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

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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 As₂O₃ as a clarifying agent and does not contain bubbles that cause display defects.

[Solution] Provided is an alkali-free glass having a composition comprising 40 to 70 wt% SiO₂, 6 to 25 wt% Al₂O₃, 5 to 20 wt% B₂O₃, 0 to 10 wt% MgO, 0 to 15 wt% CaO, 0 to 30 wt% BaO, 0 to 10 wt% SrO, 0 to 10% ZnO, and 0.05 to 2 wt% SnO₂, and being substantially free of alkali metal oxides.

[Claims]

[Claim 1] An alkali-free glass having a composition comprising 40 to 70 wt% SiO₂, 6 to 25 wt% Al₂O₃, 5 to 20 wt% B₂O₃, 0 to 10 wt% MgO, 0 to 15 wt% CaO, 0 to 30 wt% BaO, 0 to 10 wt% SrO, 0 to 10% ZnO, and 0.05 to 2 wt% SnO₂, and 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 wt% SiO₂, 6 to 25 wt% Al₂O₃, 5 to 20 wt% B₂O₃, 0 to 10 wt% MgO, 0 to 15 wt% CaO, 0 to 30 wt% BaO, 0 to 10 wt% SrO, and 0 to 10% ZnO, and being substantially free of alkali metal oxides; and molding this glass raw material mixture, wherein SnO₂ is added as a clarifying agent to the glass raw material mixture at a concentration of 0.05 to 2.0 wt%.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to alkali-free glass, more specifically, alkali-free glass used in transparent glass substrates for displays, and a method for producing the same.

[0002]

[Background 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-BaO alkali-free glass in JP S63-74935 A.

[0004]

[Problem to Be Solved by the Invention] Alkali-free glass used as a substrate for liquid crystal displays does not contain alkali metal components, making it resistant to vitrification reaction and giving it a high molten viscosity. Therefore, this type of alkali-free glass must be melted at a higher temperature than is necessary for alkali-containing glass. For this reason, the clarifying agent added to eliminate bubbles in the glass is As₂O₃, which can generate a large amount of clarifying gas when melted at this high temperature.

[0005] However, because As₂O₃ is highly toxic and may contaminate the environment during glass production and waste glass treatment, its use is being restricted.

[0006] Therefore, it is an object of the present invention to provide an alkali-free glass that does not use As₂O₃ as a clarifying agent and

does not contain bubbles that cause display defects.

[0007]

[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 SnO₂ instead of As₂O₃ as a clarifying agent, and thus proposes this finding as the present invention.

[0008] Specifically, the present invention is an alkali-free glass having a composition comprising 40 to 70 wt% SiO₂, 6 to 25 wt% Al₂O₃, 5 to 20 wt% B₂O₃, 0 to 10 wt% MgO, 0 to 15 wt% CaO, 0 to 30 wt% BaO, 0 to 10 wt% SrO, 0 to 10% ZnO, and 0.05 to 2 wt% SnO₂, and being substantially free of alkali metal oxides.

[0009] 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 wt% SiO₂, 6 to 25 wt% Al₂O₃, 5 to 20 wt% B₂O₃, 0 to 10 wt% MgO, 0 to 15 wt% CaO, 0 to 30 wt% BaO, 0 to 10 wt% SrO, and 0 to 10% ZnO, and being substantially free of alkali metal oxides; and molding this glass raw material mixture, wherein SnO₂ is added as a clarifying agent to the glass raw material mixture at a concentration of 0.05 to 2.0 wt%.

[0010]

[Operation] In order to obtain bubble-free, alkali-free glass, it is necessary to generate a clarifying gas that is effective at removing bubbles during high-temperature melting, increasing the diameter of microbubbles present in the molten glass and causing them to rise and be removed. Therefore, components that decompose at high temperatures and generate large amounts of clarifying gas are essential, and SnO₂ generates large amounts of oxygen gas via chemical reactions caused by changes in the valence of Sn ions at high temperatures above 1400°C.

[0011] In the present invention, the addition of SnO₂ as a clarifying agent results in a clarifying effect in the high temperature range, enabling the production of alkali-free glass without bubbles that cause display defects.

[0012] Next, the production method for the non-alkaline glass of the present invention will be described.

[0013] First, a glass raw material mixture is prepared to obtain a glass with the desired composition. The composition range of the glass and the reasons for restrictions on components will now be described.

[0014] SiO₂ is a component that forms the glass network, and an amount of 40 to 70%,

preferably 45 to 65%, 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.

[0015] Al_2O_3 is a component that enhances the heat resistance and opacity of glass, and an amount of 6 to 25%, preferably 10 to 20%, 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.

[0016] B_2O_3 is a component that acts as a melting agent, reducing viscosity and facilitating melting, and an amount of 5 to 20%, preferably 6 to 15%, 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.

[0017] 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%, preferably 0 to 7%, is included. When the amount of MgO exceeds 10%, the resistance of the glass to buffered hydrofluoric acid is significantly reduced. CaO has the same function as MgO , and an amount of 0 to 15%, preferably 0 to 10%, is included. When the amount of CaO exceeds 15%, the resistance of the glass to buffered hydrofluoric acid is significantly reduced. BaO is a component that improves the chemical resistance of glass and improves opacity, and an amount of 0 to 30%, preferably 0 to 20%, is included. When the amount of BaO exceeds 30%, the strain point decreases and heat resistance deteriorates. SrO has the same effect as BaO , and an amount of 0 to 10%, preferably 0 to 7%, is included. When the amount of SrO exceeds 10%, opacity increases, which is undesirable. ZnO is a component that improves resistance to buffered hydrofluoric acid and improves opacity, and an amount of 0 to 10%, preferably 0 to 7%, 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. Note that when the total amount of MgO , CaO , BaO , SrO , and ZnO is less than 5%, high-temperature viscosity increases, meltability deteriorates, and the glass becomes more prone to opacity. When the total amount

exceeds 30%, heat resistance and acid resistance deteriorate to an undesirable extent.

[0018] In addition to the components mentioned above, ZrO_2 , TiO_2 , Fe_2O_3 , etc. can be added up to a total amount of 5%.

[0019] Next, SnO_2 is added to the glass raw material mixture. The amount of SnO_2 added is 0.05 to 2.0 wt% of the glass raw material mixture. The reason for this range is that an amount less than 0.05% has no clarifying effect, and an amount more than 2.0% increases the amount of volatiles, making the glass more susceptible to deterioration.

[0020] Next, the glass raw material mixture is melted. At this point, a chemical reaction caused by the change in the valence of SnO_2 generates a large amount of oxygen gas, which removes bubbles from the glass.

[0021] The molten glass is then molded into the desired shape. For display applications, the fusion method, down-draw method, float method, or roll-out method, etc. is used to mold the glass into thin sheets.

[0022] The result is the alkali-free glass of the present invention, which has a composition comprising 40 to 70 wt% SiO_2 , 6 to 25 wt% Al_2O_3 , 5 to 20 wt% B_2O_3 , 0 to 10 wt% MgO , 0 to 15 wt% CaO , 0 to 30 wt% BaO , 0 to 10 wt% SrO , 0 to 10% ZnO , and 0.05 to 2 wt% SnO_2 , and which is substantially free of alkali metal oxides.

[0023]

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

[0024] (Example 1) Table 1 shows the effects of SnO_2 . Sample a is a conventional alkali-free glass with As_2O_3 added as a clarifying agent, sample b is an alkali-free glass prepared by removing As_2O_3 from sample a, and sample c is the alkali-free glass of the present invention prepared by adding SnO_2 instead of As_2O_3 .

[0025]

[Table 1]

Sample		a	b	c
Glass Composition (wt%)	SiO_2	60.0	60.0	60.0
	Al_2O_3	16.0	16.0	16.0
	B_2O_3	8.5	8.5	8.5
	MgO	4.0	4.0	4.0
	CaO	1.0	1.0	1.0
	BaO	6.0	6.0	6.0
	SrO	3.5	3.5	3.5
	ZnO	1.0	1.0	1.0
	SnO_2	-	-	0.3
	As_2O_3	0.3	-	-
Clarity		○	X	○

[0026] Each sample was prepared as follows.

[0027] The glass raw materials were mixed together to form glass with the compositions shown in the table and melted in an electric furnace at 1550°C for one hour before evaluating the clarity. The results are shown in Table 1.

[0028] As shown in Table 1, the glass in sample b, to which no clarifying agent was added, exhibited very poor clarity. Meanwhile, the glass in sample c, to which SnO₂ was added, exhibited good clarity similar to that of sample a, which used As₂O₃.

[0029] Clarity was evaluated by melting the glass raw material mixtures at 1550°C for one hour, pouring the molten glass onto a carbon platform, cooling it slowly, and counting the number of bubbles remaining in the glass. In the evaluation, glass with more than 1000 bubbles per 100 g of glass was assigned X, glass with 101 to 1000 bubbles was assigned Δ, and glass with 100 bubbles or fewer was assigned O.

[0030]

(Example 2) Table 2 shows examples (Samples No. 1 to 5) of alkali-free glass obtained using the method of the present invention.

[0031]

[Table 2]

Sample No.		1	2	3	4	5
Glass Composition (wt%)	SiO ₂	53.8	59.8	63.0	62.0	55.9
	Al ₂ O ₃	19.8	15.7	20.5	18.0	11.1
	B ₂ O ₃	10.7	8.5	6.3	8.7	9.2
	MgO	-	3.9	0.5	4.7	-
	CaO	3.2	0.8	6.8	-	4.8
	BaO	2.2	6.1	0.4	1.2	13.4
	SrO	9.1	3.3	0.7	0.8	4.5
	ZnO	-	1.1	-	3.1	0.8
	SnO ₂	1.2	0.8	1.8	1.5	0.3
Clarity		○	○	○	○	○
Strain Point (°C)		672	665	715	668	619
HCl Resistance		○	○	○	○	○
Buffered HF Resistance		○	○	○	○	○

[0032] Each sample was prepared as follows.

[0033] Glass raw materials were mixed together to produce glass with the compositions shown in Table 1, and clarity was evaluated in the same manner as in Example 1. These glass raw material mixtures were melted in an electric furnace at 1500 to 1600°C for 16 to 24 hours and molded to obtain the samples.

[0034] The heat resistance and chemical resistance of each sample obtained in this manner were evaluated. The results are shown in Table 2.

[0035] As shown in Table 2, all samples exhibited excellent clarity as well as good heat resistance and chemical resistance.

[0036] The heat resistance was measured based on the strain point method specified in ASTM C336-71. Chemical resistance was evaluated by immersing each sample in a 10% hydrochloric acid solution maintained at 80°C for 24 hours, then observing the surface condition of the glass substrate. Samples with discoloration of the glass substrate surface were assigned "X," and those with no discoloration were assigned "O." Resistance to buffered

hydrofluoric acid was evaluated by immersing each sample in a buffered hydrofluoric acid solution consisting of 38.7% ammonium fluoride and 1.6% hydrofluoric acid maintained at 20°C for 30 minutes, and then observing the surface condition of the glass substrate. Samples with a cloudy glass substrate surface were assigned "X," and those whose surface showed no change were assigned "O."

[0037]

[Effects of the Invention] As described above, the method of the present invention makes it possible to produce alkali-free glass with excellent clarity and no bubbles that cause display defects, by using SnO₂ as a clarifying agent.

[0038] The alkali-free glass of the present invention is also environmentally friendly because it does not contain As₂O₃. It also has no bubbles that cause display defects as well as excellent heat resistance and chemical resistance, making it particularly suitable for use as the transparent glass substrate in displays.