Feb. 27, 1968 A. R. HILTON, JR., ETAL 3,370,964

GLASSES AND METHOD OF MAKING SAME

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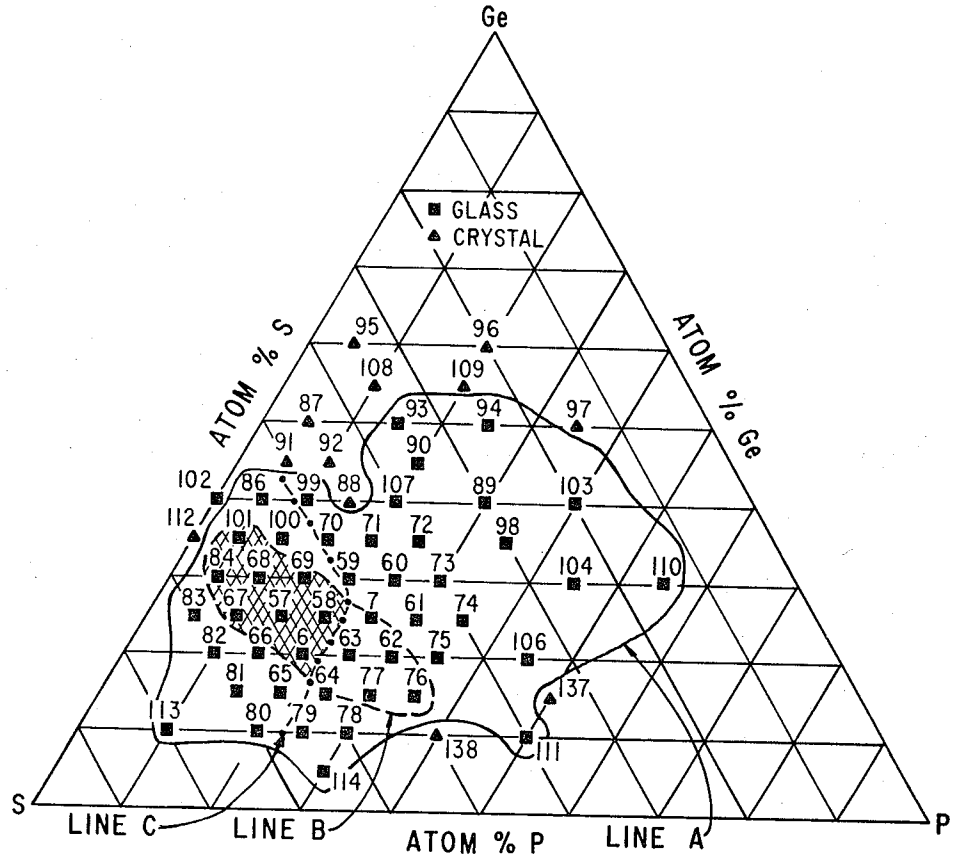


Fig. 1

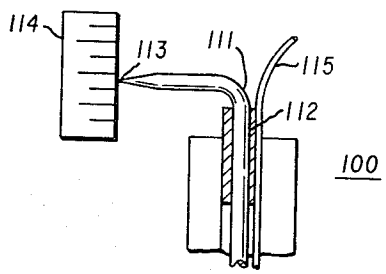
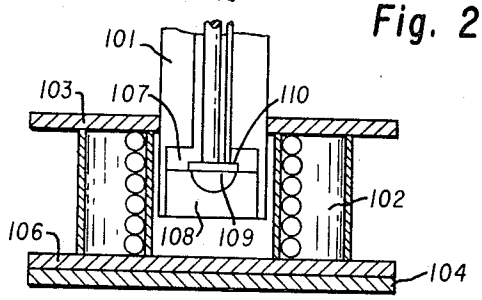


Fig. 2



ALBERT RAY HILTON, JR.
CHARLIE EARL JONES, JR.
INVENTORS
BY Harold Levine
ATTORNEY

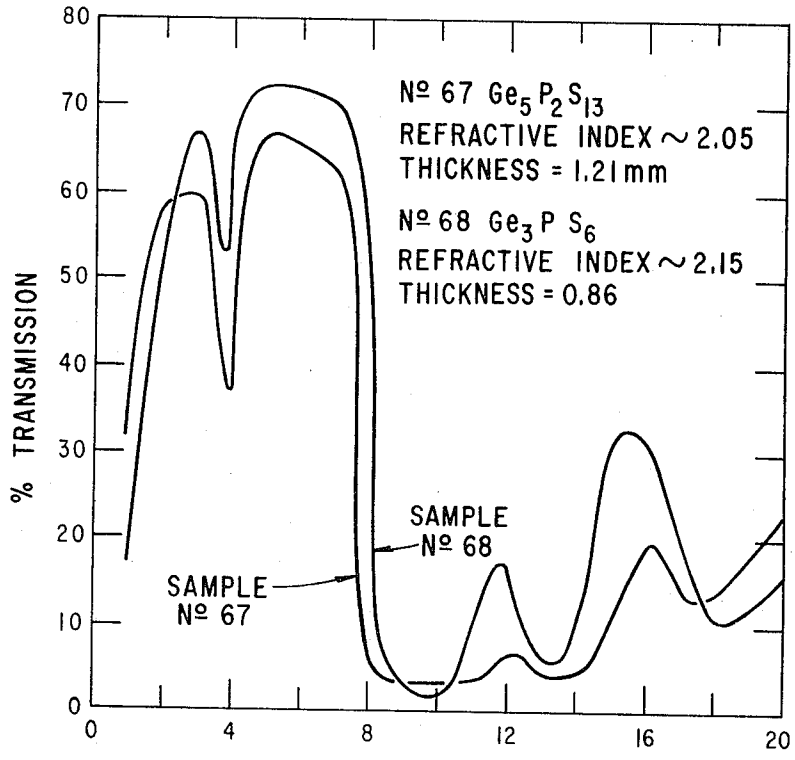


Fig. 3

ALBERT RAY HILTON, JR.
CHARLIE EARL JONES, JR.
INVENTORS
BY Harold Levine
ATTORNEY

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GLASSES AND METHOD OF MAKING SAME

Albert Ray Hilton, Jr., and Charlie Earl Jones, Jr., Richardson, Tex., assignors to Texas Instruments Incorporated, Dallas, Tex., a corporation of Delaware

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ABSTRACT OF THE DISCLOSURE

Disclosed are compositions of matter comprising germanium, phosphorus and sulfur, many samples of which have been found to be amorphous glasses transmitting in the infrared region of the electromagnetic spectrum, and some samples of which have been found to be crystalline. Also disclosed are methods of compounding said compositions, and apparatus for measuring the softening point of said glasses.

This invention relates to amorphous compositions of matter. More particularly it relates to infrared transparent glasses and to a method of making same.

The invention disclosed herein appertains to germanium-phosphorus-sulfur amorphous glass compositions which are transparent to the infrared region of the electromagnetic spectrum. Moreover, the invention provides compositions of matter having good transmission in the one to 20 micron wave-length region of the electromagnetic spectrum.

The glass of the invention may contain about up to 55 atom percent germanium, up to 50, (i.e., from 0–50) atom percent phosphorus, and 15 to 100 atom percent sulfur. The amorphous compositions of matter of the invention are either in binary or ternary form and may be made by forming a melt of the constituents and quench-cooling the melt from about 950° C. to 1000° C. to room temperature in air.

It is therefore an object of the invention to provide ternary amorphous compositions of matter comprising germanium, phosphorus, and sulfur, and binary amorphous compositions of matter comprising germanium and sulfur.

Another object of the invention is to provide binary and ternary amorphous compositions of matter exhibiting a high softening point and good transmission in the one to 20 micron wave-length region of the electromagnetic spectrum.

A further object of the invention is to provide binary and ternary amorphous compositions of matter comprising in major proportion or consisting essentially of up to 55 atom percent germanium, up to 50 (i.e., from 0–50) atom percent phosphorus, and 15 up to 100 atom percent sulfur.

A further object of the invention is to provide a method of making binary and ternary amorphous compositions of matter having good transmission in the one to 20 micron region of the electromagnetic spectrum.

These and other objects, advantages, and features of the invention will become more readily apparent from the following detailed description taken in conjunction with the appended claims and attached drawings wherein:

FIGURE 1 depicts a ternary diagram of the atomic percentages of germanium, phosphorus, and sulfur for various amorphous compositions of matter of the invention;

FIGURE 2 illustrates a Soft-Point apparatus utilized in obtaining characteristic properties of the glass;

FIGURE 3 is a graphical representation of percent transmission at room temperature of various wave lengths of the electromagnetic spectrum for various glass compositions according to this invention.

Referring to FIGURE 1, various compositions of germanium, phosphorus, and sulfur were compounded and evaluated to determine whether they were amorphous or crystalline. The general procedure for making the various compositions is described hereinafter.

Various atomic percents of germanium, phosphorus, and sulfur were chosen for each sample to be made. The appropriate amounts of the constituents were weighed and then placed in a previously cleaned quartz ampoule. An example of a suitable cleaning step for the ampoule is by etching 30 minutes in a 10% solution of concentrated hydrofluoric (48% HF) acid, rinsing in deionized water about 15 minutes, treating with aqua regia, rinsing in deionized water and then drying. The total weight of each of the samples was between 5 and 15 grams. The constituents were placed in the cleaned tube and evacuated to about 10^{-4} torr and sealed. The sealed tubes were then placed in a furnace and gradually heated to a temperature of about 950° C. to 1000° C. and held at that temperature for about 15 to 36 hours to provide sufficient time for the constituents to react completely with each other. The furnace was a rocking furnace which may be of any suitable design to provide agitation of the constituents so as to achieve maximum complete reaction thereof. The samples were then removed from the furnace and held in a vertical position in air for air quenching and allowed to cool to room temperature.

The sample compositions which failed to form amorphous glass by the air quench-cooling technique and were crystalline after quenching are presented in Table I below, whereas the compositions which formed amorphous glass are presented in Table II below with the Soft-Point results achieved for the glass. The reaction condition for the samples in Tables I and II below were the same. The samples were held at a temperature between 950° C. and 1000° C. for a period of about 15–36 hours.

TABLE I

	Composition, Atomic Percent		
	Ge	P	S
Sample No.:			
87	50	5	45
88	40	15	45
91	45	5	50
92	45	10	45
95	60	5	35
96	60	20	20
97	50	35	15
108	55	10	35
109	55	20	25
112	35		65
137	15	50	35
138	10	40	50

TABLE II

	Composition, Atomic Percent			Softening Point in ° C.
	Ge	P	S	
Sample No.:				
6	20	20	60	500
7	25	25	50	475
57	25	15	60	485
58	25	20	55	410
59	30	20	50	465
60	30	25	45	470
61	25	30	45	465
62	20	30	50	485
63	20	25	55	475
64	15	25	60	470
65	15	20	65	400
66	20	15	65	465
67	25	10	65	490
68	30	10	60	520
69	30	15	55	500
70	35	15	50	425
71	35	20	45	410
72	35	25	40	405
73	30	30	40	420
74	25	35	40	465
75*	20	35	45	----------
76	15	35	50	515
77	15	30	55	510
78	10	30	60	380
79	10	25	65	330
80	10	20	70	275
81	15	15	70	325
82	20	10	70	375
83	25	5	70	400
84	30	5	65	500
86	40	5	55	375
89	40	30	30	----------
90	45	20	35	425
93	50	15	35	455
94	50	25	25	520
98	35	35	30	450
99	40	10	50	400
100	35	10	55	420
101	35	5	60	480
102	40	--------	60	420
103	40	40	20	450
104	30	45	25	415
106	20	45	35	440
107	40	20	40	380
110	30	55	15	460
111	10	50	40	520
113	10	10	80	285
114	5	30	65	----------

* Two-Phase.

In FIGURE 1 the solid peripheral Line A, the broken dashed peripheral Line B, and the dash-dot peripheral Line C generally circumscribe the ternary amorphous compositions of germanium, phosphorus, and sulfur according to this invention. The samples which failed to form amorphous glass by the air quench-cooling technique (listed in Table I) are plotted in FIGURE 1 by black triangular dots identified by sample number and lie outside of the area circumscribed by Line A. The sample compositions forming amorphous glass listed in Table II are plotted in FIGURE 1 by black square dots identified by sample number and, except for the binary sample **102**, lie within the area generally circumscribed by one of Lines A, B, or C. Certain of the amorphous samples were discovered to show two distinct amorphous phases, indicating that an immiscible system exists in these composition regions. The measured softening points of the amorphous glass compositions of this invention have been tested as high as 520° C., and the glasses show very good transmission, particularly in the three to five micron region. The amorphous glass forming region according to this invention is generally enclosed by Line A in FIGURE 1. The area to the left of the dash-dot Line C i.e., compositions having more than 50 atom percent sulfur and circumscribed by Lines A and C, denotes the composition region in which the glasses show at least 50 percent transmission in the three to five micron region (thickness ~ 1 mm). The region within the dashed Line B is for compositions in which the measured softening point is greater than 480° C. The region common to all three areas enclosed by Lines A, B, and C is shaded in FIGURE 1 and represents the preferred composition according to this invention for high temperature transmission in the three to five micron wave-length region of the electromagnetic spectrum. The range of compositions within the shaded area in the diagram of FIGURE 1 is about 15 to 40 atomic percent germanium, up to 25 atom percent phosphorus, 50 to 65 atom percent sulfur. The range of compositions within the area circumscribed by the dashed Line B is about 15 to 40 atom percent germanium, up to 40 atom percent phosphorus, and 50 to 70 atom percent sulfur. The range of compositions within the region delineated by the dash-dot Line C and Line A of FIGURE 1 is about 5 to 45 atom percent germanium, up to 25 atom percent phosphorus, and 50 up to 100 atom percent sulfur.

Referring specifically to FIGURE 2, there is schematically illustrated an apparatus suitable for use in determining the Soft-Point listed in Table II. The apparatus, generally referred to as **100**, consists of a quartz tube **101** supported within a heating mantle **102** by mounting plate **103**. The heating mantle **102** has a base plate **106** seated on an asbestos pad **104**.The quartz tube **101** has an enlarged bore **107** which retains a boron nitride sample holder **108** having a hollow depression **109** therein. A sample slice **110** to be tested for Soft-Point is placed over the depression **109**. A quartz rod **111** is supported within the quartz tube **101**, resting against the surface of sample **110**. To maintain the quartz rod in vertical alignment with respect to the quartz tube **101**, a quartz guide **112** is provided. At the upper end of the quartz rod **111** a right angle bend is provided therein and the end of the quartz rod tapered to form a pointer **113**. A scale **114** is provided to show movement of the quartz rod **111**. The scale **114** is supported by means not illustrated in fixed relation to the sample slice **110**. A thermocouple **115** is provided abutting the sample surface for measuring the temperature of sample **110**.

In operation of the Soft-Point test apparatus **100**, an amorphous glass sample **110** is placed in its proper position and heat is applied by the heating manifold **102**. The temperature of the sample is slowly increased until the quartz rod **111**, under the influence of its weight, deforms the sample **110**, the amount of the deformation being indicated by the pointer **113** moving over the scale **114**.

The room temperature transmission of the various samples at various wave lengths of the electromagnetic spectrum are presented in Table III below.

TABLE III.—INFRARED TRANSMISSION OF SOME Ge-P-S GLASSES

	Sample No.					
	57	65	66	84	86	102
	Sample Thickness, mm.					
	1.16	0.86	1.03	1.50	1.09	0.88
	Refractive Index					
	2.0	1.95	2.05	2.15	2.1	2.15
	Percent Transmission					
Wave Length Microns:						
1	2	0	2	57	18	58
2	7	21	32	63	45	64
3	25	47	55	64	67	63
4	37	39	46	52	64	63
5	55	58	64	63	69	64
6	55	50	58	62	69	64
7	55	47	58	60	69	64
8	25	0	10	15	48	62
9	1	0	1	7	5	58
10	1	0	0	5	7	63
11	1	0	0	2	25	60
12	7	0	2.5	4	18	20
13	2	0	1	3	3	10
14	3	0	1	4	3	15
15	21	2	2.5	8	17	30
16	22	3	8	18	20	41
17	6	4	5	13	15	42
18	3	2	5	14	12	36
19	3	3	6	19	15	36
20	5	5	7	24	15	39

In FIGURE 3, the percent transmission of the electromagnetic spectrum in the one to 20 micron wave-length region is plotted for various of the glass samples contained in Table II.

It should be understood that although most of the samples tested were essentially germanium, phosphorus, and sulfur, minor percentages of silicon, selenium, tellurium, antimony, arsenic, bismuth, etc., may be used in the glass of the invention to provide variations in the softening point and transmission of the glass compositions.

Although only the air quench-cooling method has been described for making the amorphous compositions of matter of the invention, other methods could be used. Furthermore, the limits of composition for making amorphous material may be extended by more rapid quenching than provided by air quenching. Also, to achieve amorphous composition, the initial temperature for forming the melt may be extended several 100 degrees higher than described herein.

It should be appreciated that many other variations and changes to the invention will suggest themselves to those skilled in the art and such variations and changes are deemed to be within the purview and scope of the invention as defined in the appended claims.

What is claimed is:

1. A binary glass composition consisting essentially of 40 atomic percent germanium and 60 atomic percent sulfur.

2. Infrared transmitting ternary glass compositions consisting essentially of germanium, phosphorus, and sulfur having good transmission at high temperature in the 1 to 20 micron wave-length region of the electromagnetic spectrum, said compositions lying within Line B of FIGURE 1.

3. Infrared transmitting ternary glass compositions consisting essentially of germanium, phosphorus, and sulfur having good transmission at high temperature in the 1 to 20 micron wave-length region of the electromagnetic spectrum, said compositions lying within the region to the left of Line C and circumscribed by Lines A and C of FIGURE 1.

4. Infrared transmitting ternary glass compositions consisting essentially of germanium, phosphorus, and sulfur having good transmission at high temperature in the 1 to 20 micron wave-length region of the electromagnetic spectrum, said compositions lying within the shaded area of FIGURE 1.

5. Ternary glass compositions consisting essentially of germanium, sulfur and phosphorus and lying within Line A of FIGURE 1.

6. The method of making a ternary glass composition for transmitting the 1–20 micron wavelength portion of the electromagnetic spectrum said composition consisting essentially of germanium, sulfur and phosphorus and lying within the shaded area of FIGURE 1, comprising the steps of placing appropriate amounts of the constituents into a reaction vessel, evaporating and sealing said vessel, heating said vessel to a temperature of about 950° C. to 1000° C. and holding said vessel at said temperature for about 15 to 36 hours, in order to form a melt of said composition and to completely react the constituents thereof, agitating said vessel during said heating and quench-cooling said melt while sealed in said vessel in air at room temperature.

7. The method of making a binary glass composition for transmitting the 1–20 micron wave-length portion of the electromagnetic spectrum comprising the steps of placing 40 atomic percent germanium and 60 atomic percent sulfur into a reaction vessel, evacuating and sealing said vessel, heating said vessel to a temperature of about 950° C. to 1000° C. and holding said vessel at said temperature for about 15 to 36 hours in order to form a melt of said binary composition and to completely react the constituents of the melt, agitating said vessel during said heating, and quench-cooling said melt while sealed in said vessel at room temperature.

8. The method of making a ternary glass composition for transmitting the 1–20 micron wavelength portion of the electromagnetic spectrum, said composition consisting essentially of germanium, sulfur, and phosphorus and lying within Line A of FIGURE 1, comprising the steps of placing appropriate amounts of the constituents into a reaction vessel, evaporating and sealing said vessel, heating said vessel to a temperature of about 950° C. to 1000° C. and holding said vessel at said temperature for about 15 to 36 hours in order to form a melt of said composition and to completely react the constituents thereof, agitating said vessel during said heating, and quench-cooling said melt while sealed in said vessel in air at room temperature.

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HELEN M. McCARTHY, *Primary Examiner.*