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3,370,965

GLASSES AND METHOD OF MAKING SAME

Filed March 2, 1964

2 Sheets-Sheet 1

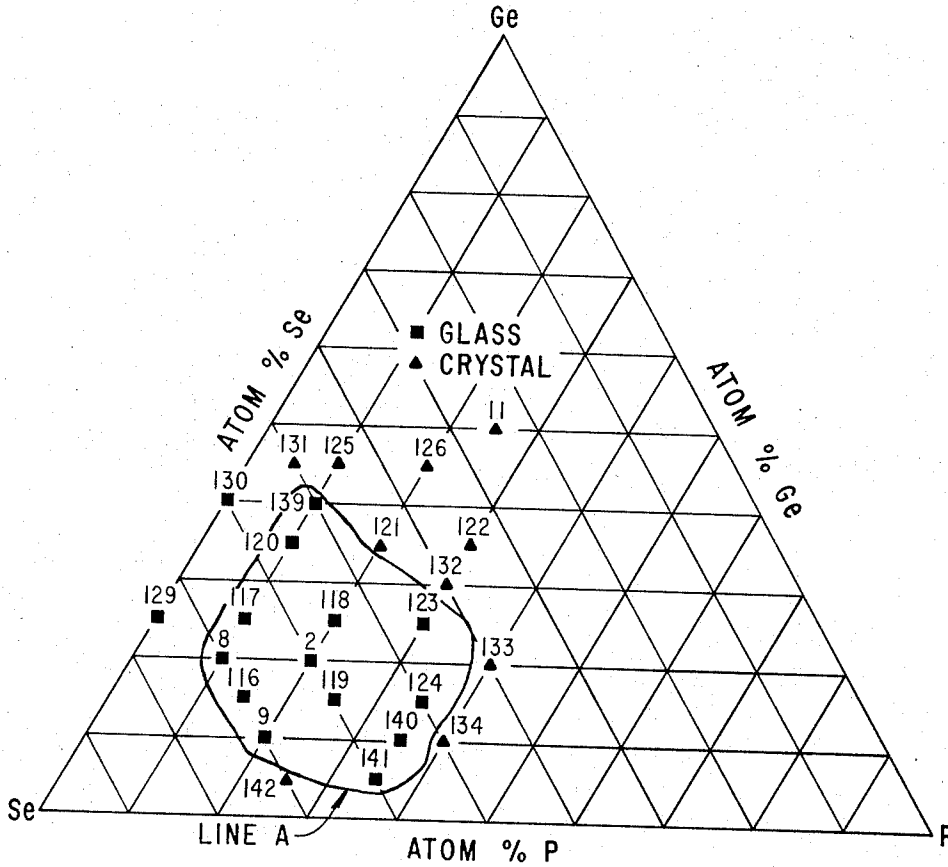


Fig. 1

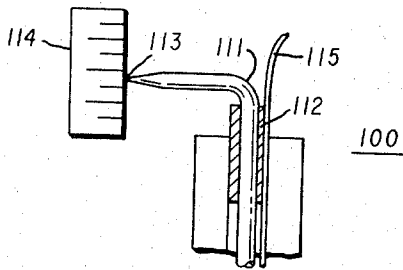
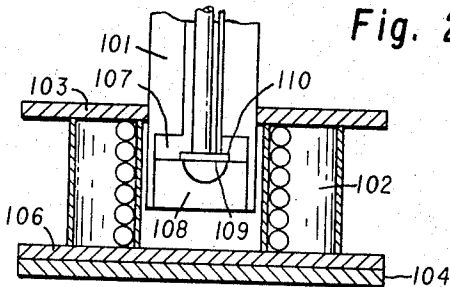


Fig. 2



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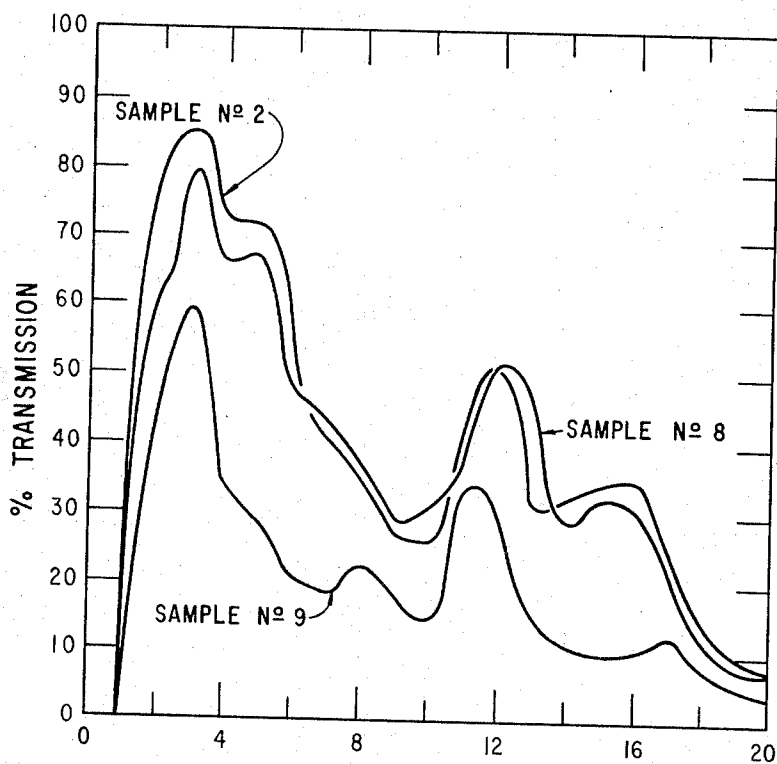


Fig. 3

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GLASSES AND METHOD OF MAKING SAME

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ABSTRACT OF THE DISCLOSURE

Disclosed are compositions of matter comprising germanium, phosphorus, and selenium, 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 for compounding these compositions and an illustration of the use of the glass compositions of this invention as a transmitting element within an infrared detection system.

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-selenium 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 45 (i.e., from greater than 0 to 45) atom percent germanium, up to 40 (i.e., from 0 to 40) atom percent phosphorus, and 45 to 100 atom percent selenium. The amorphous composition of matter of the invention is 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 consisting essentially of germanium, phosphorus, and selenium, and binary amorphous compositions of matter consisting essentially of germanium and selenium.

Another object of the invention is to provide an amorphous composition of matter having a high 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 about from greater than zero to 45 atom percent germanium, up to 40 (i.e., from 0-40) atom percent phosphorus, and 45 up to 100 percent selenium.

Another object of this invention is to provide a ger-

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manium-phosphorus - selenium or germanium-selenium amorphous composition of matter exhibiting a high softening point and having good transmission at high temperatures in the one to 20 micron wave-length region of the electromagnetic spectrum.

It is still a further object of the invention to provide a quench-freeze method of making the amorphous compositions of the invention having high softening points.

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 selenium for various amorphous compositions of matter of the invention;

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

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 selenium 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 selenium 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 five 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

Sample No.	Composition Atomic Percent		
	Ge	P	Se
11.....	50	25	25
121.....	35	20	45
122.....	35	30	35
125.....	45	10	45
126.....	45	20	35
131.....	45	5	50
132.....	30	30	40
133.....	20	40	40
134.....	10	40	50
142.....	5	25	70

TABLE II

Sample No.	Composition Atomic Percent			Softening Point in ° C.
	Ge	P	Se	
2.....	20	20	60	420
8.....	20	10	70	300
9.....	10	20	70	210
116.....	15	15	70	280
117.....	25	10	65	400
118.....	25	20	55	450
119.....	15	25	60	350
120.....	35	10	55	410
123.....	25	30	45	380
124.....	15	35	50	380
129.....	25	-----	75	300
130.....	40	-----	60	360
139.....	40	10	50	160
140.....	10	35	55	310
141.....	5	35	60	180

In FIGURE 1 the peripheral line A generally delineates the amorphous compositions of germanium, phosphorus, and selenium according to this invention. The samples which failed to form amorphous glass by the air-quench cooling technique (listed in Table I) are plotted on FIGURE 1 by a black triangular dot and identified by sample number. The sample compositions forming amorphous glass listed in Table II are also plotted in FIGURE 1 within the areas generally delineated by line A and designated by black square dots and each identified by sample numbers.

Referring specifically to FIGURE 2, the apparatus utilized in determining the Soft-Point listed in Table II is depicted therein. 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 sam-

ples at various wave lengths of the electromagnetic spectrum are presented in Table III below.

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

Sample No.....	116	117	119	120	129	130
Sample Thickness (mm.).....	1.17	1.07	0.91	0.82	1.11	0.96
Refractive Index.....	-----	-----	-----	-----	2.48	2.61

Wave Length, Microns:	Percent Transmission					
	5	4	0	5	13	43
1.....	9	7	13	10	43	55
2.....	11	15	22	15	43	55
3.....	15	19	24	20	56	63
4.....	20	26	28	25	64	64
5.....	24	45	32	32	67	64
6.....	25	31	44	28	66	65
7.....	19	16	25	19	65	54
8.....	19	17	23	20	66	64
9.....	20	19	17	24	64	61
10.....	28	29	15	22	60	54
11.....	40	33	32	41	16	8
12.....	31	44	23	35	9	7
13.....	19	23	18	33	29	18
14.....	21	25	18	30	46	25
15.....	27	25	18	26	50	36
16.....	17	13	18	16	32	32
17.....	8	8	12	10	21	25
18.....	6	8	7	10	25	24
19.....	4	5	6	10	23	26
20.....	-----	-----	-----	-----	-----	-----

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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 discussed above were essentially germanium, phosphorus, and selenium, minor percentages of silicon, tellurium, sulfur, 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. Ternary glass compositions consisting essentially of germanium, phosphorus and selenium and lying within line A of FIGURE 1.

2. The method of making a ternary glass composition for transmitting in the 1–20 micron wave-length portion of the electromagnetic spectrum, said composition consisting essentially of germanium, phosphorus and selenium and lying within line A of FIGURE 1, comprising the steps of placing appropriate amounts of the constituents 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 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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