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GLASSES FOR TEMPERATURE-STABLE ULTRASONIC DELAY LINES
OF LOW DAMPING CHARACTERISTICS
Filed June 22, 1970

FIG. 1

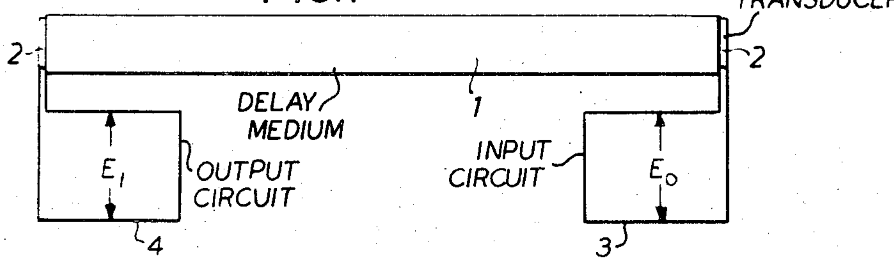


FIG. 2

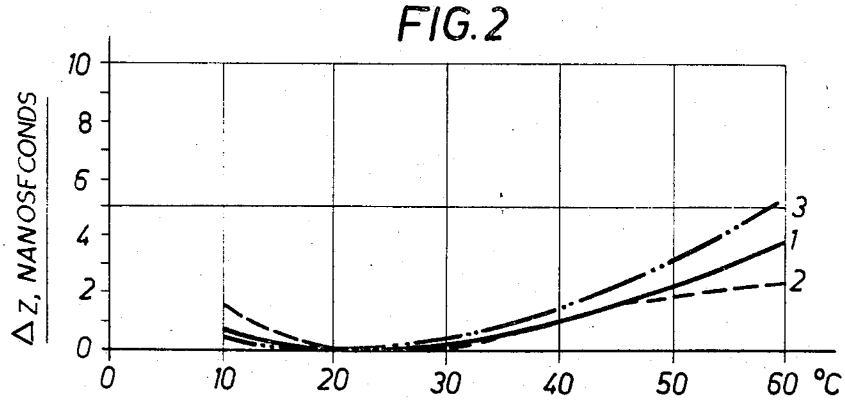
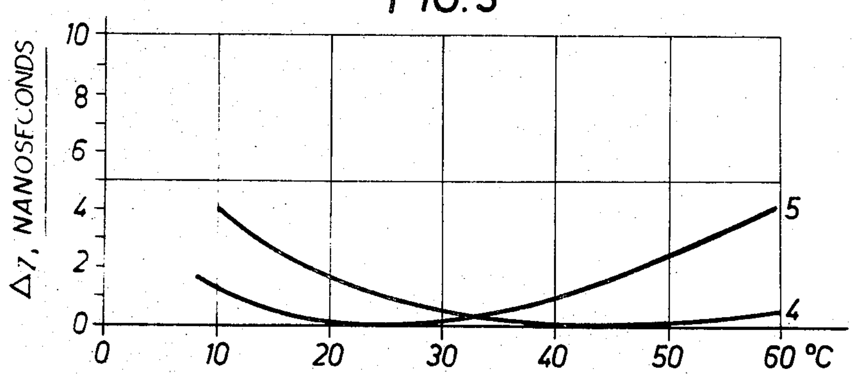


FIG. 3



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3,687,697

GLASSES FOR TEMPERATURE-STABLE ULTRASONIC DELAY LINES OF LOW DAMPING CHARACTERISTICS

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Int. Cl. C03c *3/04, 3/10;* H03h *7/30*
U.S. Cl. 106—53 9 Claims

ABSTRACT OF THE DISCLOSURE

Glass compositions for use in delay line assemblies having low temperature coefficient of propagation time for ultrasonic waves, low mechanical damping, a transformation temperature of about 540–600° C., and high acoustical impedance. Preferred compositions in percent by weight are as follows:

SiO_2	48.5–49.7
Li_2O	0–0.2
Na_2O	0–0.6
K_2O	0.7–1.0
BaO	10.5–11.5
ZnO	3.1–5.8
PbO	31–34
Sb_2O_3	0.3–0.5

the total alkali metal oxide amounting to 0.7–1.8%, with the proviso that up to 2 of the wt. percent of BaO may be replaced by CdO, SrO, CaO, WO_3, Al_2O_3 or a mixture of two or more thereof, for stabilization against devitrification.

BACKGROUND

The invention relates to glasses for electromechanical delay lines which have a very low delay time temperature coefficient. Furthermore, these glasses have a relatively low mechanical damping, so that the intensity of the signal is only slightly attenuated by passing through the delay line.

In an electromechanical delay line, the electrical signal is transformed by a piezoelectric transducer into sound vibrations. These pass through the glass body and at the end of the sound path they are transformed back into electrical vibrations by a second piezoelectric tranducer. The electrical signal at the output of the delay line is delayed by the amount of time which the sound takes to pass through the glass body. This travel time z is determined by the length L of the sound path and the velocity v of the sound in the glass, according to the equation $z=L/v$.

In a number of applications it is required that the temperature coefficient of time delay (T.C.) be very small, e.g.

$$\frac{1}{z}\frac{dz}{dT}=2\times10^{-6} \text{ per } ^\circ \text{C.}$$

Our copending application Ser. No. 687,099, filed Dec. 1, 1967, now Pat. 3,615,770 is incorporated herein by reference; it explains the stated formula. With the glasses herein described it is possible to construct, for use with piezoceramic transducers, delay lines which have a delay time temperature coefficient of this order of magnitude.

Two types of sound waves are possible in a solid: longitudinal waves and shear waves. In delay lines shear waves are preferred, because these waves have a lower velocity than longitudinal waves. The frequency, when measured, ranges around 5 megahertz.

Two factors are important in the attenuation of the electrical signal in passing through the line:

(a) The mechanical vibration damping of the glass;
(b) The intimate fastening together of transducer and glass.

THE INVENTION

The logarithmic decrement of the mechanical vibration damping (L.D.) in the case of the glasses described in this invention, at a frequency of 1 kilohertz, amounts to 0.35×10^{-3} to 0.45×10^{-3}, that is, it is lower than it is in the special glasses of the prior art for this purpose. For example, in French Pat. No. 1,546,407 and copending application Ser. No. 687,099, filed Dec. 1, 1967, glasses are described in which $\delta=2\times10^{-3}$ to 5×10^{-3}, and in German patent application p 16 96 064.8 and copending application Ser. No. 804,595, filed Mar. 5, 1969, glasses are described wherein $\delta=0.5\times10^{-3}$ to 0.8×10^{-3}.

For (b) it is important that the glass be capable of good metallization. There are a number of processes for this purpose, e.g. vapor depositing and firing. For these processes it is desirable that the glass be able to withstand heating to high temperatures. The transformation temperature (Tg) of the glasses of the invention just cited, ranges from 540 to 590° C.

The velocity of shear waves (ν_s) is lower in the glasses of the instant invention and the acoustical impedance (A.I.) is greater than in the case of the glasses hitherto described for temperature-stable ultrasonic delay lines which have a high softening temperature. Both of these factors represent technical improvements: the lower sound velocity signifies that the glass body can be made smaller, and the greater acoustical impedance means lower reflection losses in the passage of the sound waves from the glass to the transducer. The very low alkali oxide content in the glasses of the invention guards against mechanical after-effects.

The glasses of the invention have a small temperature coefficient of propagation time for ultrasonic waves, preferably for shear waves with a frequency of about 5 megahertz, with low mechanical dampening, transformation temperatures of about 540–600° C., and increased acoustical impedance. Preferred compositions are set forth in Table 2.

The total alkali metal oxide content amounts to 0.7 to 1.8%. For stabilization against devitrification, 2% of the BaO can be replaced by other alkali earth (SrO and CaO) or by CdO, WO_3, or Al_2O_3 without substantially modifying the special properties which are important to the described application of the glass.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic showing of a delay line assembly; and

FIG. 2 and FIG. 3 show change in delay time versus temperature for compositions of the invention stated infra.

Referring to FIG. 1, a delay line medium 1 is installed in an ultrasonic delay line assembly, which is of conventional construction. The delay line medium is outfitted with transducers **2** which are connected to imput circuit **3** and output circuit **4**.

Examples

In Table 1 there are listed a number of examples of glasses according to the invention. The chemical composition and the most important physical properties are stated:

TABLE 1

	1	2	3	4	5
Glass oxide:					
SiO_2	49.4	48.5	48.4	49.7	48.4
LiO_2			0.2		
Na_2O	0.6			0.6	
K_2O	0.7	1.0	0.3	0.7	1.0
BaO	11.2	10.5	11.5	11.1	11.5
ZnO	3.8	4.8	5.8	3.1	4.8
PbO	34.0	31.0	33.0	33.7	33.0
Sb_2O_3	0.3	0.3	0.3	0.3	0.3
CdO		2.0			
WO_3				0.8	
Al_2O_3					1.0
T.C.: $\frac{1}{z}\frac{dz}{dT} \times 10^6/°$ C. (10 . . . 60° C. 4.4 MHz.)	1.2	0.8	1.5	1.2	1.2
L.D.: (log. decrement$\times 10^3$) (1 kHz.)	0.36	0.41	0.38	0.37	0.43
V_s: Sound speed for shear waves, meters per sec	2,722	2,733	2,742	2,727	2,730
Density (g./cm.^{3})	3.58	3.58	3.63	3.57	3.59
A.I.: Acoustical impedance, 10^6 kg./(m.$^2\times$sec.)	9.75	9.76	9.96	9.74	9.80
Tg: Transformation temperature (° C.)	550	572	555	542	577

As can be seen from Table 1, the compositional ranges of the glasses of the examples consist essentially of:

SiO_2	48.4–49.7
Li_2O	0–0.2
Na_2O	0–0.6
K_2O	0.3–1.0
BaO	10.5–11.5
ZnO	3.1–5.8
PbO	31.0–34.0
Sb_2O_3	0.3
CdO	0–2.0
WO_3	0–0.8
Al_2O_3	0–1.0

These glasses also have the following properties:

Temperature coefficient, 10 to 60° C. at 4.4 MHz., 0.8 to 1.5×10^{-6} per ° C.; mechanical damping in terms of logarithmic decrement at 1 kilohertz of about 0.36×10^{-3} to 0.43×10^{-3}; sound speed for shear waves of 2722 to 2742 meters per second; density of 3.57 to 3.63 grams/cm.^{3}; acoustical impedance of 9.74 to 9.96×10^6 kg./m.$^2\times$sec.); and a transformation temperature in the range of about 550 to 577° C.

FIGS. 2 and 3 show the effect of temperature on the delay time in a delay line made from the glasses in the table and providing a 64 microsecond delay.

Production example

The glasses of the invention are similar in type to known optical and art glasses, and they can be produced by procedures which are conventional for production of such glasses. In the instant example, the batch mixture consists of:

Oxide	Percent by wt.	Raw material	Amount weighed in, in kg., 100 kg. of glass
SiO_2	49.5	SiO_2	49.599
K_2O	1.0	K_2CO_3	1.471
BaO	5.1	$Ba(NO_3)_2$	8.726
BaO	5.6	$BaCO_3$	7.263
ZnO	4.9	ZnO	4.907
CdO	2.0	CdO	2.007
PbO	31.6	Pb_3O_4	32.362
b_2O_3	0.3	Sb_2O_3	0.301

The well-mixed batch is continuously fed into a conventional glass melting tank, melted at about 1440° C. in about 16 hours, refined for about 14 hours, at about 1480–1500° C. and until it is free of bubbles, and, at a viscosity between 300 and 500 poises (corresponding to temperatures of 1420 to 1360° C.), depending on the throughput, it is poured off and worked directly into the desired molded objects or bars. In this example, the viscosity at pouring off is about 6,000 poises. The melt can also be cast in blocks from which the desired objects can afterwards be pressed. The molded objects are annealed in accordance with conventional optical glass practice. The glass can also be produced in any smaller volume desired in platinum crucibles or appropriate ceramic crucibles.

A summary of the invention is contained in Table 2.

TABLE 2

	Preferred range	Optimum range
Weight percent:		
SiO_2	48.5–49.7	48.5–49.5
Li_2O	0–0.2	0
Na_2O	0–0.6	0–0.6
K_2O	0.7–1.0	0.7–1.0
BaO	10.5–11.5	10.5–11.5
ZnO	3.1–5.8	3.1–4.8
PbO	31–34	31–34
Sb_2O_3	0.3–0.5	0.3
SrO, CaO, CdO, WO_3, Al_2O_3	0–2 of the BaO	
T.C.[1]	0.8–1.5	0.8–1.2
L.D.[1]	0.36–0.43	0.36–0.43
V_s [1]	2,720–2,745	2,722–2,742
Density [1]	3.58–3.63	3.58–3.63
A.I.[1]	9.74–9.96	9.74–9.96
Tg [1]	550–577	550–577

[1] Units as in Table 1.

What is claimed is:

1. Glass having a low temperature coefficient of the propagation time for ultrasonic waves, mechanical dampening in terms of logarithmic decrement at 1 kilohertz of about 0.36×10^{-3} to 0.43×10^{-3}, a transformation temperature in the range of about 550–577° C. and high acoustical impedence, consisting essentially of the following chemical composition in percent by weight:

SiO_2	48.4–49.7
Li_2O	0–0.2
Na_2O	0–0.6
K_2O	0.3–1.0
BaO	10.5–11.5
ZnO	3.1–5.8
PbO	31.0–34.0
Sb_2O_3	0.3
CdO	0–2.0
WO_3	0–0.8
Al_2O_3	0–1.0

2. Glass according to claim **1**, having the following properties:

temperature coefficient, 10 to 60° C. at 4.4 MHz, 0.8 to 1.5×10^{-6} per ° C.; sound speed for shear waves of 2722 to 2742 meters per second; density of 3.57 to 3.63 grams/cm.^{3}; acoustical impedance of 9.74 to 9.96×10^6 kg./m.$^2\times$sec.).

3. Glass according to claim **1**, characterized by the following chemical composition in percent by weight:

SiO_2	49.4
Na_2O	0.6
K_2O	0.7
BaO	11.2
ZnO	3.8
PbO	34.0
Sb_2O_3	0.3

4. Glass according to claim 1, characterized by the following composition in percent by weight:

SiO_2	49.7
Na_2O	0.6
K_2O	0.7
BaO	11.1
ZnO	3.1
PbO	33.7
Sb_2O_3	0.3
WO_3	0.8

5. Glass according to claim 1, characterized by the following composition in percent by weight:

SiO_2	48.4
K_2O	1.0
BaO	11.5
ZnO	4.8
PbO	33.0
Sb_2O_3	0.3
Al_2O_3	1.0

6. Glass according to claim 1, characterized by the following composition in percent by weight:

SiO_2	48.5
K_2O	1.0
BaO	10.5
ZnO	4.8
PbO	31.0
Sb_2O_3	0.3
CdO	2.0

7. Glass according to claim 1, characterized by the following composition in percent by weight:

SiO_2	48.4
Li_2O	0.2
K_2O	0.3
BaO	11.5
ZnO	5.8
PbO	33.0
Sb_2O_3	0.3

8. Glass having a low temperature coefficient of the propagation time for ultrasonic waves, mechanical dampening in terms of logarithmic decrement at 1 kilohertz of about 0.36×10^{-3}–0.43×10^{-3}, a transformation temperature in the range of about 550–577° C. and high acoustical impedance, consisting essentially of the following chemical composition in percent by weight:

SiO_2	48.5–49.7
Li_2O	0.0–0.2
Na_2O	0.0–0.6
K_2O	0.7–1.0
BaO	10.5–11.5
ZnO	3.1–5.8
PbO	31–34
Sb_2O_3	0.3–0.5

with the proviso that up to 2 of the wt. percent of BaO may be replaced by CdO, SrO, CaO, WO_3, Al_2O_3 or a mixture of two or more thereof, for stabilization against devitrification.

9. Glass according to claim 8, having the following properties:

temperature coefficient, 10 to 60° C. at 4.4 MHz., 0.8 to 1.5×10^{-6} per ° C.; sound speed for shear waves of 2720 to 2745 meters per second; density of 3.58 to 3.63 grams/cm.^{3}; acoustical impedance of 9.74 to 9.96×10^6 kg./m.$^2\times$sec.).

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U.S. Cl. X.R.

333—30

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,687,697 Dated August 29, 1972

Inventor(s) Marga Faulstich et al.

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 75, change "b_2O_3" to -- Sb_2O_3 --.

Signed and sealed this 9th day of January 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents