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National Aeronautics and Space Administration

Washington, D.C. 20546

JUN 21 1982

Reply to Attn of: GP-4

TO: NST-44/Scientific and Technical Information Division Attn: Shirley Peigare

FROM: GP-4/Office of Assistant General Counsel for Patent Matters

SUBJECT: Announcement of NASA-Owned U.S. Patents in STAR

In accordance with the procedures agreed upon by Code GP-4 and Code NST-44, the attached NASA-owned U.S. Patent is being forwarded for abstracting and announcement in NASA STAR.

The following information is provided:

U.S. Patent No. :	3,947,281
Government or Contractor Employee:	United Technologies Corporation Haitford, Conn.
NASA Case No. :	$H_{QN} - 10,595 - 1$

NOTE - If this patent covers an invention made by a contractor employee under a NASA contract, the following is applicable:



Pursuant to Section 305(a) of the National Aeronautics and Space Act, the name of the Administrator of NASA appears on the first page of the patent; however, the name of the actual <u>inventor</u> (author) appears at the heading of Column No. 1 of the specification, following the words "...with respect to an invention of...."



(NASA-Case-HQN-10595-1) HIGH MODULUS RARE N82-29455 EARTH AND BERYLLIUM CONTAINING SILICATE GLASS COMPOSITIONS Patent (National Aeronautics and Space Administration) 5 p Unclas CSCL 11B 00/27 24155

United States Patent [19]

Bacon

[54] HIGH MODULUS RARE EARTH AND BERYLLIUM CONTAINING SILICATE GLASS COMPOSITIONS

- [75] Inventor: James F. Bacon, Manchester, Conn.
- [73] Assignce: United Technologies Corporation, Hartford, Conn.
- [22] Filed: June 2, 1972
- [21] Appl. No.: 259,056

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 874,675, Nov. 6, 1969, abandoned.

[52]	U.S. Cl	
1511	Int. CL ²	C03C 3/04: C03C 13/00

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[45] Mar. 30, 1976

[11]

HQN-10,595-1

3,947,281

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Primary Examiner—Helen M. McArthur Assistant Examiner—Mark Bell Attorney, Agent, or Firm—John D. Del Ponti

[57] ABSTRACT

Glass compositions having a Young's modulus of at least 16 million psi and a specific modulus of at least 110 million inches consisting essentially of approximately, by weight, 20-43% SiO₂, 8-21% Al₂O₃, 4-10% BeO, 27-58% of at least one oxide selected from a first group consisting of Y₂O₃, La₂O₃, Nd₂O₃, Ce₂O₃ and the mixed rare earth oxides and 3-12% of at least one oxide selected from a second group consisting of MgO, ZrO₂, ZnO and CaO, the molar ratio of BeO to the total content of said first group oxides being from 1.0-3.0.

12 Claims, No Drawings

HIGH MODULUS RARE EARTH AND BERYLLIUM CONTAINING SILICATE GLASS COMPOSITIONS

BACKGROUND OF THE INVENTION

This is a continuation-in-part of application Ser. No. 874,675 filed Nov. 6, 1969, now abandoned by the same inventor.

The invention described herein was made in the performance of work under NASA contract and is subject 10 ing a Young's modulus ranging from at least 16 to at to the provisions of Section 305 of the National Aeronautics and Space Act of 1958, Public Law 85-568 (72 Stat. 435; 42 USC 2457).

This invention in general relates to high modulus glass and glass compositions and more particularly 15 relates to beryllia containing glasses having a Young's modulus of at least 16 million psi and a specific modulus of at least 110 million inches, some having a liquidus-viscosity relationship suitable for fiberization.

In the present age, there has been a continuing search 20 for glasses of high modulus and low density, capable for use as reinforcements, preferably in fiber form in composite structures such as those ranging from high strength missile cases and helicopter blades to propeller spinners and gas turbine engine parts. Glass offers 25 promise as the reinforcement in such applications since it may be quickly and cheaply produced by relatively conventional techniques and, generally, presents no compatability problems with the matrix materials with which it is normally used. There is a need however to 30 provide glass formulations which possess a high modulus of elasticity, and particularly a high modulus-density ratio. It is even more preferable if the glass possesses the aforementioned two characteristics in combination with an appropriate liquidus-viscosity relation 35 ship to permit fiberization.

There is dislosed in my copending application Ser. No. 683,465 filed on Nov. 16, 1967, now U.S. Pat. No. 3,573,078, glass compositions comprising silica, alumina and magnesia with substantial quantities of an 40 uncommon oxide such as lanthana, ceria or yttria which provide a formulation capable of fiberization to produce filaments having a high modulus of elasticity. It has now been found that the fiberizing properties of this type of glass composition, which shal be referred to 45 as rare earth or zirconia-cordierite base glasses, may be most markedly enhanced by including beryllia in a similar type glass and maintaining its content in a particular molar ratio to the total content of yttria, lanthana, neodymia, ceria and mixed rare earth oxides 50 present.

SUMMARY OF THE INVENTION

The glass compositions of the present invention are a high modulus, low density glass which, in their pre- 55 ferred form consist essentially of a combination of silica, beryllia, alumina, one or more oxides selected from a first group consisting of yttria, lanthana, neodymia, ceria and the mixed rare earth oxides and one or more oxides selected from a second group consisting of 60 magnesia, zirconia, zinc oxide and calcia, with the molar ratio of beryllia to the total content of the first group oxides being 1.0-3.0. In particular, the inventive glasses contemplated are those having a Young's modulus of at least 16 million psi and a specific modulus of 65 at least 110 million inches which consist essentially of, by weight, approximately 20-43% SiO., 4-10% BeO. 8-215-1-20, 27-58% of at least one oxide selected

from a first group consisting of Y2O2, La2O3, Nd2O3, Ce_2O_3 and the mixed rate earth oxides and 3-12% of at least one oxide selected from a second group consisting of MgO, ZrO₂, ZnO and CaO, the molar ratio of BeO to the total content of the first group oxides being from 1.0 to 3.0. In general, there are not more than two first group oxides nor more than three second group oxides in a given glass composition.

In several preferred embodiments, formulations havleast 21 million psi and a specific modulus ranging from at least 120 to at least 160 million inches that are readily formed into fibers having a relatively high fiber modulus ranging from above 15 to above 19 million psi are described. These include glasses consisting essentially of, by weight, approximately:

37% SiO2, 8% BeO, 10% Al2O3, 33% La2O3 and 12% ZrO₂;

- 30% SiO₂, 8% BeO, 16% Al₂O₃, 34% Y₂O₃ and 12% ZnO;
- 36% SiO₂, 5% BeO, 21% Al₂O₃, 30% Y₂O₃ and 8% MgO;
- 38% SiO₂, 8% BeO, 11% Al₂O₃, 34% La₂O₃ and 9% ZnO;
- 37% SiO₂, 8% BeO, 10% Al₂O₂, 33% La₂O₃ and 12% ZrO₂;
- 31% SiO₂, 8% BeO, 16% Al₂O₃, 30% Y₂O₃, 9% Ce₂O₃ and 6% MgO;
- 30% SiO₂, 8% BeO, 16% Al₂O₃, 29% Y₂O₃, 8% Ce₂O₂, 3% MgO and 6% ZnO;
- 30% SiO₂, 8% BeO, 15% Al₂O₃, 29% Y₂O₃, 8% Ce2O3, 6% ZnO and 4% CaO;
- 30% SiO₂, 8% BeO, 16% Al₂O₃, 29% Y₂O₃, 8% Ce2O3, 2% MgO, 4% ZnO and 3% CaO;
- 32% SiO₂, 4% BeO, 18% Al₂O₃, 39% mixed rare earth oxides and 7% MgO;
- 32% SiO₂, 4% BeO, 18% Al₂O₃, 39% La₂O₃ and 7% MgO; and
- 33% SiO₂, 8% BeO, 11% Al₂O₂, 36% La₂O₃, 4% Nd₂O₃ and 8% MgO.

The features of the invention will be discussed in greater detail in the description which follows or will be evident therefrom to those skilled in the art.

DESCRIPTION OF THE PREFERRED **EMBODIMENTS** · · · ÷ C

In a generic sense, the glasses of the present invention may be characterized as of the cordierite variety (Mg2Al4Si5O18-a three-dimensional ring-former), but with the inclusion of beryllia and with the addition of substantial amounts of oxides selected from the group consisting of yttria, lanthana, ceria, neodymia and mixed rare earth oxides, this addition in some instances being so large as to equal or exceed the contributed weight of the cordierite components.

In the preliminary work only pure materials, particularly those of lanthana, ceria, zirconia and beryllia were utilized so that the characterization and property data could be unequivocally interpreted. In later experiments much less costly and impure formulations were substituted, such as would be used in actual glass-making operations. The normal impurities found in the less pure starting materials, including some of the less common rare earths, have been found to exert no significant detrimental effect on the properties of the desired end product when present in the normal amounts.

With repsect to the form of the materials added, it has been the practice to add the ceria, lanthana, yttria,

neodymia and mixed rare earths as oxalates, the zirconia, beryllia, zinc and calcium as carbonates, and the other materials as oxides. Any form of the addition is satisfactory, however, as long as it is reducible in the melt to the oxide. And the addition of the ingredients in ⁵ a form which provides some gas evolution during the melting operation furnishes an advantageous stirring or "fining" effect in the melt.

Many of the inventive glasses are capable of fiberization which is the ability of the glass to be readily drawn 10 into filamentary form. In general, therefore, the glasses over a reasonable temperature range, depending on the particular composition, will display a viscosity of ap-

and bubbles due to the fining action of the oxalates when held at a temperature of at least 1500°C or higher for a period of time of at least two hours or longer. With the above-mentioned preparation technique alumina crucibles of even slightly lower purity (99.3–99.7%) cannot be used, nor can the temperature of about 1540°-1460°C be exceeded even with the alumina crucibles of highest purity. The more refractory glasses were melted in either platinum alloy crucibles, or in tungsten crucibles under argon cover.

The compositions of some of the representative glasses formulated in the course of the experimental program are set forth in Table I.

		-		Comp	ositions of	Represent	ative Glass	ies (Weigł	t Percen	t)			
Example	SiO ₂	BeO	Al ₂ O ₃	Y ₂ O ₃	La ₂ O ₃	Nd ₂ O3	Ce ₂ O ₃	R.E. Oxides	MgO	ZrO,	ZnO	CaO	Molar Ratio BcO/1st Group Oxides
. 1	36.6	7.5	10.4		33.1					12.5			3.0
2	25.8	6.9	13.5		43.1						10.8		2.1
3 .	29.8	7.9	15.5	34.4		•			•		. 12.4		2.1
-4.	24.9	8.9	18.1	• • • •	38.5					•	9.6		3.0
5	28.1	. 10.1	20.5	30.3							10.9		,3.0
6 .	19.7	8.2	16.7		44.5						11.1.		2.4
·7 ·	36.2	5.0	20.5	30.2					8.1				1.5
8	.38.2	7.9	10.8		34.4						8.6		3.0
.9	36.6	7.6	10.4	· .	33.1			•		. 12.5			3.0
10	38.1	7.4	10.9				34.5				8.6		3.0
	31.0	8.2	16.2	29.9			8.6		. 6.4				
12 .	29.9	8.0	15.6	28.8			8.4		3.1		6.2		2.1
13	30.2	8.1	15.8	29.1	•		8.4				•	8.7	2.1
-14	29.5	7.9	15.4	28:5	•		8.3			• *	. 1 6.2	4.2	2.1
15	30.0	8.0	15.7	28.9			8.4		2.1	•	4.2	2.9	2.1
16	25.7	6.9	13.4		7.2			36.1			10.7		2.1
17	38.2	7.9	10.8			. •		34.6			8.6		3.0
18	31.O ·	7.3	12.0		38.2						9.6		2:5
19	25.5	6.9	13.5	· . ·	43.1				¥		10.7		2.1
20	31.9	. 4.4	18.0	•	•			38.7	7.1			•	1.5
21	32.0	-4.4	.18.1		38.4				7.1				1.5
. 22	24.6	3.8	15.6		49.9		-		6.2	•		•	1.0
23	42.8	8.9	12.1	26.8							- 9.6		3.0
24	29.2	9.1	12.4		39.6						9.9	•	3.0
25	24.6	6.2	8.4		26.7	26.7				•	-6.7	· .	- 1.5
26	25.4	6.4	8.6		27.6	28.5			3:4				- 1.5
27	31.9	8.0	10.8		34.6	7.1			. 7.7				.2.5
28	33:3	-8.1	10.9		36.1	3.6			7.8				2.7

proximately 20,000 poises, the optimum viscosity being about 300-1,000 poises.

Typically, the glasses were prepared in 500 gram batches in high purity (99.9%) alumina crucibles in a Super-Kanthal hairpin kiln. The starting materials were 5 micron particle size high purity silica, 325 mesh high purity alumina, high purity precipitated magnesia, high purity lump-free beryllium carbonate, high purity precipitated zinc carbonate, zirconium carbonate, lithium carbonate and calcium carbonate, lanthanum, yttrium and/or cerium oxalates of 99% purity and a mixed rare earth oxalate of which a typical sample analyzed as:

	Rc,	(C,	20,}	x	H ₂ O	
~	0-:4		A		1	

La ₁ O ₃ *CeO ₅	_	11.2	
Pr _e O ₁₁ Nd ₂ O ₂	•	 2.4 8.0	
Sm ₂ O ₂ Gd ₂ O ₂		1.4 0.9	
Y ₂ O ₂ Others		0.1 0.4	н

Valence of ceriem in the oxalate = 3

In order to characterize the various glasses, measurements of the density and Young's modulus of bulk samples as well as Young's modulus of mechanically 45 drawn fibers were made. As a standard density measuring technique, the heavy-liquid-of-known density comparison procedure was used for samples with densities less than 3.00 gms/cm³ while the Archimedean method was employed for samples with densities greater than 50 3.00 gms/cm³.

Bulk samples for modulus measurement were prepared using the technique whereby the samples were drawn directly from the crucibles of molten glass into fused silica tubes previously dusted lightly with pow-55 dered magnesia. Controlled suction for pulling the sample into the tube was supplied by a hypodermic syringe. Since all of the experimental glasses had coefficients of thermal expansion at least higher than that of fused silica, the aspirated bars shrank away from the tube upon cooling and thus were readily removable.

Table II lists the values for a number of glasses made and tested in accordance with the teachings herein.

Iaurei

			ruote in	· ·	
55	Ğla	iss Density,	Young's Modulus and	Specific Modulus	•
	Example	Density Ib./in. 3	Young's Modulus psi × 10 ⁴	Specific Modulus 10 ^s in.	· .
		0.1318	16.7	127	

The ingredients were completely mixed dry by tumbling, and briquetted for ease of handling. The yield, in general, is a water-white optical grade glass free of seed

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Table	III-continue
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Frema	. 5	Specific Modulus	Young's Modulus	Density	Framale
	-	120	10.6	0.1//2	~~~~~~
3		129	18.0	0.1452	4
		138	20.9	0.1322	3
. ' 8	·	130	19.0	0.1392	- 4
9.4		100	21.0	0.1203	5
11	**	130	17.4	0.1500	
12	-10	170	20.3	0.1193	
14 -	•	104	21.0	0.1312	8
a: 15	ъ. 1	134	11.1	0.1317	
20		132	10.8	0.1273	10
· 21		149	19.0	0.12//	-41
28		144	19.1	0.1320	12
		139	17.8	0.12//	13
	:42	142	18.6	0.1320	14
	•.	144	18.5	0.1289	15
The particu		118	. 17.3	0.1473	- 10
	,	138	18.1	0.1312	17
cation will be		131	18.3	0.1393	18
properties of	• •	132	.19.2	0.1457	19
Abo Succession			18.2	0.1311	20
the ingredien	20	134	18.0	0.1340	21
high volume of		121	17.9	0,1477	22 5
White the i	•	154	19.1	0.1239	23
while the t		-134	18.7	0.1402	24
tion with a r	• •	123	. 19.3	0.1570	25
manta than a		128	19.6	0.1540	26
ments, they a		144	. 19_3	0.1345	5 27
limitation is ir	25	146	19.1	0.1308	28

Table II-continued

As is evident from the Tables, several of the formulations have proved to display extremely high modulus as well as modulus/density ratios superior to the best of 30 glass compositions heretofore known. The particular formulation selected in a given application, however, will be dependent usually not only upon the properties of the end product but also upon the cost of the ingredients included. This is particularly true in commercial 35 production.

Several of the glasses proved to be fiberizable. In order to evaluate these glasses, a "poor man's bushing" was used to prepare mechanically drawn fibers. The bushing comprises a 20 cm³ platinum crucible with a 40 reinforced bottom and central orifice. The orifice is formed by welding several thicknesses of platinum foil to the bottom of a normal platinum crucible until a bottom thickness of 3/16 in. is obtained. A central orifice .088 in. at top, .063 in. at bottom and 3/16 in. 45 long in the crucible is made by taper reaming. Once the orifice is made, the crucible is filled with glass and introduced into a platform furnace having high temperature Super-Kanthal hairpin heating elements together with a first ring orifice to provide water cooling imme- 50 diately below the crucible and a second ring orifice to cool the fiber with helium jets as it forms. The fibers were drawn at speeds of 4000-8000 feet/minute and yielded circular glass fibers having a diameter of approximately one mil. The fibers were then evaluated on 55 at least 16 million psi and a specific modulus of at least an Instron CRE tester operated with a machine speed of 0.2 in./minute, a chart speed of 20 in./minute, a gage length of 5 in. and a full scale capacity of 1.0 lb. The specimens were held in air actuated clamps with flat 60 rubber coated faces.

Table III lists the values for several glasses which were mechanically drawn into fibers.

Table III

······	Fiber Modul	128	
Example	e ,`	Young's Modulus psi × 10 ⁴	• .
	- · · · · · · · · · · · · · · · · · · ·	15.9	

	Fiber M	odulus
5	Example	Young's Modulus psi × 10 ⁴
	3	19.8
	7	18.6
:	8	17.4
	9	17.5
	11	17.5
10	12	18.8
	14	17.7
	ar 15	18.4
	28	17.8
	21	15.6
	28	17.4

lar formulation selected in a given applidependent, usually, not only upon the the end product but also upon the cost of ts included. This is particularly true in commercial production.

nvention has been described in connecumber of particular preferred embodire considered illustrative only, and no tended thereby. Numerous substitutions, alterations and modifications will be evident to those skilled in the art within the true spirit and scope of the invention as set forth in the appended claims.

What is claimed is:

1. A glass composition having a Young's modulus of at least 16 million psi and a specific modulus of at least 110 million inches consisting essentially of, by weight, approximately:

20-43% SiO2, 4-10% BeO, 8-21% Al2O3, 27-58% of at least one oxide selected from a first group consisting of Y2O3, La2O3, Nd2O3, Ce2O3 and mixtures thereof and 3-12% of at least one oxide selected from a second group consisting of MgO, ZrO, and ZnO, the molar ratio of BeO to the total content of said first group oxides being from 1.0 to 3.0.

2. A glass composition having a Young's modulus of at least 16 million psi and a specific modulus of at least 110 million inches consisting essentially of approximately, by weight:

20-43% SiO2, 4-10% BeO, 8-21% Al2O3, 27-58% of at least one but not more than two oxides selected from a first group consisting of YzO3, LazO3, Nd2O3 and Ce2O2 and 3-12% of not more than three oxides selected from a second group consisting of MgO, ZrO₂, and ZnO, the molar ratio of BeO to the total content of said first group oxides being from 1.0 to 3.0.

3. A glass composition having a Young's modulus of 110 million inches consisting essentially of, by weight, approximately:

20-43% SiO2, 4-10% BeO, 8-21% Al2O3, 27-58% of at least one oxide selected from a first group consisting of Y₂O₃, Nd₂O₃, Ce₂O₂ and mixtures thereof. and 3-12% of at least one oxide selected from a second group consisting of MgO, ZrO₂, ZnO and CaO, the molar ratio ratio of BeO to the total content of said first group oxides being from 1.0 to 3.0. 4. A glass composition having a Young's modulus of

at least 16 million psi and a specific modulus of at least 110 million inches consisting essentially of approximately, by weight:

5

-30

35

50

20-43% SiO₂, 4-10% BeO, 8-21% Al₂O₃, 27-58% of at least one but not more than two oxides selected from a first group consisting of Y_2O_3 , Nd₂O₃ and Ce₂O₃ and 3-12% of not more than three oxides selected from a second group consisting of MgO, ZrO₂, ZnO, and CaO, the molar ratio of BeO to the total content of said first group oxides being from 1.0 to 3.0.

5. A fiberizable glass composition having a Young's modulus of at least 20 million psi and a specific modulus of at least 150 million inches consisting essentially of about, by weight:

30% SiO₂, 8% BeO, 16% Al₂O₃, 34% Y₂O₃ and 12% ZnO.

6. A fiberizable glass composition having a Young's modulus of at least 20 million psi and a specific modulus of at least 160 million inches consisting essentially of about, by weight:

36% SiO₂, 5% BeO, 21% Al₂O₃, 30% Y₂O₃ and 8% 20 MgO.

7. A fiberizable glass composition having a Young's modulus of at least 20 million psi and a specific modulus of at least 160 million inches consisting essentially of about, by weight:

38% SiO₂, 8% BeO, 11% Al₂O₃, 34% La₂O₃ and 9% ZnO.

8. A fiberizable glass composition having a Young's modulus of at least 19 million psi and a specific modu-

lus of at least 140 million inches consisting essentially of about, by weight:

31% SiO₂, 8% BeO, 16% Al₂O₃, 30% Y₂O₃, 9% Ce₂O₃ and 6% MgO.

9. A fiberizable glass composition having a Young's modulus of at least 19 million psi and a specific modulus of at least 140 million inches consisting essentially of about, by weight:

30% SiO₂, 8% BeO, 16% Al₂O₃, 29% Y₂O₃, 8% Ce₂O₃, 3% MgO and 6% ZnO.

10. A fiberizable glass composition having a Young's modulus of at least 18 million psi and a specific modulus of at least 140 million inches consisting essentially of about, by weight:

30% SiO₂, 8% BeO, 15% Al₂O₃, 29% Y₂O₃, 8% Ce₂O₃, 6% ZnO and 4% CaO.

11. A fiberizable glass composition having a Young's modulus of at least 16 million psi and a specific modulus of at least 120 million inches consisting essentially of, by weight:

37% SiO₂, 8% BeO, 10% Al₂O₃, 33% La₂O₃ and 12% ZrO₂.

12. A fiberizable glass composition having a Young's modulus of at least 18 million psi and a specific modu²⁵ lus of at least 140 million inches consisting essentially of, by weight:

30% SiO₂, 8% BeO, 16% Al₂O₃, 29% Y₂O₃, 8% Ce₂O₃, 2% MgO, 4% ZnO and 3% CaO.