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Date: 4/21/2025

To whom it may concern:

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- Japanese

To:

- English

The documents are designated as:

- D3-JPA 1998059741-000000.pdf
- D6-JP2004299947A.pdf
- JPA 2003192377-000000.pdf

Prince Williams, Project Coordinator in this company, attests to the following:

"To the best of my knowledge, the aforementioned documents are a true, full and accurate translation of the specified documents."

Signature of Prince Williams

(19) Japan Patent Office (JP)

(12) Gazette of Unexamined
Patent Applications (A)(11) Publication Number
2004-299947
(P2004-299947A)

(43) Publication Date October 28, 2004 (2004.10.28)

(51) Int.Cl.⁷
C03C 3/093
C03C 3/091FI
C03C 3/093
C03C 3/091Theme Codes (Ref.)
4G062

Examination Request Not Yet Received No. of Claims 2 OL (Total of 8 pages)

(21) Appl. No. 2003-93356 (P2003-93356)
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(54) [Title of the Invention] Alkali-Free Glass and Method For Producing the Same

(57) [Abstract]

[Problem] To provide an alkali-free glass that does not use As_2O_3 as a clarifying agent and does not contain bubbles that cause display defects, even when used as a glass substrate for displays.

[Solution] Provided is an alkali-free glass comprising 40 to 70 mass% SiO_2 , 6 to 25 mass% Al_2O_3 , 5 to 20 mass% B_2O_3 , 0 to 10 mass% MgO , 0 to 15 mass% CaO , 0 to 30 mass% BaO , 0 to 10 mass% SrO , 0 to 10 mass% ZnO , 0.0001 to 0.03 mass% SO_3 , and 0.05 to 2 mass% SnO_2 , the glass being substantially free of alkali metal oxides.

[Selected Drawing] None

[Claims]

[Claim 1]

An alkali-free glass comprising 40 to 70 mass% SiO₂, 6 to 25 mass% Al₂O₃, 5 to 20 mass% B₂O₃, 0 to 10 mass% MgO, 0 to 15 mass% CaO, 0 to 30 mass% BaO, 0 to 10 mass% SrO, 0 to 10 mass% ZnO, 0.0001 to 0.03 mass% SO₃, and 0.05 to 2 mass% SnO₂, the glass being substantially free of alkali metal oxides.

[Claim 2]

A method for producing an alkali-free glass comprising: melting a glass raw material mixture mixed together to become a glass having a composition comprising 40 to 70 mass% SiO₂, 6 to 25 mass% Al₂O₃, 5 to 20 mass% B₂O₃, 0 to 10 mass% MgO, 0 to 15 mass% CaO, 0 to 30 mass% BaO, 0 to 10 mass% SrO, 0 to 10% ZnO, and being substantially free of alkali metal oxides; and molding this glass raw material mixture, wherein a sulfate is added as a clarifying agent to the glass raw material mixture at a concentration of 0.005 to 1 mass% in terms of SO₃ and SnO₂ is added at a concentration of 0.05 to 2 mass%.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention]

The present invention relates to an alkali-free glass, and more specifically to alkali-free glass used as transparent glass substrate for displays, and a method for producing the same.

[0002]

[Prior Art]

Alkali-free glass has been used as the transparent glass substrate in liquid crystal displays and other applications. In addition to properties such as heat resistance and chemical resistance, alkali-free glass used in display applications must not contain bubbles that cause display defects.

[0003]

Various types of glass have been proposed as alkali-free glass, and the applicant has also proposed a SiO₂-Al₂O₃-B₂O₃-CaO-SrO-BaO alkali-free glass in Patent Document 1.

[0004]

[Patent Document 1] JP H06-263473 A

[0005]

[Problem to Be Solved by the Invention]

In order to obtain bubble-free glass, it is important to select a clarifying agent that generates clarifying gas during the vitrification reaction process using solid-state reactions and solid state/liquid reactions, and the clarification process during which degassing of molten glass occurs. This is done to remove gas generated when the raw materials undergo a vitrification reaction from the molten glass using a clarifying gas, and then enlarging the remaining minute bubbles using clarifying gas generated again during the clarification process to raise and remove them.

[0006]

Alkali-free glass used in liquid crystal display glass substrates has a high viscosity when molten and is melted at higher temperatures than glass containing alkali components. In this type of alkali-free glass, the vitrification reaction usually occurs at 1200 to 1300°C, and degassing and homogenization are performed at high temperatures of 1400°C or higher. As₂O₃ is known to be a clarifying agent capable of generating clarifying gas during the vitrification reaction process and clarification process under such high-temperature conditions, and Patent Document 1 discloses that As₂O₃ is used as a clarifying agent.

[0007]

However, because As₂O₃ is highly toxic and may contaminate the environment during glass production and waste glass treatment, its use is being restricted.

[0008]

Therefore, in view of these circumstances, it is an object of the present invention to provide an alkali-free glass as a glass substrate for displays that does not use As₂O₃ as a clarifying agent and does not contain bubbles that cause display defects.

[0009]

[Means for Solving the Problem]

As a result of various experiments, the present applicant found that the object of the present invention could be realized by using a sulfate and stannic oxide instead of As₂O₃ as clarifying agents, and thus proposes this finding as the present invention.

[0010]

Specifically, the present invention is an alkali-free glass comprising 40 to 70 mass% SiO₂, 6 to 25 mass% Al₂O₃, 5 to 20 mass% B₂O₃, 0 to 10 mass% MgO, 0 to 15 mass% CaO, 0 to 30 mass% BaO, 0 to 10 mass% SrO, 0 to 10 mass% ZnO, 0.0001 to 0.03 mass% SO₃, 0.05 to 2 mass% SnO₂, the glass being substantially free of alkali metal oxides.

[0011]

The present invention is also a method for producing an alkali-free glass comprising: melting a glass raw material mixture mixed together to become a glass having a composition comprising 40 to 70 mass% SiO₂, 6 to 25 mass% Al₂O₃, 5 to 20 mass% B₂O₃, 0 to 10 mass% MgO, 0 to 15 mass% CaO, 0 to 30 mass% BaO, 0 to 10 mass% SrO, 0 to 10% ZnO, and being substantially free of alkali metal oxides; and molding this glass raw material mixture, wherein a sulfate is added as a clarifying agent to the glass raw material mixture at a concentration of 0.005 to 1 mass% in terms of SO₃ and SnO₂ is added at a concentration of 0.05 to 2 mass%.

[0012]

[Embodiment of the Invention]

The sulfate used in the present invention decomposes at a temperature ranging from approximately 1200 to 1500°C and generates a large amount of clarifying gas (sulfur dioxide, oxygen gas) upon decomposition. SO₃ decomposes even at high temperatures of 1400°C, making it ideal for glass with high-temperature vitrification reactions such as alkali-free glass. In other words, SO₃ acts effectively as a clarifying agent when melting glass with a viscosity equivalent to 10^{2.5} dPa·s at temperatures above 1500°C. However, in general, the solubility of SO₃ in glass decreases as the alkali content decreases, so in the case of alkali-free glass, the solubility of SO₃ is very low. In other words, SO₃ releases a large amount of gas during the vitrification reaction process, but after vitrification, the clarification effect is reduced because there is little SO₃ remaining.

[0013]

SnO₂ undergoes a chemical reaction caused by a change in the valence of Sn ions at temperatures above 1400°C, especially above 1500°C, releasing large amounts of clarifying gas (oxygen gas). In other words, SnO₂ (tetravalent) changes to SnO (bivalent) as the temperature rises, releasing large amounts of clarifying gas in the process.

[0014]

Therefore, by using SnO₂ in addition to SO₃ to generate clarifying gas via changes in valence rather than decomposition, where these valence changes occur at temperatures at which non-alkaline glass melts, high clarification effects can be obtained over a wide range of temperatures from the vitrification reaction process that occurs at relatively low temperatures to the clarification process that occurs at high temperatures, enabling the production of low-bubble, alkali-free glass.

[0015]

Next, the production method for the non-alkaline glass of the present invention will be described.

[0016]

First, a glass raw material mixture is prepared to obtain a glass comprising a composition of 40 to 70 mass% SiO₂, 6 to 25 mass% Al₂O₃, 5 to 20 mass% B₂O₃, 0 to 10 mass% MgO, 0 to 15 mass% CaO, 0 to 30 mass% BaO, 0 to 10 mass% SrO, and 0 to 10 mass% ZnO.

[0017]

Next, a sulfate and SnO₂ are added to this glass raw material mixture. BaSO₄ and CaSO₄ can be used as a sulfate. The amount of sulfate added is 0.005 to 1 mass% of the glass raw material mixture in terms of SO₃, and this amount results in an amount of SO₃ in the glass of 0.0001 to 0.03%. When the amount of sulfate is less than 0.005%, it becomes difficult to expel the gas generated during the vitrification process, and when the amount is more than 1%, the glass raw material mixture becomes prone to formation of new bubbles, resulting in bubbles remaining in the glass. The preferred amount of sulfate added is 0.01 to 1% in terms of SO₃, and more preferably 0.05 to 1%. The preferred amount of SO₃ is 0.001 to 0.03%, preferably 0.005 to 0.03%. Also, the amount of SnO₂ added is 0.05 to 2 mass% per 100 mass% of glass raw material mixture. When the amount of SnO₂ is less than 0.05%, it becomes difficult to remove bubbles remaining in the glass melt during the clarification process, and when the amount exceeds 2%, the glass becomes prone to opacity. The preferred amount of SnO₂ added is 0.05 to 1%, and more preferably 0.1 to 0.5%.

[0018]

In the present invention, in addition to the sulfate and SnO₂, Sb₂O₃ can be added up to 3% and a chloride can be added (in terms of Cl₂) up to 1% as clarifying agents. Fluorides are not added because they are toxic, albeit not as toxic as As₂O₃. Fe₂O₃ is also a component with clarifying properties, but when present in large amounts, it reduces the visible light transmissivity of glass, making it unsuitable for display applications. Therefore, it is preferable to keep the amount below 800 ppm, and preferably below 500 ppm.

[0019]

Next, the mixed glass raw materials are melted. As the glass raw materials are heated, a vitrification reaction occurs, and sulfur dioxide and oxygen gas are generated by the decomposition of the sulfate. The gases generated during the vitrification reaction are then expelled from the molten glass. Then, as the temperature rises during the clarification process, the valence of SnO₂ changes, generating oxygen gas that removes the minute bubbles remaining in the molten glass.

[0020]

The molten glass is then molded into the desired shape. For display applications, methods such as the overflow down-draw method, slot down-draw method, float method, and roll-out method are used to form thin plates. In particular, forming thin plates using the overflow down-draw method or the slot down-draw method is preferable because it produces glass plates with excellent surface properties.

[0021]

In this way, an alkali-free glass is obtained that contains 40 to 70 mass% SiO_2 , 6 to 25 mass% Al_2O_3 , 5 to 20 mass% B_2O_3 , 0 to 10 mass% MgO , 0 to 15 mass% CaO , 0 to 30 mass% BaO , 0 to 10 mass% SrO , 0 to 10 mass% ZnO , 0.0001 to 0.03 mass% SO_3 , and 0.05 to 2 mass% SnO_2 , and that is substantially free of alkali metal oxides. Here, substantially free of alkali metal oxides means that alkali metal oxides (Li_2O , Na_2O , K_2O) are not added as glass raw materials, and if mixed in as impurities at a level of 0.2 mass% or less, do not hinder the invention.

[0022]

The following are the reasons for applying limitations on the composition of the alkali-free glass.

[0023]

SiO_2 is a component that forms the glass network, and an amount from 40 to 70% is included. When the amount SiO_2 is less than 40%, chemical resistance deteriorates, the strain point decreases, and heat resistance worsens. When the amount exceeds 70%, high-temperature viscosity increases, meltability deteriorates, and cristobalite impurities are more likely to precipitate. The amount of SiO_2 is preferably from 45 to 65%.

[0024]

Al_2O_3 is a component that enhances the heat resistance and opacity of glass, and an amount from 6 to 25% is included. When the amount of Al_2O_3 is less than 6%, the opacity temperature significantly increases, making the glass more prone to opacity. When the amount exceeds 25%, acid resistance, particularly resistance to buffered hydrofluoric acid, decreases, making the glass substrate surface more prone to cloudiness. The amount of Al_2O_3 is preferably from 10 to 20%.

[0025]

B_2O_3 is a component that acts as a melting agent, reducing viscosity and facilitating melting, and an amount of 5 to 20% is included. When the amount of B_2O_3 is less than 5%, its melting effect is insufficient. When the amount exceeds 20%, acid resistance decreases and the strain point decreases, leading to reduced heat resistance. The amount of B_2O_3 is preferably from 7.5 to 15%, and more preferably from 8.5 to 15%.

[0026]

MgO is a component that lowers the high-temperature viscosity without lowering the strain point, facilitating glass melting, and an amount of 0 to 10% is included. When the amount of MgO exceeds 10%, the resistance of the glass to buffered hydrofluoric acid is significantly reduced. The amount of MgO is preferably from 0 to 3.5%, and more preferably from 0 to 3%.

[0027]

CaO has the same function as MgO , and an amount of 0 to 15% is included. When the amount of CaO exceeds 15%, the resistance of the glass to buffered hydrofluoric acid is significantly reduced. The amount of CaO is preferably from 0 to 10%, and more preferably from 6 to 10%.

[0028]

BaO is a component that improves the chemical resistance of glass and improves opacity, and an amount of 0 to 30% is included. When the amount of BaO exceeds 30%, the strain point decreases and heat resistance deteriorates. The amount of BaO is preferably from 0 to 20%.

[0029]

SrO has the same effect as BaO, and an amount of 0 to 10% is included. When the amount of SrO exceeds 10%, opacity increases, which is undesirable. The amount of SrO is preferably from 0 to 7%.

[0030]

Mobile devices such as mobile phones and notebook PCs require light weight for ease of carrying, and the glass substrates used in these devices must also be lightweight. Therefore, a low density is required. Also, since this type of glass substrate tends to warp when the thermal expansion coefficient of thin-film transistor (TFT) materials increases, it is desirable for the glass substrate to have a low thermal expansion coefficient that is close to that of TFT materials (approximately 30 to $33 \times 10^{-7}/^{\circ}\text{C}$), specifically 28 to $35 \times 10^{-7}/^{\circ}\text{C}$. BaO and SrO are components that also affect the density and thermal expansion coefficient of glass. To obtain low-density, low-expansion glass, these should be limited to 6% or less, preferably 4% or less, in total.

[0031]

ZnO is a component that improves resistance to buffered hydrofluoric acid and improves opacity, and an amount of 0 to 10% is included. When the amount of ZnO exceeds 10%, the glass becomes more prone to opacity, and the strain point decreases, resulting in a loss of heat resistance. The amount of ZnO is preferably from 0 to 7%.

[0032]

In addition to the components mentioned above, ZrO_2 , TiO_2 , Fe_2O_3 , P_2O_5 , Y_2O_3 , Nb_2O_3 , and La_2O_3 , etc. can be added to the present invention up to a total amount of 5%.

[0033]

[Examples]

The present invention will now be described with reference to examples.

[0034]

Table 1 shows the effects of SO_3 and SnO_2 on alkali-free glass. In this table, the glass in sample a is conventional alkali-free glass with As_2O_3 added as a clarifying agent, the glass in sample b is an alkali-free glass prepared by removing As_2O_3 from sample a, the glass in sample c is an alkali-free glass with only a sulfate (BaSO_4) added, the glass in sample d is an alkali-free glass with only SnO_2 added, and the glass in samples e and f are alkali-free glass containing both the sulfate and SnO_2 .

[0035]

[Table 1]

		(mass%)					
Sample		a	b	c	d	e	f
Glass Raw Material Mix	SiO ₂	60.5	60.5	60.5	60.5	60.5	60.5
	Al ₂ O ₃	15.5	15.5	15.5	15.5	15.5	15.5
	B ₂ O ₃	10.0	10.0	10.0	10.0	10.0	10.0
	CaO	5.5	5.5	5.5	5.5	5.5	5.5
	SrO	6.0	6.0	6.0	6.0	6.0	6.0
	BaO	2.0	2.0	2.0	2.0	2.0	2.0
	ZnO	0.5	0.5	0.5	0.5	0.5	0.5
	SO ₃	-	-	0.1	-	0.05	0.1
	SnO ₂	-	-	-	0.2	0.2	0.2
	As ₂ O ₃	0.5	-	-	-	-	-
Clarity	1600°C · 4 hr	○	X	Δ	Δ	Δ	Δ
	1600°C · 8 hr	○	Δ	○	Δ	○	○
	1600°C · 4 hr + 1650°C · 4 hr	⊙	Δ	○	○	⊙	⊙
Strain Point (°C)		660	665	665	665	665	665
Temp. (°C) at Viscosity of 10 ^{2.5} dPa · s		1575	1580	1580	1580	1580	1580
HCl Resistance		⊙	⊙	⊙	⊙	⊙	⊙
Buffered HF Resistance		⊙	⊙	⊙	⊙	⊙	⊙

[0036]

Each sample glass in the table was prepared as follows.

[0037]

First, the glass raw materials were prepared so that the total amount of SiO₂, Al₂O₃, B₂O₃, CaO, SrO, BaO, and ZnO was 100 mass%, and then clarifying agents (SO₃, SnO₂, As₂O₃) were added to (inserted into) this mixture and melted in an electric furnace. To evaluate the clarity during the vitrification reaction process, the sample was melted at 1600°C for 4 hours and then at 1600°C for 8 hours. To evaluate the clarity during the clarification process, the sample was melted at 1600°C for 4 hours and then at 1650°C for 4 hours. Note that because SO₃ decomposes during melting, the amount of SO₃ remaining in the glass in samples c, e, and f was 0.001 mass% under all melting conditions.

[0038]

Next, molten glass was poured onto a carbon plate and slowly cooled. The size of the cast glass plate was approximately 10 cm long, 6 cm wide, and 1 cm high. The number of bubbles in the glass was observed visually using a microscope in the first 1.5 to 7 cm of the cast glass plate, and the results are shown in the table. This bubble count refers to bubbles with a maximum diameter of 20 μm or greater. If there were more than 10,000 bubbles per 100 g of glass, X was assigned. If there were 1,001 to 10,000 bubbles, Δ was assigned. If there were 101 to 1,000 bubbles, ○ was assigned. If there were 100 bubbles or fewer, ⊙ was assigned.

[0039]

The strain points in the table were measured using the method specified in ASTM C336-71. The temperature corresponding to a viscosity of 10^{2.5} dPa · s was calculated with Fulcher's equation from the high-temperature viscosity measured using the platinum ball pull-up method. Acid resistance was tested by immersing each sample glass in a 10 mass% hydrochloric acid solution maintained at 80°C for 24 hours, then observing the surface condition of the glass. Buffered hydrofluoric acid resistance was tested by immersing each sample glass in a buffered hydrofluoric acid solution consisting of 38.7 mass% ammonium fluoride and 1.6 mass% hydrofluoric acid maintained at 20°C for 30 minutes, then observing the surface condition of the glass. For acid resistance and buffered hydrofluoric acid resistance, glass with no change in appearance was assigned ⊙ and glass that had experienced a change in appearance was assigned X.

[0040]

As seen in the table, the glass in sample a, to which As_2O_3 was added, had good clarity, but the glass in sample b, to which no clarifying agent was added, had very poor clarity. The glass in sample c, to which only a sulfate (SO_3) was added, produced a large amount of clarifying gas during the vitrification process, but insufficient clarifying gas was produced during the clarification process, resulting in poor clarity. The glass in sample d, to which only SnO_2 was added, generated a large amount of gas during the clarification process, but insufficient clarification gas was generated during the vitrification process, resulting in poor clarity.

[0041]

Meanwhile, the glass in samples e and f, to which a sulfate and SnO_2 were added, had approximately the same excellent clarity as that of sample a, to which As_2O_3 was added. The glass in samples e and f also exhibited excellent heat resistance, with a strain point of 665°C , and exhibited no apparent changes in appearance even after treatment with hydrochloric acid or buffered hydrofluoric acid, demonstrating excellent chemical resistance.

[0042]

[Effects of the Invention]

As described above, by adding a predetermined amount of a sulfate and SnO_2 as clarifying agents using the method of the present invention, alkali-free glass can be produced with excellent clarifying properties and few bubbles without using As_2O_3 .

[0043]

The alkali-free glass of the present invention is particularly suitable for use as a glass substrate for displays because it has excellent clarity, few bubbles, and excellent heat resistance and chemical resistance.

Continued from front page

F Terms (Reference) 4G062 AA01 BB01 DA05 DA06 DB03 DB04 DC03 DC04 DD01 DE01 DE02
DE03 DF01 EA01 EA10 EB01 EC01 ED01 ED02 ED03 EE01 EE02 EE03
EE04 EF01 EF02 EF03 EG01 EG02 EG03 EG04 FA01 FB01 FC01 FD01
FE02 FF01 FG01 FH01 FJ01 FK01 FL01 GA01 GB02 GC01 GD01 GE01
HH01 HH03 HH05 HH07 HH09 HH11 HH13 HH15 HH17 HH20 JJ01 JJ03
JJ04 JJ05 JJ06 JJ07 JJ10 KK01 KK03 KK05 KK07 KK10 MM27 NN40