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(54) Titre : VERRES SANS PLOMB PRESENTANT LES CARACTERISTIQUES DU CRISTAL

(54) Title: LEAD-FREE GLASSES EXHIBITING CHARACTERISTICS OF CRYSTAL

SiO ₂	51-63	Al ₂ O ₃	0-5
Li ₂ O	0-3	ZrO ₂	0-6
Na ₂ O	0-8	SiO ₂ +Al ₂ O ₃ +ZrO ₂	55-66
K ₂ O	0-12	TiO ₂	0-3
Li ₂ O+Na ₂ O+K ₂ O	7-15	CaO	0-5
SrO	0-<8	MgO	0-3
BaO	>13-21	B ₂ O ₃	0-3
ZnO	5-15	La ₂ O ₃	0-8
SrO+BaO+ZnO	27-34		

(57) Abrégé/Abstract:

The present invention relates to the production of lead-free glasses exhibiting densities of at least 2.9 g/cm³ and refractive indices of at least 1.545 which consist essentially, in weight percent, of (see above figure).



Abstract

The present invention relates to the production of lead-free glasses exhibiting densities of at least 2.9 g/cm^3 and refractive indices of at least 1.545 which consist essentially, in weight percent, of

SiO_2	51-63	Al_2O_3	0-5
Li_2O	0-3	ZrO_2	0-6
Na_2O	0-8	$\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{ZrO}_2$	55-66
K_2O	0-12	TiO_2	0-3
$\text{Li}_2\text{O} + \text{Na}_2\text{O} + \text{K}_2\text{O}$	7-15	CaO	0-5
SrO	0-<8	MgO	0-3
BaO	>13-21	B_2O_3	0-3
ZnO	5-15	La_2O_3	0-8 .
$\text{SrO} + \text{BaO} + \text{ZnO}$	27-34		

LEAD-FREE GLASSES EXHIBITING CHARACTERISTICS OF CRYSTAL

5 This invention relates to glasses essentially free from lead displaying the physical characteristics of lead-containing crystal glasses.

Background of the Invention

10 Among the glasses used for the aesthetics or decoration of the table, crystal occupies an exceptional place: its brightness, its density, and its sonority make it a much esteemed material. In addition, it exhibits the characteristics of formability at moderate temperatures, of
15 having a long working range, and of being able to be easily cut and polished.

Traditionally these properties are achieved by the presence of lead oxide in the glass composition. But lead is a toxic, and nowadays is considered problematical for
20 handling, manufacturing and use, especially the latter, as lead in the glass can migrate into food in contact with the glass, and lead poisoning, particularly after contact with an acid medium, for example, fruit juices or alcohol.

Strengthening safety concerns create a need for

glasses without lead but having the properties and manufacturing cost similar to those of lead crystal.

The present invention solves the problem by lead free glasses suitable for use as tableware and/or decorative crystal glassware meeting the following requirements:

- (1) a glass density of at least 2.9 g/cm^3 ;
- (2) an index of refraction of at least 1.545;
- (3) the glass displays a pleasant sonority;
- (4) the glass exhibits a moderate linear coefficient of thermal expansion (lower than $100 \times 10^{-7}/^\circ\text{C}$ between $0^\circ\text{--}300^\circ\text{C}$) in order not to be too sensitive to thermal shock;
- (5) the viscosity of the glass at high temperature is close to that of crystal; the temperature at which the glass exhibits a viscosity of 10 Pa.s (100 poises) does not exceed 1470°C ; and
- (6) the viscosity of the glass at the liquidus temperature is greater than 600 Pa.s (6000 poises).

Summary of the Invention

More precisely, the invention relates to glasses essentially free from lead (no lead additions to the batch, except as incidental batch impurities) having the following compositions, expressed in terms of weight percent on the oxide basis.

	SiO ₂	51-63	Al ₂ O ₃	0-5
	Li ₂ O	0-3	ZrO ₂	0-6
	Na ₂ O	0-8	SiO ₂ +Al ₂ O ₃ +ZrO ₂	55-66
5	K ₂ O	0-12	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	7-15	CaO	0-5
	SrO	0-<8	MgO	0-3
	BaO	>13-21	B ₂ O ₃	0-3
	ZnO	5-15	La ₂ O ₃	0-8
10	SrO+BaO+ZnO	27-34		

BaO, ZnO, and SiO₂ are utilized in order to obtain the required density and index of refraction.

15 BaO is the most effective component for raising the index and the density. In addition, it provides a lower cost increase than ZnO and SrO. However, its level must be maintained below 21% to avoid unacceptable devitrification.

20 ZnO is preferred to SrO because SrO tends to give a yellow color to the glass, its cost is relatively high, and it raises the thermal expansion of the glass more than ZnO.

The level of SiO₂+Al₂O₃+ZrO₂ must be maintained at least 55% to impart acceptable chemical durability to the glass.

25 Li₂O plays a favorable role regarding the viscosity of the glass. However, its content is limited to 3% because of its cost.

The other components such as ZrO₂, B₂O₃, TiO₂, CaO, MgO, and La₂O₃ can be added to adjust the properties of the glass. To illustrate:

30 ZrO₂ exhibits an interesting effect with respect to the density and the refractive index of the glass. But in amounts higher than 6%, it leads to glasses difficult to melt and displaying an acceptable devitrification.

35 TiO₂ demonstrates an interesting effect on the refractive index of the glass, but it leads to a yellow coloration in the glass, this color being more intense as

the level of Fe_2O_3 comprising an impurity in the batch materials increases. Its amount must be limited to 3% and is preferably essentially excluded when a colorless glass is desired.

In order to obtain a colorless or very low colored material having a high visible transmission, as is often valued for articles designed for the table or for decoration, it is necessary that the level of impurities in the glass be low. A level of Fe_2O_3 less than 150 ppm is, for example, desirable.

Coloring components such as the transition metal oxides or the rare earth metal oxides can also be added in a total amount less than 0.1% to mask the tint imparted by the impurities. These components can also be added in higher amounts to color the material, if one desires a colored glass.

As_2O_3 and Sb_2O_3 can also be added in the usual proportions to perform their customary role as fining agents.

The preferred glasses of the invention have the following compositions, expressed in terms of weight percent on the oxide basis:

SiO_2	53-62	ZnO	8-13
Li_2O	0-2	$\text{SrO}+\text{BaO}+\text{ZnO}$	27-32
Na_2O	2-7	CaO	0-5
K_2O	3-11	Al_2O_3	0-3
$\text{Li}_2\text{O}+\text{Na}_2\text{O}+\text{K}_2\text{O}$	8-14	ZrO_2	0-4
SrO	0-3	$\text{SiO}_2+\text{Al}_2\text{O}_3+\text{ZrO}_2$	56-65
BaO	15-19		

Glasses having compositions within those ranges exhibit an interesting compromise between the different properties, those related to the ease of manufacturing as well as those related to the final product. For example,

the low levels of Li_2O and SrO enable the cost of the composition to be limited. The simultaneous presence of Na_2O and K_2O facilitates melting of the glass.

Prior Art

The concern regarding the release of lead where a glass is to be used in tableware application has given rise to the production of lead-free enamels and glazes for use in coating and decorating food service ware. Illustrations of such materials can be found in the following United States patents: 4,084,976 (Hinton), 4,224,074 (Nigrin), 4,282,035 (Nigrin), 4,285,731 (Nigrin), and 4,590,171 (Nigrin). The properties of those glasses, however, do not correspond to those exhibited by fine crystal glass.

Lead-free glasses have also been utilized in the fabrication of faceplates for television receiver tubes in order to avoid the development of a brownish discoloration resulting from the impingement of high velocity electrons, with accompanying X-radiation, upon PbO -containing glasses. The following United States patents are illustrative of such glasses: 3,464,932 (Connelly et al.), 3,805,107 (Boyd), 4,089,693 (LaGrouw et al.), 4,277,286 (Boyd et al.), 4,734,388 (Cameron et al.), 4,830,990 (Connelly), and 5,108,960 (Boek et al.). The glasses disclosed therein vary in composition and properties from those of the present invention.

United States Patent No. 5,270,269 (Hares et al.) is also directed to the production of lead-free fine crystal glassware and, as such, is deemed to comprise the most pertinent prior art. The glasses disclosed therein consist essentially, in weight percent, of

	SiO ₂	54-64	BaO	8-13
	Li ₂ O	0-3	SrO	8-13
	Na ₂ O	0-6.5	ZnO	5.5-9
5	K ₂ O	0-7	BaO+SrO+SnO	22-33
	Li ₂ O+Na ₂ O+K ₂ O	8-15		

wherein at least two of Li₂O, Na₂O, and K₂O are present and are present in essentially equimolar ratios.

10 As can be observed, however, the BaO content of the subject inventive glasses is greater than the maximum permitted in the glasses described in the patent, and the level of SrO is lower than the minimum demanded in the glasses of the patent. Furthermore, the present inventive
15 glasses have no requirement that at least two alkali metal oxides be present in equimolar amounts.

Description of Preferred Embodiments

20 The invention will now be illustrated through the following non-limiting examples.

EXAMPLES

25 The appended table presents examples of compositions and properties. The compositions are recorded in terms of parts by weight, but, because the sum of the components totals or closely approximates 100, for all practical purposes, the individual values can be deemed to reflect
30 weight percent. In each case, 3000 grams of batch materials were melted for 4 hours at 1500°C in a platinum crucible. Thereafter, the molten glasses were formed into bars and measurements performed thereon. Whereas these examples reflect only laboratory experiments, the glasses
35 of the invention can be manufactured in industrial plants

utilizing classical glass melting and forming techniques.

In order to evaluate the chemical durability of the glasses, three tests have been carried out.

(1) A test of hydrolytic resistance (DIN 12111). In order to have a durability comparable to that of crystal, the level of the Na_2O analyzed after attack by water must be less than $120 \mu\text{g/g}$.

(2) A test of acid durability (ACID). The test is carried out on polished samples immersed for 3 hours in a boiling aqueous solution of 20% by volume HCl . To have a satisfactory durability, the weight loss must be less than 30 mg/dm^2 .

(3) A test of alkali durability (ISO 695). The test is carried out on polished samples immersed into an alkaline solution. To have a satisfactory durability, the weight loss must be less than 230 mg/dm^2 .

The viscosity-temperature values in terms of Pa.s and $^{\circ}\text{C}$, the viscosity at the liquidus temperature in terms of Pa.s, the linear coefficient of thermal expansion ($0^{\circ}\text{--}300^{\circ}\text{C}$) in terms of $\times 10^{-7}/^{\circ}\text{C}$, the density in terms of g/cm^3 , the softening point (S.P.), annealing point (A.P.), and strain point (St.P.) in terms of $^{\circ}\text{C}$, and the index of refraction were determined in accordance with measuring techniques conventional in the glass art.

Examples 1-6 belong to the preferred composition area.

Examples 7-10 are outside of the preferred area but are within the scope of the invention.

Examples 11-15 are outside of the scope of the invention for the following reasons:

In Examples 11, 12, and 13 the level of BaO and that of $\text{BaO}+\text{SrO}+\text{ZnO}$ are too low and the glasses do not exhibit the required density or refractive index.

In Example 14 the level of BaO is too high and the glass demonstrates unacceptable devitrification.

In Example 15 the sum $\text{BaO}+\text{ZnO}+\text{SrO}$ is too high and the

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viscosity at the liquidus is too low.

Example 1 is the most preferred glass.

TABLE

		1	2	3	4	5	6
	SiO ₂	57.5	57.1	57.0	59.0	56.2	53.9
	Li ₂ O	0.4	--	0.4	1.6	1.6	1.5
5	Na ₂ O	4.8	5.15	3.0	4.9	4.8	4.7
	K ₂ O	7.1	7.75	9.7	3.7	3.6	3.6
	Li ₂ O+Na ₂ O+K ₂ O	12.3	12.9	13.1	10.2	10.0	9.8
	SrO	--	--	--	--	--	2.9
	BaO	17.7	17.5	17.5	18.1	17.8	17.6
10	ZnO	11.2	11.2	11.1	11.5	11.3	11.2
	SrO+Bao+ZnO	28.9	28.7	28.7	29.6	29.1	31.7
	Al ₂ O ₃	1.0	0.95	0.95	1.0	1.0	1.0
	ZrO ₂	--	--	--	--	3.4	3.4
	SiO ₂ +Al ₂ O ₃ +ZrO ₂	58.5	58.05	57.95	60.0	60.6	58.3
15	Sb ₂ O ₃	0.28	0.28	0.28	0.29	0.28	0.28
	Temp. for a Viscosity of 10 Pa.s	1420	1427	1433	1396	1391	1350
	" 100 Pa.s	1181	1190	1193	1146	1167	1137
20	" 1000 Pa.s	1021	1032	1034	983	1015	993
	S.P.	711	723	--	682	713	--
	A.P.	519	532	--	497	521	--
	St.P.	474	485	--	451	474	--
25	Liquidus Viscosity	1400	5000	2000- 5000	1000	>1300	1000- 2000
	Expansion	94	--	--	--	--	--
	Density	2.93	--	2.92	2.93	3.0	3.06
	Refractive Index	1.547	1.545	--	1.55	1.563	1.571
30	DIN 12111	65	47	66	--	--	--
	ACID	8	10.7	--	1.5	2.0	1.65
	ISO 695	162	137.4	--	135	52.4	55.0

TABLE (Cont.)

		7	8	9	10	11
	SiO ₂	57.8	54.6	58.8	57.6	59.5
5	Li ₂ O	0.6	0.6	2.75	0.4	1.7
	Na ₂ O	4.5	4.4	2.4	3.6	3.6
	K ₂ O	6.9	6.7	3.7	8.4	5.4
	Li ₂ O+Na ₂ O+K ₂ O	12.0	11.7	8.85	12.4	10.7
	SrO	7.8	7.0	7.3	--	10.5
10	BaO	13.8	17.2	18.0	18.3	10.5
	ZnO	7.3	5.5	5.7	9.5	7.5
	SrO+Bao+ZnO	28.9	29.7	31.0	27.8	28.5
	Al ₂ O ₃	1.0	3.7	1.0	0.1	1.0
	SiO ₂ +Al ₂ O ₃ +ZrO ₂	58.8	58.3	59.8	57.7	60.5
15	Sb ₂ O ₃	0.29	0.28	0.29	0.29	0.28
	B ₂ O ₃	--	--	--	1.5	--
	Temp. for a Viscosity of 10 Pa.s	1396	1415	--	1386	1375
20	" 100 Pa.s	1160	1173	--	1149	1130
	" 1000 Pa.s	1000	1014	--	994	971
	S.P.	699	--	--	--	675
	A.P.	513	--	--	--	498
	St.P.	469	--	--	--	456
25	Liquidus Viscosity	2500	1200	>600	2000	--
	Expansion	93	--	--	--	88
	Density	2.919	--	2.95	2.92	2.88
30	Refractive Index	1.548	--	1.556	--	1.548
	DIN 12111	--	--	--	--	53
	ACID	10	15	--	--	2.08
	ISO 695	175.5	--	--	--	159

TABLE (Concl.)

	12	13	14	15
SiO ₂	59.2	60.2	56.6	56.8
Li ₂ O	--	0.6	1.6	1.6
Na ₂ O	5.3	4.7	3.4	4.8
K ₂ O	8.0	7.2	5.1	1.0
Li ₂ O+Na ₂ O+K ₂ O	13.3	12.5	10.1	7.4
SrO	--	4.8	--	2.9
BaO	10.4	12.0	24.8	17.9
ZnO	15.7	3.8	7.1	13.7
SrO+BaO+ZnO	26.1	20.6	31.9	34.5
Al ₂ O ₃	1.0	1.0	0.95	1.0
SiO ₂ +Al ₂ O ₃ +ZrO ₂	60.2	61.2	57.55	57.8
Sb ₂ O ₃	0.29	0.3	0.28	0.29
B ₂ O ₃	--	--	--	--
CaO	--	5.2	--	--
Temp. for a Viscosity of 10 Pa.s	1469	1405	1354	1358
" 100 Pa.s	1230	1167	1117	1126
" 1000 Pa.s	1068	1012	961	976
S.P.	748	--	--	--
A.P.	551	--	--	--
St.P.	501	--	--	--
Liquidus Viscosity	>10000	3000- 10000	<600	<600
Expansion	88	--	--	--
Density	--	2.82	3.0	3.03
Refractive Index	1.539	1.546	1.556	1.561
DIN 12111	62	--	--	--
ACID	--	4	10.5	0.4
ISO 695	--	--	204	--

1. A glass having a density of at least 2.9 g/cm^3 and an index of refraction of at least 1.545, and consisting essentially of the following components, expressed in terms of weight percent on the oxide basis, of

5	SiO ₂	53-62	Al ₂ O ₃	0-3
	Li ₂ O	0-2	ZrO ₂	0-4
	Na ₂ O	2-7	SiO ₂ +Al ₂ O ₃ +ZrO ₂	56-65
	K ₂ O	3-11	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	8-14	CaO	0-5
10	SrO	0-3	MgO	0-3
	BaO	15-19	B ₂ O ₃	0-3
	ZnO	8-13	La ₂ O ₃	0-8
	SrO+BaO+ZnO	27-32		

15 wherein said glass is essentially free from lead.

2. The glass according to claim 1, further comprising up to 0.1% total of at least one transition metal oxide or rare earth metal oxide.

20 3. Tableware and/or decorative crystal glassware consisting of glasses essentially free from lead characterized in that they exhibit a density of at least 2.9 g/cm^3 and an index of refraction of at least 1.545, and which consist essentially of the following compositions, expressed in terms of weight percent on the oxide basis, of

25	SiO ₂	51-63	Al ₂ O ₃	0-5
	Li ₂ O	0-3	ZrO ₂	0-6
	Na ₂ O	0-8	SiO ₂ +Al ₂ O ₃ +ZrO ₂	55-66
	K ₂ O	0-12	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	7-15	CaO	0-5
30	SrO	0-8	MgO	0-3
	BaO	>13-21	B ₂ O ₃	0-3
	ZnO	5-15	La ₂ O ₃	0-8
	SrO+BaO+ZnO	27-34		

4. Tableware and/or decorative crystal glassware according to claim 3 characterized in that they consist essentially of the following compositions, expressed in terms of weight percent on the oxide basis, of

5	SiO ₂	53-62	Al ₂ O ₃	0-3
	Li ₂ O	0-2	ZrO ₂	0-4
	Na ₂ O	2-7	SiO ₂ +Al ₂ O ₃ +ZrO ₂	56-65
	K ₂ O	3-11	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	8-14	CaO	0-5
10	SrO	0-3	MgO	0-3
	BaO	15-19	B ₂ O ₃	0-3
	ZnO	8-13	La ₂ O ₃	0-8 .
	SrO+BaO+ZnO	27-32		

15 5. Tableware and/or decorative crystal glassware according to claim 3 also containing up to 0.1% total of at least one transition metal oxide or rare earth metal oxide.

20 6. Tableware and/or decorative crystal glassware according to claim 4 also containing up to 0.1% total of at least one transition metal oxide or rare earth metal oxide.

25 7. A use of a glass having a density of at least 2.9 g/cm³ and an index of refraction of at least 1.545, and consisting essentially of the following components, expressed in terms of weight percent on the oxide basis, of

	SiO ₂	51-63	Al ₂ O ₃	0-5
	Li ₂ O	0-3	ZrO ₂	0-6
	Na ₂ O	0-8	SiO ₂ +Al ₂ O ₃ +ZrO ₂	55-66
30	K ₂ O	0-12	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	7-15	CaO	0-5
	SrO	0-8	MgO	0-3
	BaO	>13-21	B ₂ O ₃	0-3
	ZnO	5-15	La ₂ O ₃	0-8

SrO+BaO+ZnO 27-34

wherein said glass is essentially free from lead, in the preparation of tableware or decorative crystal glassware.

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8. The use according to claim 7, wherein said glass consists essentially of the following components, expressed in terms of weight percent on the oxide basis, of

	SiO ₂	53-62	Al ₂ O ₃	0-3
10	Li ₂ O	0-2	ZrO ₂	0-4
	Na ₂ O	2-7	SiO ₂ +Al ₂ O ₃ +ZrO ₂	56-65
	K ₂ O	3-11	TiO ₂	0-3
	Li ₂ O+Na ₂ O+K ₂ O	8-14	CaO	0-5
	SrO	0-3	MgO	0-3
15	BaO	15-19	B ₂ O ₃	0-3
	ZnO	8-13	La ₂ O ₃	0-8 .
	SrO+BaO+ZnO	27-32		

9. The use according to claim 7 or 8, wherein said glass further comprises up to
20 0.1% total of at least one transition metal oxide or rare earth metal oxide.

SiO ₂	51-63	Al ₂ O ₃	0-5
Li ₂ O	0-3	ZrO ₂	0-6
Na ₂ O	0-8	SiO ₂ +Al ₂ O ₃ +ZrO ₂	55-66
K ₂ O	0-12	TiO ₂	0-3
Li ₂ O+Na ₂ O+K ₂ O	7-15	CaO	0-5
SrO	0-<8	MgO	0-3
BaO	>13-21	B ₂ O ₃	0-3
ZnO	5-15	La ₂ O ₃	0-8
SrO+BaO+ZnO	27-34		