a high-modulus glass fiber composition, a glass fiber and composite material thereof. The high-modulus glass fiber composition comprises the following components expressed as percentage by weight: 42-56.8% of SiO_2 , 15.8-24% of Al_2O_3 , 9.2-18% of MgO , 0.1-6.5% of CaO , greater than 8% but less than or equal to 20% of Y_2O_3 , 0.01-4% of TiO_2 , 0.01-1.5% of Fe_2O_3 , 0.01-1.5% of Na_2O , 0-1.5% of K_2O , 0-0.7% of Li_2O , 0-3% of SrO , and 0-2.9% of La_2O_3 ; wherein, the total weight percentage of the above components is greater than or equal to 98%, and the range of the weight percentage ratio $C1=\text{Y}_2\text{O}_3/\text{CaO}$ is greater than 2.1. The composition can significantly increase the modulus of glass fiber, significantly reduce the refining temperature and bubbles content in molten glass; it can also remarkably improve the cooling performance of glass fiber and effectively reduce the crystallization rate. The composition is suitable for large-scale production of high-modulus glass fiber.

HIGH-MODULUS GLASS FIBER COMPOSITION, GLASS FIBER AND COMPOSITE MATERIAL THEREOF

FIELD OF THE INVENTION

The invention relates to a high-modulus glass fiber composition, in particular, to a composition of high-modulus glass fiber that can be used as a reinforcing base material for advanced composites, and to the glass fiber and composite material thereof.

BACKGROUND OF THE INVENTION

As a reinforcing base material for advanced composite materials, high-modulus glass fibers were originally used mainly in the aerospace industry or the national defense industry. With the progress of science and technology and the development of economy, high-modulus glass fibers have been widely used in civil and industrial fields such as large wind blades, pressure vessels, optical cable cores and auto industry. Taking the field of wind power as an example, with the rapid development of large wind blades, the proportion of high modulus glass fiber used in place of ordinary glass fiber is increasing. At present, the pursuit of glass fiber having better modulus properties and the realization of mass production for this glass fiber has become an important trend of development for high modulus glass fibers.

The original high-strength and high-modulus glass is S-glass. Its composition is based on an $\text{MgO-Al}_2\text{O}_3\text{-SiO}_2$ system. As defined by ASTM, it is a type of glass mainly comprising the oxides of magnesium, aluminum and silicon. A typical solution of S-glass is S-2 glass developed by America. The combined weight percentage of SiO_2 and Al_2O_3 in the S-2 glass

composition is up to 90%, and the weight percentage of MgO is about 10%. As a result, the S-2 glass is not easy to melt and refine, and there are many bubbles in the molten glass. What's more, the forming temperature of S-2 glass fiber is up to 1571 °C and the liquidus temperature is as high as 1470 °C, and its crystallization rate is also very high. Consequently, the large-scale tank furnace production of S-2 glass fiber cannot be achieved, as it is too difficult to form S-2 glass fiber, and even one-step production is hard to secure. For these reasons, the production scale and efficiency of S-2 glass fiber are both very low while its price is high, making it impractical to achieve a large-scale industrial use.

An HS high-strength glass that is comparable to S-glass has been developed by China. The composition of the HS glass primarily contains SiO₂, Al₂O₃ and MgO while also including relatively high contents of Li₂O, B₂O₃ and Fe₂O₃. Its forming temperature is in a range from 1310°C to 1330°C and its liquidus temperature is from 1360°C to 1390°C. The temperatures of these two ranges are much lower than those of S glass. However, since the forming temperature of HS glass is lower than its liquidus temperature, the ΔT value is negative, which is unfavorable for efficient formation of glass fiber, the forming temperature has to be increased and special bushings and bushing tips have to be used to prevent a glass crystallization phenomenon from occurring in the fiber drawing process. This causes difficulty in temperature control and also makes it difficult to realize large-scale industrial production. In addition, due to the introduction of high contents of Li₂O and B₂O₃, with the combined content generally being over 2% or even 3%, the mechanical properties and corrosion resistance of glass are adversely affected. Moreover, the elastic modulus of HS glass is only similar to that of S-glass.

Japanese patent JP8231240 discloses a glass fiber composition which contains 62-67% of SiO₂, 22-27% of Al₂O₃, 7-15% of MgO, 0.1-1.1% of CaO and 0.1-1.1% of B₂O₃, expressed in percentage by weight on the basis of the total composition. Compared with S glass, the amount of bubbles formed with this composition is significantly lowered, but the fiber formation remains difficult, as its forming temperature goes beyond 1460 °C.

To sum up, the production of high-modulus glass fibers in the prior arts described above generally faces great production difficulties, specifically manifested by high forming temperature and high liquidus temperature, high rate of crystallization, narrow temperature ranges (ΔT) for fiber formation, great melting and refining problems, and many bubbles in the molten glass. To reduce these difficulties, most companies and institutions tend to sacrifice some of the glass properties, thus making it impossible to substantially improve the modulus of above-mentioned glass fibers.

SUMMARY OF THE INVENTION

In order to solve the issue described above, the present invention aims to provide a high-modulus glass fiber composition. The composition can significantly increase the modulus of glass fiber, significantly reduce the refining temperature of molten glass, and improve the refining performance of molten glass; it can also remarkably improve the cooling performance of glass fiber and effectively reduce the crystallization rate. The composition is suitable for large-scale production of high-modulus glass fiber.

In accordance with one aspect of the present invention, there is provided a composition for producing high-modulus glass fiber, the composition comprising percentage by weight of the following components:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and $\leq 20\%$
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%

Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, and the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1.

In a class of this embodiment, the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

In a class of this embodiment, the weight percentage ratio $C3 = Y_2O_3/(Al_2O_3 + MgO)$ is greater than or equal to 0.31.

In a class of this embodiment, the weight percentage ratio $C1 = Y_2O_3/CaO$ is further greater than or equal to 2.85.

In a class of this embodiment, the content range of Y_2O_3 is greater than 10% and less than or equal to 18% by weight.

In a class of this embodiment, the content range of SiO_2 is 44-55.9% by weight.

In a class of this embodiment, the content range of Al_2O_3 is 15.8-20.4% by weight.

In a class of this embodiment, the content range of MgO is 9.4-13.5% by weight.

In a class of this embodiment, the content range of CaO is 0.5-5.9% by weight.

In a class of this embodiment, the weight percentage ratio of Y_2O_3/MgO is greater than or equal to 0.8.

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO_2	44-55.9%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%

Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio C1= Y₂O₃/CaO is greater than or equal to 2.1, and the weight percentage ratio C2=MgO/CaO is greater than 2.

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-20.4%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

In a class of this embodiment, the composition further contains one or more components selected from the group consisting of ZrO_2 , CeO_2 , ZnO , B_2O_3 , F_2 and SO_3 , the combined weight percentage being less than 2%.

In a class of this embodiment, the composition further contains 0-0.9% by weight of ZrO_2 .

In a class of this embodiment, the composition further contains 0-0.6% by weight of CeO_2 .

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO_2	44-55.9%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y_2O_3	> 10% and $\leq 18\%$
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%
Li_2O	0-0.7%
SrO	0-3%
La_2O_3	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, the weight percentage ratio $C2 = MgO/CaO$ is greater than 2, and the weight percentage ratio $C3 = Y_2O_3/(Al_2O_3 + MgO)$ is greater than or equal to 0.31.

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-20.4%
MgO	9.2-18%
CaO	0.1-6.5%

Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.85, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

In a class of this embodiment, the composition comprises the following components expressed as percentage by weight:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 99.5%, and the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1.

In a class of this embodiment, the composition may be free of B_2O_3 .

In a class of this embodiment, the composition may produce a molten glass that has a refining temperature of less than or equal to $1460^{\circ}C$.

According to another aspect of this invention, a glass fiber produced with said glass fiber composition is provided.

According to yet another aspect of this invention, a composite material incorporating said glass fiber is provided.

In the high-modulus glass fiber composition according to the present invention, by introducing a high content of Y_2O_3 and a lowered amount of SiO_2 , and controlling the ratio of Y_2O_3/CaO , the respective contents of alkali earth metal oxides and alkali metal oxides, and the ratios of MgO/CaO , $Y_2O_3/(Al_2O_3+MgO)$ and Y_2O_3/MgO respectively, while reasonably configuring the content ranges of Al_2O_3 , SiO_2 , Y_2O_3 , MgO and CaO , and utilizing the special compensation effect and accumulation effect of yttrium ions in the glass structure as well as the synergistic effects between yttrium ions and calcium ions, between magnesium ions and calcium ions, and among yttrium ions, aluminum ions and magnesium ions, the composition enables a more compact stacking structure of the glass and a higher difficulty of ions reorganization and arrangement during the crystallization process. Therefore, the composition for producing a glass fiber of this invention significantly increases the glass modulus, effectively reduces the glass crystallization rate, and helps improve the refining effect of molten glass and cooling performance of glass fiber.

Specifically, the high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO_2	42-56.8%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y_2O_3	$> 8\%$ and $\leq 20\%$

TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

In addition, the total weight percentage of the above components is greater than or equal to 98%, and the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1.

The effect and content of each component in said glass fiber composition is described as follows:

SiO₂ is a main oxide forming the glass network. Compared with the S-glass, in order to increase the glass modulus, the glass fiber composition according to the present invention contains a significantly reduced amount of silica while including a high content of yttrium oxide. Thus, in the glass fiber composition of the present invention, the content range of SiO₂ is 42-56.8%. Preferably, the SiO₂ content range can be 44-55.9%, more preferably 44-54.9%, even more preferably 45-54%, and still even more preferably 45-53%.

Al₂O₃ is another main oxide forming the glass network. When combined with SiO₂, it can have a substantive effect on the mechanical properties of the glass. Too low of an Al₂O₃ content will make it impossible to obtain sufficiently high mechanical properties, while too high of an Al₂O₃ content will significantly increase the risk of crystallization. Therefore, the content range of Al₂O₃ in this invention is set to be 15.8-24%. Preferably, the Al₂O₃ content can be 15.8-21%, more preferably 15.8-20.4%, even more preferably 16.5-19.8%, and still even more preferably 17.5-19.8%.

Further, the sum of the weight percentages of SiO₂+Al₂O₃ can be 65-78%, which will not only ensure sufficiently high mechanical properties of glass fiber but also enable a

large-scale production at relatively low temperatures. Preferably, the sum of the weight percentages of $\text{SiO}_2 + \text{Al}_2\text{O}_3$ can be 65-76%, more preferably 66-74%, and even more preferably 66-72.5%.

Y_2O_3 is an important rare earth oxide. As the external ions of the glass network, Y^{3+} ions have large coordination numbers, high field strength and high electric charge, and high accumulation capability, which would help improve the structural stability of the glass and increase the glass modulus and strength. Meanwhile, the Y^{3+} ions and Ca^{2+} ions can replace each other well for network filling, as their ionic radii are almost the same, 0.09nm for the Y^{3+} ion and 0.1nm for the Ca^{2+} ion, both being noticeably larger than that of either Al^{3+} (0.0535nm) or Mg^{2+} (0.072nm). In the present invention, by introducing a high amount of Y_2O_3 while properly controlling the ratio of $\text{Y}_2\text{O}_3/\text{CaO}$, the movement and arrangement of other ions in the glass would be effectively inhibited, so that the crystallization tendency of the glass is minimized; also, the hardening rate of molten glass would be effectively adjusted and the cooling performance of the glass would be improved.

Therefore, in the glass fiber composition of this invention, the content range of Y_2O_3 is greater than 8% and less than or equal to 20%. Preferably, the content range of Y_2O_3 is 8.5-20%, more preferably 9.2-20%, even more preferably greater than 10% and less than or equal to 18%, and still even more preferably 10.5-18%. Furthermore, the content range of Y_2O_3 is preferably 12.0-18%, and more preferably 12.9-18%.

In the glass fiber composition according to the present invention, the weight percentage ratio $C1 = \text{Y}_2\text{O}_3/\text{CaO}$ is greater than or equal to 2.1. Preferably, the weight percentage ratio $C1$ is greater than or equal to 2.3, more preferably greater than or equal to 2.85, and even more preferably greater than or equal to 3.

In the present invention, MgO and CaO mainly play the role of regulating the viscosity and crystallization of the glass. In the glass fiber composition of this invention, the weight percent range of MgO is 9.2-18%. Preferably, the weight percent range of MgO can be 9.4-16%, more preferably 9.4-13.5%, even more preferably 9.4-12.6%, and still even more

preferably 9.4-12%. In the glass fiber composition of this invention, the weight percent range of CaO is 0.1-6.5%. Preferably, the weight percent range of CaO can be 0.5-5.9%, more preferably 0.5-4.9%, and even more preferably 1-4.4%.

Further, the weight percentage ratio $C2 = \text{MgO}/\text{CaO}$ is greater than 2. Preferably, the weight percentage ratio C2 is greater than or equal to 2.2, more preferably greater than or equal to 2.5, and even more preferably greater than or equal to 3.

At the same time, considering the difference of field strength between Y^{3+} ions and Ca^{2+} ions, as well as the differences of ionic radius and field strength between Ca^{2+} ions and Mg^{2+} ions, the ratios of $\text{Y}_2\text{O}_3/\text{CaO}$ and MgO/CaO are rationally controlled in this invention, so that not only can a better effect of structural stacking be achieved, but also the crystal phases formed in the glass crystallization can be effectively inhibited due to a strengthened competition among the crystal phases; and thus the crystallization tendency of the glass would be effectively controlled. The main crystal phases include cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_8$), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), diopside ($\text{CaMgSi}_2\text{O}_6$), or a mixture thereof.

Further, in another embodiment of this invention, an excellent modulus and refining performance of glass can be achieved with a glass fiber composition containing Y_2O_3 in an amount from greater than 10% to 18% by weight, CaO in an amount from 0.5% to 5.9% by weight, and SiO_2 in an amount from 44% to 55.9% by weight.

Further, in yet another embodiment of this invention, an excellent modulus and crystallization performance of glass can be achieved with a glass fiber composition containing Y_2O_3 in an amount from 13.1% to 18% by weight and CaO in an amount from 0.5% to 4.9% by weight.

Furthermore, in order to further increase the glass modulus and improve crystallization performance of the glass, the weight percentage ratio $C3 = \text{Y}_2\text{O}_3/(\text{Al}_2\text{O}_3 + \text{MgO})$ can be greater than or equal to 0.29. Preferably, the weight percentage ratio C3 can be greater than or equal to 0.31, and more preferably greater than or equal to 0.33. Further, the weight percentage ratio

of $\text{Y}_2\text{O}_3/\text{MgO}$ can be greater than or equal to 0.8, preferably greater than or equal to 1.0, and more preferably greater than or equal to 1.1.

Furthermore, the combined weight percentage of $\text{CaO}+\text{MgO}$ can be 9.5-20%. Preferably, the combined weight percentage of $\text{CaO}+\text{MgO}$ can be 9.5-17%, more preferably can be 9.5-16%, and even more preferably can be 10-15%.

Both Na_2O and K_2O can reduce glass viscosity and are good fluxing agents. Compared with Na_2O and K_2O , Li_2O can not only significantly reduce glass viscosity thereby improving the glass melting performance, but also help improve the mechanical properties of glass. However, the introduced amount of alkali metal oxides should be controlled, as the raw materials containing these oxides are very costly and, when there is an excessive amount of alkali metal ions in the glass fiber composition, the structural stability of the glass will be affected and thus the corrosion resistance of the glass will be noticeably impaired. Therefore, in the glass fiber composition according to the present invention, the content range of Na_2O is 0.01-1.5%, preferably 0.01-1%, more preferably 0.05-0.8%, and even more preferably 0.05-0.45%.

In the glass fiber composition according to the present invention, the content range of K_2O is 0-1.5%, preferably 0-1%, more preferably 0-0.8%, and even more preferably 0-0.5%.

In the glass fiber composition according to the present invention, the content range of Li_2O is 0-0.7%, preferably 0-0.5%, more preferably 0-0.3%. In another embodiment of this invention, the glass fiber composition can be free of Li_2O .

Further, the combined weight percentage of $\text{Na}_2\text{O}+\text{K}_2\text{O}+\text{Li}_2\text{O}$ can be 0.01-1.5%, preferably 0.05-0.9%, and more preferably 0.05-0.6%. Further, the combined weight percentage of $\text{Na}_2\text{O}+\text{K}_2\text{O}$ can be 0.01-1%, preferably 0.05-0.6%.

TiO_2 can reduce the viscosity of glass at high temperatures and, with a synergistic effect produced in combination with titanium ions and yttrium ions, can improve the stacking effect and mechanical properties of the glass. In the glass fiber composition of this invention,

the content range of TiO_2 is 0.01-4%, preferably 0.01-2%, more preferably 0.05-1.5%, and even more preferably 0.05-0.9%.

Fe_2O_3 facilitates the melting of glass and can also improve the crystallization performance of glass. However, since ferric ions have a coloring effect, the introduced amount should be limited. In the glass fiber composition of this invention, the content range of Fe_2O_3 is 0.01-1.5%, preferably 0.01-1%, and more preferably 0.01-0.8%.

SrO can reduce the glass viscosity and produce a synergistic effect of alkaline earth metal ions with calcium ions and magnesium ions, which can help further reduce the glass crystallization tendency. In the glass fiber composition of this invention, the content range of SrO is 0-3%, preferably 0-1.5%, more preferably 0-1%, and even more preferably 0-0.5%. In another embodiment of this invention, the glass fiber composition can be free of SrO .

La_2O_3 can reduce the glass viscosity and improve the mechanical properties of glass, and has a certain synergistic effect with yttrium ions, which can further reduce the crystallization tendency of glass. In the glass fiber composition of this invention, the content range of La_2O_3 is 0-2.9%, preferably 0-2%, more preferably 0-1%, and even more preferably 0-0.5%. In another embodiment of this invention, the glass fiber composition can be free of La_2O_3 .

In addition to the above-mentioned main components, the glass fiber composition according to the present invention can also contain a small amount of other components with a combined content less than or equal to 2%.

Further, the glass fiber composition according to the present invention contains one or more components selected from the group consisting of ZrO_2 , CeO_2 , ZnO , B_2O_3 , F_2 and SO_3 , and the total amount of ZrO_2 , CeO_2 , ZnO , B_2O_3 , F_2 and SO_3 is less than 2% by weight. Further, the total amount of ZrO_2 , CeO_2 , ZnO , B_2O_3 , F_2 and SO_3 is less than 1% by weight.

Further, the glass fiber composition according to the present invention contains one or more components selected from the group consisting of Sm_2O_3 , Sc_2O_3 , Nd_2O_3 , Eu_2O_3 and

Gd₂O₃, and the total amount of Sm₂O₃, Sc₂O₃, Nd₂O₃, Eu₂O₃ and Gd₂O₃ is less than 2% by weight.

Further, the glass fiber composition according to the present invention contains one or more components selected from the group consisting of Ho₂O₃, Er₂O₃, Tm₂O₃, Tb₂O₃ and Lu₂O₃, and the total amount of Ho₂O₃, Er₂O₃, Tm₂O₃, Tb₂O₃ and Lu₂O₃ is less than 2% by weight.

Further, the glass fiber composition according to the present invention contains either or both of Nb₂O₅ and Ta₂O₅ with a combined content of less than 1% by weight.

Further, the glass fiber composition according to the present invention contains ZrO₂ with a content range of 0-1.5%. Further, the content range of ZrO₂ can be 0-0.9%, and still further can be 0-0.3%. In another embodiment of this invention, the glass fiber composition can be free of ZrO₂.

Further, the glass fiber composition according to the present invention contains CeO₂ with a content range of 0-0.6%. Further, the content range of CeO₂ can be 0-0.3%. In another embodiment of this invention, the glass fiber composition can be free of CeO₂.

Further, the glass fiber composition according to the present invention contains B₂O₃ with a content range of 0-1%. In another embodiment of this invention, the glass fiber composition can be free of B₂O₃.

Further, the glass fiber composition according to the present invention contains F₂ with a content range of 0-0.5%. Further, the glass fiber composition according to the present invention contains SO₃ with a content range of 0-0.5%. Further, the glass fiber composition can be free of MnO.

Further, the combined weight percentage of other components can be less than or equal to 1%, and still further can be less than or equal to 0.5%.

Further, the refining temperature of glass fiber composition according to the present invention can be less than or equal to 1480 °C. Further, the refining temperature can be less than or equal to 1460 °C, and still further less than or equal to 1450 °C.

Further, the modulus of glass fiber formed from the glass fiber composition of this invention can be greater than or equal to 96 GPa. Further, the modulus of glass fiber can be greater than or equal to 98 GPa, and still further can be 98-110 GPa.

In the glass fiber composition according to the present invention, the beneficial effects produced by the aforementioned selected ranges of the components will be explained by way of examples through the specific experimental data.

The following are examples of preferred content ranges of the components contained in the glass fiber composition according to the present invention.

Preferred example 1

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-21%
MgO	9.4-16%
CaO	0.5-5.9%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1%
Li ₂ O	0-0.5%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, and the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1.

Preferred example 2

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-21%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 99.5%, and the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1.

Preferred example 3

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-21%
MgO	9.4-16%
CaO	0.5-5.9%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-2%

Fe_2O_3	0.01-1%
Na_2O	0.01-1.5%
K_2O	0-1%
Li_2O	0-0.5%
SrO	0-3%
La_2O_3	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = \text{Y}_2\text{O}_3/\text{CaO}$ is greater than or equal to 2.1, and the weight percentage ratio $C2 = \text{MgO}/\text{CaO}$ is greater than 2.

Preferred example 4

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO_2	44-55.9%
Al_2O_3	15.8-20.4%
MgO	9.4-13.5%
CaO	0.5-5.9%
Y_2O_3	$> 10\%$ and $\leq 18\%$
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%
Li_2O	0-0.7%
SrO	0-3%
La_2O_3	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

Preferred example 5

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO_2	42-56.8%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y_2O_3	> 8% and $\leq 20\%$
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%
Li_2O	0-0.7%
SrO	0-3%
La_2O_3	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, the weight percentage ratio $C2 = MgO/CaO$ is greater than 2, and the composition further comprises 0-0.3% by weight of ZrO_2 .

Preferred example 6

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
SiO ₂ +Al ₂ O ₃	66-74%
MgO	9.2-18%
CaO	0.1-6.5%
CaO+MgO	9.5-16%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

Preferred example 7

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	> 10% and ≤18%
TiO ₂	0.01-4%

Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.85, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

Preferred example 8

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-24%
MgO	9.4-16%
CaO	0.1-6.5%
Y ₂ O ₃	> 8% and ≤20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.1, the weight

percentage ratio $C2=MgO/CaO$ is greater than 2, and the weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

Preferred example 9

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO_2	44-55.9%
Al_2O_3	16.5-19.8%
MgO	9.4-13.5%
CaO	0.5-5.9%
Y_2O_3	> 10% and $\leq 18\%$
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%
Li_2O	0-0.7%
SrO	0-3%
La_2O_3	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1= Y_2O_3/CaO$ is greater than or equal to 2.1, and the weight percentage ratio $C2=MgO/CaO$ is greater than 2.

Preferred example 10

The high-modulus glass fiber composition according to the present invention comprises the following components expressed as percentage by weight:

SiO_2	44-54.9%
Al_2O_3	16.5-19.8%
MgO	9.4-13.5%

CaO	0.5-4.9%
Y ₂ O ₃	> 10% and ≤18%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein, the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1 = Y_2O_3/CaO$ is greater than or equal to 2.85, and the weight percentage ratio $C2 = MgO/CaO$ is greater than 2.

DETAILED DESCRIPTION OF THE INVENTION

In order to better clarify the purposes, technical solutions and advantages of the examples of the present invention, the technical solutions in the examples of the present invention are clearly and completely described below. Obviously, the examples described herein are just part of the examples of the present invention and are not all the examples. All other exemplary embodiments obtained by one skilled in the art on the basis of the examples in the present invention without performing creative work shall all fall into the scope of protection of the present invention. What needs to be made clear is that, as long as there is no conflict, the examples and the features of examples in the present application can be arbitrarily combined with each other.

The basic concept of the present invention is that the components of the glass fiber composition expressed as percentage by weight are: 42-56.8% of SiO₂, 15.8-24% of Al₂O₃, 9.2-18% of MgO, 0.1-6.5% of CaO, greater than 8% and less than or equal to 20% of Y₂O₃,

0.01-4% of TiO_2 , 0.01-1.5% of Fe_2O_3 , 0.01-1.5% of Na_2O , 0-1.5% of K_2O , 0-0.7% of Li_2O , 0-3% of SrO , and 0-2.9% of La_2O_3 , wherein the total weight percentage of the above components is greater than or equal to 98%, and the range of the weight percentage ratio $C1=\text{Y}_2\text{O}_3/\text{CaO}$ is greater than 2.1. The composition can significantly increase the modulus of glass fiber, significantly reduce the refining temperature and bubbles content in molten glass; it can also remarkably improve the cooling performance of glass fiber and effectively reduce the crystallization rate. The composition is suitable for large-scale production of high-modulus glass fiber.

The specific content values of SiO_2 , Al_2O_3 , MgO , CaO , Y_2O_3 , TiO_2 , Fe_2O_3 , Na_2O , K_2O , Li_2O , SrO , La_2O_3 , CeO_2 and ZrO_2 in the glass fiber composition of the present invention are selected to be used in the examples, and comparisons with the improved R glass, designated as B1, as disclosed in the patent WO2016165506A2, traditional R glass designated as B2 and S glass designated as B3 are made in terms of the following eight property parameters,

(1) Forming temperature, the temperature at which the glass melt has a viscosity of 10^3 poise and which represents the typical temperature for fiber formation.

(2) Liquidus temperature, the temperature at which the crystal nucleuses begin to form when the glass melt cools off—i.e., the upper limit temperature for glass crystallization.

(3) Refining temperature, the temperature at which the glass melt has a viscosity of 10^2 poise and which represents the relative difficulty in refining molten glass and eliminating bubbles from the glass. Generally, when a refining temperature is lower, it will be more efficient to refine molten glass and eliminate bubbles under the same temperature.

(4) ΔT value, which is the difference between the forming temperature and the liquidus temperature and indicates the temperature range at which fiber drawing can be performed.

(5) ΔL value, which is the difference between the refining temperature and the forming temperature and indicates the hardening rate of molten glass. It can be used to represent the difficulty of glass melt cooling during fiber formation. Generally speaking, if the ΔL value is

relatively small, the glass melt will be easier to cool off under the same fiberizing conditions, which is conducive to efficient drawing of glass fiber.

(6) Elastic modulus, the modulus defining the ability of glass to resist elastic deformation, which is to be measured on bulk glass according to ASTM E1876. It can be used to represent the modulus property of glass fiber.

(7) Crystallization area ratio, to be determined in a procedure set out as follows: Cut the bulk glass appropriately to fit in with a porcelain boat trough and then place the cut glass bar sample into the porcelain boat. Put the porcelain boat with the pretreated glass bar sample into a gradient furnace for crystallization and keep the sample for heat preservation for 5 hours. Take the boat with the sample out of the gradient furnace and air-cool it to room temperature. Finally, examine and measure the amounts and dimensions of crystals on the surfaces of each sample within a temperature range of 1050-1150°C. from a microscopic view by using an optical microscope, and then calculate the relative area ratio of crystallization with reference to S glass. A high area ratio would mean a high crystallization tendency and a high crystallization rate.

(8) Bubbles content, to be determined in a procedure set out as follows: Use special molds to compress the glass batch materials in each example into samples of same shape and dimension, which will then be placed on the sample platform of a high temperature microscope. Heat the samples according to standard procedures up to the pre-set temperature of 1500°C. and then directly cool them off with the cooling hearth of the microscope to the ambient temperature without heat preservation. Finally, each of the glass samples is examined under an optical microscope to determine the amount of bubbles in the samples, and then calculate the relative bubbles content with reference to S glass. The higher the bubbles content is, the more difficult the refining of the glass will be, and the quality of the molten glass will be hard to be guaranteed. Wherein the amounts of bubbles are identified according to the magnification of the microscope.

The aforementioned eight parameters and the methods of measuring them are well-known to one skilled in the art. Therefore, these aforementioned parameters can be effectively used to explain the properties of the glass fiber composition according to the present invention.

The specific procedures for the experiments are as follows: Each component can be acquired from the appropriate raw materials. Mix the raw materials in the appropriate proportions so that each component reaches the final expected weight percentage. The mixed batch is melted and refined. Then the molten glass is drawn out through the tips of the bushings, thereby forming the glass fiber. The glass fiber is attenuated onto the rotary collet of a winder to form cakes or packages. Of course, traditional methods can be used to further process these glass fibers to meet the expected requirements.

Comparisons of the property parameters of the examples of the glass fiber composition according to the present invention with those of the S glass (B3), traditional R glass (B2) and improved R glass (B1) are further made below by way of tables, wherein the component contents of the compositions for producing glass fibers are expressed as weight percentage. What needs to be made clear is that the total amount of the components in an example is slightly less than 100%, and it should be understood that the remaining amount is trace impurities or a small amount of components which cannot be analyzed.

Table 1A

		A1	A2	A3	A4	A5	A6	A7
Component	SiO ₂	53.2	52.0	53.0	54.4	54.4	54.4	54.4
	Al ₂ O ₃	18.7	19.3	18.7	17.5	18.1	18.7	18.7
	CaO	2.9	5.9	4.9	4.0	3.4	3.4	4.8
	MgO	11.5	9.2	10.4	13.5	12.6	12.0	10.6
	Y ₂ O ₃	12.4	12.4	11.5	9.2	10.1	10.1	10.1
	Na ₂ O	0.15	0.05	0.05	0.25	0.25	0.25	0.25
	K ₂ O	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	Li ₂ O	0	0	0	0	0	0	0
	Fe ₂ O ₃	0.35	0.35	0.35	0.35	0.35	0.35	0.35
	TiO ₂	0.45	0.45	0.45	0.45	0.45	0.45	0.45
	SrO	0	0	0	0	0	0	0
	La ₂ O ₃	0	0	0	0	0	0	0
	CeO ₂	0	0	0.30	0	0	0	0
Ratio	C1	4.28	2.10	2.35	2.30	2.97	2.97	2.10
	C2	3.97	1.56	2.12	3.38	3.71	3.53	2.21
	C3	0.41	0.44	0.40	0.30	0.33	0.33	0.34
Parameter	Forming temperature /°C	1283	1274	1280	1279	1284	1286	1290
	Liquidus temperature /°C	1236	1220	1225	1253	1248	1242	1230
	Refining temperature /°C	1443	1432	1440	1439	1445	1447	1452
	ΔT/°C	47	54	55	26	36	44	60
	ΔL/°C	160	158	160	160	161	161	162
	Elastic modulus /GPa	105.0	103.0	104.0	103.2	103.8	103.0	102.2
	Crystalliza-	9	4	5	15	12	10	5

	tion area ratio /%							
	Bubbles content/%	6	4	3	5	7	8	9

Table 1B

		A8	A9	A10	A11	A12	A13	A14
Component	SiO ₂	54.0	49.8	51.0	52.5	55.9	52.5	56.8
	Al ₂ O ₃	19.0	21.0	20.4	19.8	18.6	18.6	16.5
	CaO	3.8	4.0	4.0	4.0	4.0	4.0	3.3
	MgO	11.0	9.4	10.0	10.0	10.0	10.0	10.4
	Y ₂ O ₃	10.5	14.4	13.2	12.3	10.1	13.5	11.6
	Na ₂ O	0.10	0.45	0.45	0.45	0.45	0.45	0.20
	K ₂ O	0.40	0.20	0.20	0.20	0.20	0.20	0.30
	Li ₂ O	0.30	0	0	0	0	0	0
	Fe ₂ O ₃	0.20	0.35	0.35	0.35	0.35	0.35	0.40
	TiO ₂	0.60	0.30	0.30	0.30	0.30	0.30	0.40
	SrO	0	0	0	0	0	0	0
	La ₂ O ₃	0	0	0	0	0	0	0
	CeO ₂	0	0	0	0	0	0	0
Ratio	C1	2.76	3.60	3.30	3.08	2.53	3.38	3.52
	C2	2.89	2.35	2.50	2.50	2.50	2.50	3.15
	C3	0.35	0.47	0.43	0.41	0.35	0.47	0.43
Parameter	Forming temperature /°C	1281	1276	1278	1284	1295	1280	1294
	Liquidus temperature /°C	1235	1245	1238	1235	1230	1220	1232
	Refining temperature /°C	1443	1433	1437	1445	1460	1440	1460
	ΔT/°C	46	31	40	49	65	60	62

	$\Delta L/^{\circ}\text{C}$	162	157	159	161	165	160	166
	Elastic modulus /GPa	103.5	106.0	105.3	103.8	102.6	105.0	102.0
	Crystallization area ratio /%	7	16	7	6	6	4	6
	Bubbles content/%	6	5	4	6	11	5	10

Table 1C

		A15	A16	A17	A18	A19	A20	A21
Component	SiO ₂	53.5	52.0	54.0	56.5	55.0	53.5	52.2
	Al ₂ O ₃	18.9	18.9	18.9	18.5	18.5	18.7	18.7
	CaO	2.4	1.0	3.3	3.7	3.7	3.0	3.5
	MgO	10.7	10.7	10.2	10.4	10.8	11.0	10.0
	Y ₂ O ₃	13.1	16.0	12.0	8.5	8.1	11.4	13.5
	Na ₂ O	0.30	0.30	0.30	0.30	0.30	0.30	0.30
	K ₂ O	0.20	0.20	0.20	0.20	0.20	0.20	0.20
	Li ₂ O	0	0	0.50	0	0	0	0
	Fe ₂ O ₃	0.40	0.40	0.30	0.30	0.30	0.40	0.30
	TiO ₂	0.40	0.40	0.30	1.50	0.90	0.40	0.30
	SrO	0	0	0	0	0	1.00	0
	La ₂ O ₃	0	0	0	0	2.00	0	0
	CeO ₂	0	0	0	0	0.10	0	0
	ZrO ₂	0	0	0	0	0	0	0.90
Ratio	C1	5.46	16.00	3.64	2.30	2.19	3.80	3.86
	C2	4.46	10.70	3.09	2.81	2.92	3.67	2.86
	C3	0.44	0.54	0.41	0.29	0.28	0.38	0.47
Parameter	Forming temperature / $^{\circ}\text{C}$	1291	1287	1269	1290	1285	1288	1286

	Liquidus temperature /°C	1238	1255	1231	1238	1225	1230	1224
	Refining temperature /°C	1452	1445	1429	1455	1449	1450	1446
	$\Delta T/^{\circ}\text{C}$	53	32	38	52	60	58	62
	$\Delta L/^{\circ}\text{C}$	161	158	160	165	164	162	160
	Elastic modulus /GPa	104.5	106.3	105.2	101.5	100.5	103.5	105.5
	Crystallization area ratio /%	10	14	8	12	3	5	5
	Bubbles content/%	8	7	3	6	7	8	7

Table 1D

		A22	A23	A24	A25	B1	B2	B3
Component	SiO ₂	54.9	54.9	53.0	51.9	60.1	60	65
	Al ₂ O ₃	18.0	19.2	19.2	19.2	17.0	25	25
	CaO	3.0	3.0	3.0	3.0	10.2	9	0
	MgO	11.4	10.4	10.4	10.4	9.8	6	10
	Y ₂ O ₃	11.0	11.0	12.9	14.0	0.5	0	0
	Na ₂ O	0.20	0.20	0.20	0.20	0.21	Trace amount	Trace amount
	K ₂ O	0.30	0.30	0.30	0.30	0.41	Trace amount	Trace amount
	Li ₂ O	0	0	0.10	0.10	0.65	0	0
	Fe ₂ O ₃	0.40	0.40	0.40	0.40	0.44	Trace amount	Trace amount
	TiO ₂	0.40	0.40	0.40	0.40	0.44	Trace amount	Trace amount
	SrO	0	0	0	0	0	0	0
	La ₂ O ₃	0	0	0	0	0	0	0
	CeO ₂	0	0.10	0	0	0	0	0
	ZrO ₂	0.30	0	0	0	0	0	0
Ratio	C1	3.67	3.67	4.30	4.67	0.05	0	-

	C2	3.80	3.47	3.47	3.47	0.96	0.67	-
	C3	0.37	0.37	0.44	0.47	0.02	0	0
Parameter	Forming temperature /°C	1288	1293	1284	1276	1300	1430	1571
	Liquidus temperature /°C	1236	1233	1230	1225	1208	1350	1470
	Refining temperature /°C	1451	1457	1445	1434	1498	1620	>1700
	$\Delta T/^{\circ}\text{C}$	52	60	54	51	92	80	101
	$\Delta L/^{\circ}\text{C}$	163	164	161	158	198	200	-
	Elastic modulus /GPa	103.5	103.0	104.5	105.7	90.9	89	90
	Crystallization area ratio /%	8	7	6	5	20	70	100
	Bubbles content/%	8	10	6	4	30	75	100

It can be seen from the values in the above tables that, compared with the composition of S glass, the glass fiber composition according to the present invention has the following advantages: (1) much higher elastic modulus; (2) much lower refining temperature and bubbles content, which means the molten glass of this invention is easier to refine and the bubbles are easier to be discharged; and (3) much lower fiber forming temperature, liquidus temperature and crystallization area ratio.

Compared with the composition of the traditional R glass, the glass fiber composition according to the present invention has the following advantages: (1) much higher elastic modulus; (2) much lower refining temperature and bubbles content, which means the molten glass of this invention is easier to refine and the bubbles are easier to be discharged; (3) much lower ΔL value, which helps increase the fiber drawing efficiency as the molten glass is easier to cool off; and (4) much lower fiber forming temperature, liquidus temperature and crystallization area ratio.

Compared with the composition of the improved R glass, the glass fiber composition according to the present invention has the following advantages: (1) much higher elastic modulus; (2) much lower refining temperature and bubbles content, which means the molten glass of this invention is easier to refine and the bubbles are easier to be discharged; (3) much lower ΔL value, which helps increase the fiber drawing efficiency as the molten glass is easier to cool off; and (4) a lower crystallization area ratio, which means the molten glass of this invention has relatively low crystallization rate and thus help reduce the crystallization risk.

Therefore, it can be concluded that the glass fiber composition according to the present invention has made a breakthrough in terms of glass modulus, refining and cooling performance, and crystallization rate. According to the present invention, under equal conditions, the modulus of glass is greatly raised, the refining temperature of molten glass is significantly lowered, the amount of bubbles in the molten glass is reduced and the glass shows excellent cooling performance. The overall technical solution of this invention is excellent.

The glass fiber composition according to the present invention can be used for making glass fibers having the aforementioned excellent properties.

The glass fiber composition according to the present invention in combination with one or more organic and/or inorganic materials can be used for preparing composite materials having excellent performance, such as glass fiber reinforced base materials.

It is to be noted that, in this text, the terms “comprise/comprising”, “contain/containing” and any other variants thereof are non-exclusive, so that any process, method, object or device containing a series of elements contains not only such factors, but also other factors not listed clearly, or further contains inherent factors of the process, method, object or device. Without further restrictions, a factor defined by the statement “comprises/comprising an/a ...”, “contain/containing an/a ...” or any other variants thereof does not exclude other identical factors in the process, method, object or device including said factors.

The foregoing embodiments are provided only for describing instead of limiting the technical solutions of the present invention. While particular embodiments of the invention have been shown and described, it will be obvious to one skilled in the art that modifications can be made to the technical solutions embodied by all the aforementioned embodiments, or that equivalent replacements can be made to some of the technical features embodied by all the aforementioned embodiments, without departing from the spirit and scope of the technical solutions of the present invention.

INDUSTRIAL APPLICABILITY OF THE INVENTION

The high-modulus glass fiber composition according to the present invention can significantly increase the modulus of glass fiber, significantly reduce the refining temperature of molten glass, and improve the refining performance of molten glass; it can also remarkably improve the cooling performance of glass fiber and effectively reduce the crystallization rate. The composition is suitable for large-scale production of high-modulus glass fiber.

Compared with conventional glass fiber compositions, the glass fiber composition according to the present invention has made a breakthrough in terms of glass modulus, refining and cooling performance, and crystallization rate. According to the present invention, under equal conditions, the modulus of glass is greatly raised, the refining temperature of molten glass is significantly lowered, the amount of bubbles in the molten glass is reduced and the glass shows excellent cooling performance. The overall technical solution of this invention is excellent.

Therefore, the present invention has good industrial applicability.

CLAIMS:

1. A high-modulus glass fiber composition, comprising the following components with corresponding amounts by weight percentage:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	greater than 8% and less than or equal to 20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein a total weight percentage of the above components is greater than or equal to 98%, a weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, and a weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

2. The high-modulus glass fiber composition of claim 1, wherein a weight percentage ratio $C2=MgO/CaO$ is greater than 2.

3. The high-modulus glass fiber composition of claim 1, wherein the weight percentage of Y₂O₃ is greater than 10% and less than or equal to 18%.

4. The high-modulus glass fiber composition of claim 1, wherein the weight percentage of SiO_2 is 44-55.9%.
5. The high-modulus glass fiber composition of claim 1, wherein the weight percentage of Al_2O_3 is 15.8-20.4%.
6. The high-modulus glass fiber composition of claim 1, wherein the weight percentage of MgO is 9.4-13.5%.
7. The high-modulus glass fiber composition of claim 1, wherein the weight percentage of CaO is 0.5-5.9%.
8. The high-modulus glass fiber composition of claim 1, wherein a weight percentage ratio of $\text{Y}_2\text{O}_3/\text{MgO}$ is greater than or equal to 0.8.
9. The high-modulus glass fiber composition of claim 1, comprising the following components with corresponding amounts by weight percentage:

SiO_2	44-55.9%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y_2O_3	greater than 8% and less than or equal to 20%
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%

Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, a weight percentage ratio $C2=MgO/CaO$ is greater than 2, and a weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

10. The high-modulus glass fiber composition of claim 1, comprising the following components with corresponding amounts by weight percentage:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-20.4%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	greater than 8% and less than or equal to 20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, a weight percentage ratio $C2=MgO/CaO$ is greater than 2, and a weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

11. The high-modulus glass fiber composition of claim 1, further comprising one or more components selected from the group consisting of ZrO_2 , CeO_2 , ZnO , B_2O_3 , F_2 and SO_3 , with a combined weight percentage being less than 2%.

12. The high-modulus glass fiber composition of claim 1, further comprising ZrO_2 with a weight percentage range of 0-0.9%.

13. The high-modulus glass fiber composition of claim 1, further comprising CeO_2 with a weight percentage range of 0-0.6%.

14. The high-modulus glass fiber composition of claim 1, comprising the following components with corresponding amounts by weight percentage:

SiO_2	44-55.9%
Al_2O_3	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y_2O_3	greater than 10% and less than or equal to 18%
TiO_2	0.01-4%
Fe_2O_3	0.01-1.5%
Na_2O	0.01-1.5%
K_2O	0-1.5%
Li_2O	0-0.7%
SrO	0-3%
La_2O_3	0-2.9%

wherein the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, a weight percentage ratio $C2=MgO/CaO$ is greater than 2, and a weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

15. The high-modulus glass fiber composition of claim 1, comprising the following components with corresponding amounts by weight percentage:

SiO ₂	44-55.9%
Al ₂ O ₃	15.8-20.4%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	greater than 8% and less than or equal to 20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein the total weight percentage of the above components is greater than or equal to 98%, the weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, a weight percentage ratio $C2=MgO/CaO$ is greater than 2, and a weight percentage ratio $C3=Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

16. The high-modulus glass fiber composition of claim 1, comprising the following components with corresponding amounts by weight percentage:

SiO ₂	42-56.8%
Al ₂ O ₃	15.8-24%
MgO	9.2-18%
CaO	0.1-6.5%
Y ₂ O ₃	greater than 8% and less than or equal to 20%
TiO ₂	0.01-4%
Fe ₂ O ₃	0.01-1.5%
Na ₂ O	0.01-1.5%
K ₂ O	0-1.5%
Li ₂ O	0-0.7%
SrO	0-3%
La ₂ O ₃	0-2.9%

wherein the total weight percentage of the above components is greater than or equal to 99.5%, and the weight percentage ratio $C1=Y_2O_3/CaO$ is greater than or equal to 2.85, and a weight percentage ratio $C3= Y_2O_3/(Al_2O_3+MgO)$ is greater than or equal to 0.31.

17. The high-modulus glass fiber composition of claim 1, being free of B₂O₃.
18. The high-modulus glass fiber composition of claim 1, having a glass refining temperature being less than or equal to 1460 °C.
19. A glass fiber, being produced using the composition according to any one of claims 1 to 18.
20. A composite material, incorporating the glass fiber of claim 19.