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(21) International Application Number: PCT/IT95/00215 (22) International Filing Date: 11 December 1995 (11.12.95) (30) Priority Data: FI94A000223 13 December 1994 (13.12.94) IT (71) Applicant (for all designated States except US): C.A.L.P. CRISTALLERIA ARTISTICA LA PIANA S.P.A. [IT/IT]; Via Senese, Località Catarelli, I-53034 Colle Val d'Elsa (IT). (72) Inventors; and (75) Inventors/Applicants (for US only): BOSCHI, Giancarlo [IT/IT]; Via R. Sanzio, 13, I-53034 Colle Val d'Elsa (IT). PALOSCHI, Fabio [IT/IT]; Via Trebbia, 22, I-26100 Cremona (IT). (74) Agents: MANNUCCI, Gianfranco et al.; Via della Scala, 4, I-50123 Firenze (IT).		(81) Designated States: AM, AU, BB, BG, BR, BY, CA, CN, CZ, EE, FI, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LV, MD, MG, MN, MW, MX, NO, NZ, PL, RO, RU, SD, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, LS, MW, SD, SZ, UG). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: VITRIFIABLE MIXTURE FOR QUALITY GLASSES (57) Abstract The glass has a chemical composition as a percentage by weight within the following range: silica 50-58, potash 0-13, soda 0-9, lithium oxide 0-4, calcium oxide 0-3, magnesium oxide 0-4, boric anhydride 0-2, zinc oxide 16-30, barium oxide 0-12, titanium oxide 0-6, zirconium oxide 0-5, yttrium oxide 0-5, alumina 0-3, tin oxide 0-5, lanthanum oxide 0-9, niobium oxide 0-9, bismuth oxide 0-12, germanium oxide 0-5.		

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"Vitrifiable mixture for quality glasses"

DESCRIPTION

5 Technical field

The present invention relates to the composition of a glass with the characteristics of lead crystal, but without the presence of lead.

10 State of the art

Lead crystal is well known as a glass characterized in particular by exceptional brilliance, refractive index, density and sonority.

According to the definition given by EEC
15 standard 69/493 - adopted in Italian Law No. 827 of 26/11/73, Annex b, columns e and f, line 2 - for a glass to be called "lead crystal" it must among other things, as well as containing at least 24% of lead, have a density greater than 2.90 g/cm^3 and a refractive
20 index greater than 1.545. These characteristics are ensured by the lead content, which also endows the glass with good workability, sonority and gloss.

The need to invent a new glass with the same characteristics as crystal arises from the fact that
25 lead has already been banished from some production processes because of its potential toxicity and it is possible that this restriction will be extended in the near future.

For this reason alternatives have been
30 investigated for obtaining glasses without lead but with the physical characteristics of "crystal" stated above. To achieve this, the lead can be replaced by a mixture of elements such as barium, zinc, calcium, strontium, bismuth, titanium, and others which are non-
35 toxic and increase the values of density and refractive

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index. However, along with these properties, many of these elements have a high price and can impair the workability or the colour of the glass, so that their use can be unsuitable in industrial applications.

5 The researchers therefore endeavoured to determine the most favourable composition for obtaining lead-free "crystals" with characteristics suitable for both craft work and industrial processing, as for example the glass that is the subject of International
10 Application WO 93/16964 in the name of Compagnie des Cristalleries de Baccarat, with the composition given in the following table.

 This composition is characterized by replacement of the lead with a mixture of zinc,
15 strontium and calcium, and the corresponding glass has a satisfactory density and refractive index, but it proves to be difficult to work, as it has a high melting point and softening point and a devitrification temperature that is unsuitable for continuous melting.

20

Oxides	% by weight
SiO ₂	53 - 58
Li ₂ O	0-0.3
Na ₂ O	4.5 - 7.5
25 K ₂ O	6 - 10
SrO	0 - 12
BaO	
ZnO	16 - 21
SrO+CaO+ZnO	26.5 - 31
30 Al ₂ O ₃	0 - 1.5
Sb ₂ O ₃	0.5 - 1.5

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TiO ₂	0 - 2
CaO	0 - 9
SnO ₂	0 - 2.5
B ₂ O ₃	0 - 1.2
La ₂ O ₃	0 - 3

Another lead-free crystal is that envisaged in European Patent Application published under No. 0 594 422 A1 in the name of Toyo Glass Co. Ltd., with the composition according to the following table. According to this invention, the lead is replaced by a mixture of barium, zinc, titanium and boron, and the glass has satisfactory values of the physical parameters, in particular density and refractive index, at a reasonable cost.

SiO ₂	50.0 - 60.0
CaO	1.0 - 5.0
BaO	10.0 - 15.0
Na ₂ O	3.0 - 10.0
K ₂ O	5.0 - 13.0
Li ₂ O	0 - 1.0
TiO ₂	5.0 - 8.0
ZnO	5.0 - 10.0
ZrO ₂	0 - 2.0
B ₂ O ₃	1.0 - 2.0
Sb ₂ O ₃	0.3 - 0.8

However, glasses with the chemical composition given in this table can, because of the

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high titanium content, be difficult to decolorize and to work by hand.

Disclosure of the invention

5 In order to overcome the drawbacks of the known lead-free glasses, in accordance with the present invention a composition for a vitrifiable mixture has been devised according to the following table:

Table 1

10

SiO ₂	50-58	TiO ₂	0-6
K ₂ O	0-13	ZrO	0-5
Na ₂ O	0-9	Y ₂ O ₃	0-5
Li ₂ O	0-4	Al ₂ O ₃	0-3
15 CaO	0-3	SnO ₂	0-5
MgO	0-4	La ₂ O ₃	0-9
B ₂ O ₃	0-2	Nb ₂ O ₅	0-9
ZnO	16-30	Bi ₂ O ₃	0-12
BaO	0-12	GeO ₂	0-5

20

In this composition lead is replaced by a mixture comprising mainly zinc, plus barium, lanthanum, niobium and bismuth, to give a total content of the oxides of the said elements that ranges from 26% to 25 33%. The sum of these oxides excluding zinc oxide must be between 7% and 14%, and furthermore it is possible to add zirconium, yttrium and titanium with a total combined content of their oxides of less than 6% for further improvement of the chemical resistance and 30 refractive index of the glass.

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Other features defining the mixture of oxides for formation of the glass according to the invention are:

- 5 - the fact that the total weight content of SiO_2 and Al_2O_3 is between 52% and 58% to guarantee sufficient chemical resistance;
- the fact that the total weight content of the oxides of potassium, sodium and lithium is between 12% and 18% to improve workability and fusibility;
- 10 - the fact that the molar ratio between potash and soda is between 0.9 and 2 to ensure low transfers of heavy metal ions;
- the presence of oxides of arsenic, antimony, nickel, cobalt, manganese, erbium, neodymium, selenium, and
- 15 cerium, as refining and decolorizing agents, in total quantity below 2%;
- the presence of alumina and of the oxides of calcium and magnesium in total quantity below 4%, to increase the hydrolysis resistance;
- 20 - the presence of tin and germanium in total amount by weight of up to 5%, to achieve the desired density and refractive index.

Within the framework of the possible compositions in the range stated above, the following are of particular interest:

A) a glass with composition in the range shown in Table 2 below:

Table 2

30

SiO_2	53-57	ZnO	16-22
K_2O	7-12	BaO	7-13
Na_2O	3-6	B_2O_3	0-1
Li_2O	0-2	$\text{ZnO}+\text{BaO}$	26-30

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$K_2O+Na_2O+Li_2O$	12-17	ZrO_2	0-3
MgO	0-2	TiO_2+ZrO_2	0-6
TiO_2	0-6	Sb_2O_3	0-1

5

These values correspond to glasses with density and refractive index equal to or greater than the values stipulated by the aforementioned EEC standard, at a reasonable cost, and with good chemical resistance, for example the following glasses (Table 2/1), which can be used as substitutes for lead crystal:

10

Table 2/1

15

	1	2	3	4
SiO_2	53.5-54.5	55.5-56.5	54.5-55.5	53.5-54.5
K_2O	7.5-8.5	8-9	7.5-8.5	10-11
Na_2O	4.5-5.5	4-5	4.5-5.5	5-6
ZnO	18-19	16.5-17.5	15.5-16.5	18.5-19.5
BaO	9.5-10.5	10.5-11.5	10.5-11.5	9.5-10.5
Sb_2O_3	0.22-0.27	0.73-0.77	0.73-0.77	0.73-0.77
TiO_2	3.5-4.5	1.5-2.5	3.5-4.5	-

20

25

More particularly, the next table (Table 2/2) gives the compositions and the measured values of some parameters of glasses with composition according to the fields defined by Table 2/1:

30

Table 2/2

		1	2	3	4
5	SiO ₂	54	56.25	55	54.15
	K ₂ O	7.84	8.50	7.84	10.8
	Na ₂ O	5.16	4.5	5.16	5.5
	ZnO	18.5	17	16	18.8
	BaO	10	11	11	10
10	Sb ₂ O ₃	0.25	0.75	0.75	0.75
	TiO ₂	4.25	2	4.25	-
	K ₂ O+Na ₂ O+ Li ₂ O	13	13.0	13	16.3
	ZnO+BaO	28.5	28	27	28.8
15	D.I.N. 12111	0.12	0.14	0.13	0.30
	d	2.9575	2.9316	2.9441	2.938
	n _d	1.5720	1.5570	1.5695	1.5510
	α	91.8	90.5	89	103.0
	Abbe n°	50.5	55.3	53.5	53
20	Tg	563	569	567	523
	Mg	635	626	632	600

In this and subsequent tables, values are given for the various glasses, with notation as follows: "DIN 12111" is the value of the chemical resistance measured according to that standard; "d" is the density in kg/dm³ measured according to ASTM standard C729-75; "α" is the value of the coefficient of thermal expansion in °C⁻¹×10⁻⁶, according to UNI standard 7460 in the range 0-300; "Tg" is the glass

transition temperature in °C; "Mg" is the softening temperature in °C; "Abbe No." is the value of the expression $(n_D - 1)/(n_F - n_C)$, the Abbe number being an index of optical dispersion, with low values of the index corresponding to increased dispersions.

B) a glass which, in comparison with the preceding one, has a lower quantity of barium and is of better quality - with equal or better physical parameters, such as sonority and dispersion - but a much higher cost, according to the following restricted range of composition (Table 3):

Table 3

15	SiO ₂	53-57	TiO ₂	0-6
	K ₂ O	7-12	Bi ₂ O ₃	1-13
	Na ₂ O	3-6	Bi ₂ O ₃ +ZnO+BaO	26-30
	Li ₂ O	0-1	Bi ₂ O ₃ +BaO	7-14
	K ₂ O+Na ₂ O+Li ₂ O	12-17	B ₂ O ₃	0-1
20	Al ₂ O ₃	0-1	ZrO ₂	0-2
	SiO ₂ +Al ₂ O ₃	53-57	Y ₂ O ₃	0-1
	ZnO	16-22	TiO ₂ +Y ₂ O ₃ +ZrO ₂	0-6
	BaO	0-13	Sb ₂ O ₃	0-1

The next table (Table 3/1) shows two ranges of composition according to this last, restricted field:

Table 3/1

	5	6
SiO ₂	54.5-55.5	54.5-55.5
K ₂ O	10.5-11.5	10.5-11.5
Na ₂ O	5-6	5-6
ZnO	18.5-19.5	18.5-19.5
BaO	5.5-6.5	-
Bi ₂ O ₃	2.5-3.5	8.5-9.5
Sb ₂ O ₃	0.73-0.77	0.73-0.77

More particularly, Table 3/2 shown below gives the compositions and the measured values of some parameters of two glasses possessing compositions according to the ranges defined in Table 3/1:

Table 3/2

	5	6
SiO ₂	55.15	55.15
K ₂ O	10.8	10.8
Na ₂ O	5.5	5.5
ZnO	18.8	18.8
BaO	6	-
Bi ₂ O ₃	3	9
Sb ₂ O ₃	0.75	0.75
K ₂ O+Na ₂ O+Li ₂ O	16.3	16.3
ZnO+BaO+Bi ₂ O ₃ +Nb ₂ O ₅	27.8	27.8

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	BaO+Bi ₂ O ₃ +Nb ₂ O ₅	9	9
	SiO ₂ +Al ₂ O ₃	55.15	55.15
	D.I.N. 12111	0.24	0.26
5	d	2,911	2,939
	n _d	1.5495	1.5570
	α	98.0	97.7
	n°Abbe	55	52.5
	Tg	528	529
10	Mg	617	609

It can be seen from the two examples given above that simply on replacing barium with bismuth there is an increase in optical dispersion.

15 Tests that have been carried out show that with suitable combinations of oxides it is possible to achieve values of the parameters that are comparable to those of lead crystal, benefiting from one or more of the following characteristics, depending on the
20 circumstances: inexpensiveness of the product, workability, colour and optical dispersion. Moreover, the composition range stated is able to produce glasses with improved optical qualities, high density and
25 considerable chemical resistance, without the use of potentially toxic or polluting elements; the specific subranges described above define compositions that are particularly interesting from the standpoint of industrial manufacture and/or of the market.

30 It is intended that the examples are given only as practical demonstrations of the invention, this invention being able to vary without, however, departing from the scope of the concept defined by the invention itself.

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CLAIMS

1. A lead-free glass with density greater than 2.9 g/cm³ and refractive index greater than 1.545, characterized in that it has a percentage by weight of oxides in the ranges given in the following table:

	SiO ₂	50-58	TiO ₂	0-6
	K ₂ O	0-13	La ₂ O ₃	0-9
10	Na ₂ O	0-9	Nb ₂ O ₅	0-9
	Li ₂ O	0-4	Bi ₂ O ₃	0-12
	K ₂ O+Na ₂ O+Li ₂ O	12-18	Bi ₂ O ₃ +ZnO+BaO+ La ₂ O ₃ +Nb ₂ O ₅	26-33
15	CaO	0-3	Bi ₂ O ₃ +BaO+La ₂ O ₃ + Nb ₂ O ₅	7-14
	MgO	0-4	GeO ₂	0-5
	Al ₂ O ₃	0-3	B ₂ O ₃	0-2
	Al ₂ O ₃ +MgO+CaO	0-4	ZrO ₂	0-5
	SiO ₂ +Al ₂ O ₃	52-58	Y ₂ O ₃	0-5
20	ZnO	16-30	SnO ₂	0-5
	BaO	0-12	TiO ₂ +Y ₂ O ₃ +ZrO ₂	0-6

the sum of the oxides of other minor elements, such as Ni, Mn, Nd, Er, Co, Sb, As, Se and Ce, remaining below 2% by weight.

2. A glass as in Claim 1, characterized in that it has the following chemical composition as percentages by weight:

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5	SiO ₂	53-57	ZnO	16-22
	K ₂ O	7-12	BaO	7-13
	Na ₂ O	3-6	B ₂ O ₃	0-1
	Li ₂ O	0-2	ZnO+BaO	26-30
	K ₂ O+Na ₂ O+Li ₂ O	12-17	ZrO ₂	0-3
	MgO	0-2	TiO ₂ +ZrO ₂	0-6
	TiO ₂	0-6	Sb ₂ O ₃	0-1

10 and contains other oxides of minor elements (as impurities or decolorants), such as to obtain, at reasonable cost, the values of the physical parameters within the range of crystal.

3. A glass as in Claim 2, characterized in that
 15 it has a chemical composition within the following limits:

20		1	2	3	4
	SiO ₂	53.5-54.5	55.5-56.5	54.5-55.5	53.5-54.5
	K ₂ O	7.5-8.5	8-9	7.5-8.5	10-11
	Na ₂ O	4.5-5.5	4-5	4.5-5.5	5-6
	ZnO	18-19	16.5-17.5	15.5-16.5	18.5-19.5
	BaO	9.5-10.5	10.5-11.5	10.5-11.5	9.5-10.5
	Sb ₂ O ₃	0.22-0.27	0.73-0.77	0.73-0.77	0.73-0.77
25	TiO ₂	3.5-4.5	1.5-2.5	3.5-4.5	-

and contains other oxides of minor elements (as impurities or decolorants).

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4. A glass as in Claim 1, characterized in that its chemical composition as a percentage by weight is within the following restricted range:

5

10

SiO ₂	53-57	TiO ₂	0-6
K ₂ O	7-12	Bi ₂ O ₃	1-13
Na ₂ O	3-6	Bi ₂ O ₃ +ZnO+BaO	26-30
Li ₂ O	0-1	Bi ₂ O ₃ +BaO	7-14
K ₂ O+Na ₂ O+Li ₂ O	12-17	B ₂ O ₃	0-1
Al ₂ O ₃	0-1	ZrO ₂	0-2
SiO ₂ +Al ₂ O ₃	53-57	Y ₂ O ₃	0-1
ZnO	16-22	TiO ₂ +Y ₂ O ₃ +ZrO ₂	0-6
BaO	0-13	Sb ₂ O ₃	0-1

15

and in that it contains other oxides of minor elements (as impurities or decolorants), to obtain a glass of better quality than those in Claim 2, at the expense of a considerable increase in cost.

20

5. Glasses as in Claim 4, characterized in that they have the following values of chemical composition:

25

SiO ₂	54.5-55.5	54.5-55.5
K ₂ O	10.5-11.5	10.5-11.5
Na ₂ O	5-6	5-6
ZnO	18.5-19.5	18.5-19.5
BaO	5.5-6.5	-
Bi ₂ O ₃	2.5-3.5	8.5-9.5
Sb ₂ O ₃	0.73-0.77	0.73-0.77

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and contain other oxides of minor elements (as impurities or decolorants).

6. A glass not containing lead, with physical characteristics corresponding for the most part to those of a lead crystal; the whole being as defined above.
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INTERNATIONAL SEARCH REPORT

International Application No

PCT/IT 95/00215

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 C03C4/00 C03C3/078

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CHEMICAL ABSTRACTS, vol. 121, no. 12, 19 September 1994 Columbus, Ohio, US; abstract no. 140000, page 408; see abstract & JP,A,06 107 425 (OHARA KK) 19 April 1994	1-3,6
X	--- US,A,4 098 596 (C.K. WU) 4 July 1978 see claims 1-5	1-3
X	--- EP,A,0 553 586 (COMPAGNIE DES CRISTALLERIES DE BACCARAT) 4 August 1993 cited in the application see abstract -----	1-3,6

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Information on patent family members

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