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(54) High transmittance glass sheet and method of manufacture the same

Glasscheibe mit hoher Durchlässigkeit und Verfahren zu deren Herstellung

Plaque en verre à haute transmission et méthode de sa production

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(56) References cited:
EP-A- 0 701 976 DE-U1- 29 819 347
GB-A- 2 274 841 US-A- 5 030 593

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Description

TECHNICAL FIELD

5 **[0001]** The present invention relates to a high transmittance glass sheet, more specifically, a soda-lime glass sheet having high light beam transmittance that is suitable for use for buildings, solar cell panels and the like. Furthermore, this invention relates to a glass sheet that emits fluorescence efficiently under ultraviolet irradiation and is suitable for interior use and use for showcases. Moreover, this invention relates to a method of manufacturing these glass sheets.

10 BACKGROUND ART

[0002] For substantially colorless high transmittance glass sheets, a high purity raw material is used so that an iron content is extremely low with respect to that of a conventional soda-lime glass sheet, thereby obtaining a light colored and high transmittance glass sheet.

15 **[0003]** For example, an edge coloration clear glass disclosed in JP 7(1995)-29810 B is a soda-lime glass that contains as a coloring agent, expressed in wt. %, less than 0.02% of total iron oxide in terms of Fe_2O_3 , and has a ratio of ferrous oxide (FeO) to this total iron oxide of at least 0.4. This allows the glass to achieve low coloration and high transmittance. The glass has a luminous transmittance (illuminant C) of at least 87% on a 5.66 mm thickness basis.

20 **[0004]** In order to attain the above-mentioned properties, this glass has the following features. That is, in terms of a manufacturing method, the glass has a low SO_3 content, and a melting operation includes a liquefaction stage and a refining stage as separate stages. Further, in terms of a material, a batch free from limestone and dolomite is used so that an iron content in the glass is lowered.

25 **[0005]** Furthermore, an edge coloration clear glass disclosed in JP 8(1996)-715 B is obtained by adding trace amounts of Se and CoO to a glass composition having an iron oxide content equivalent to that of the above-mentioned glass so that the glass exhibits a dominant wavelength of 570 to 590 nm that is compatible with wood tones.

[0006] In order to obtain a light color tone and high transmittance glass having an iron oxide content equivalent to that of a conventional glass, a method has been known in which an oxidizing agent such as cerium oxide is added so that the content of FeO is lowered, which causes coloration and a decrease in transmittance.

30 **[0007]** For example, JP 5(1993)-221683 A discloses a clear glass whose radiation light transmittance is regulated. The clear glass has a conventional clear soda-lime glass composition containing, expressed in wt. %, 0.06 to 0.12% of iron as an impurity in terms of Fe_2O_3 . In the glass, 0.1 to 0.5% of CeO_2 is contained as an oxidizing agent so that a ratio of $\text{Fe}^{2+} / \text{Fe}^{3+}$ in the glass is lowered from a ratio of about 38% in the conventional soda-lime glass sheet to 3 to 10%, thereby attaining high transmittance in a wavelength region in the vicinity of 600 nm or higher.

35 **[0008]** A method also has been proposed, in which a base composition of a soda-lime glass having a content of iron as an impurity equivalent to that of the conventional glass is changed so that lower coloration is attained.

40 **[0009]** For example, JP 8(1996)-40742 A discloses a clear glass composition for glass windows that is a soda-lime-silica glass composition containing, expressed in wt. %, a total amount of 0.02 to 0.2% of iron oxide in terms of ferric oxide and having a base composition that contains 69 to 75% of SiO_2 , 0 to 3% of Al_2O_3 , 0 to 5% of B_2O_3 , 2 to 10% of CaO, less than 2% of MgO, 9 to 17% of Na_2O , 0 to 8% of K_2O , and optionally, fluorine, zinc oxide, zirconium oxide, and less than 4% of barium oxide. In the glass composition, a total content of alkaline-earth metal oxides is not more than 10%. Thus, an absorption band of FeO is shifted to a longer wavelength side, or a slope of the absorption band by FeO is straightened at an infrared side end of the visible region. This allows window glasses to have lower coloration and exhibit more excellent infrared absorption than a soda-lime-silica glass having a conventional base composition.

45 **[0010]** The edge coloration clear glass disclosed in JP 7(1995)-29810 B is required to have a ratio of the ferrous oxide (FeO) to the total iron oxide of at least 0.4 so that a pure and bright azure color can be obtained as desired.

[0011] In order to attain this ratio, a particular manufacturing method in which the melting operation includes the liquefaction stage and the refining stage as separate stages is desirable, and the content of SO_3 should be limited to a low level. This results in an excessive cost increase of the glass sheet thus obtained.

50 **[0012]** In the edge coloration clear glass disclosed in JP 8(1996)-715 B, Se and CoO are contained as coloring agents, thereby causing a decrease in transmittance. Accordingly, the glass is not suitable for applications requiring high transmittance.

55 **[0013]** In the clear glass disclosed in JP 5(1993)-221683 A, iron oxide contained in an amount equivalent to an iron oxide content of the conventional soda-lime glass sheet is oxidized by adding a required amount of an oxidizing agent such as cerium oxide, so that the ratio of $\text{Fe}^{2+} / \text{Fe}^{3+}$ of the contained iron oxide is made lower than that in the case of the conventional soda-lime glass sheet.

[0014] According to this method, by reducing the absorption of FeO, the absorption in a wavelength region having its peak at a wavelength in the vicinity of 1,000 nm can be reduced. However, the absorption is not reduced to a sufficient degree. Further, the absorption by Fe_2O_3 at a wavelength in the vicinity of 400 nm is increased, so that a color tone of

the glass becomes yellowish. Thus, the glass is not preferred for use as a high transmittance glass sheet.

[0015] Furthermore, since the iron oxide is contained in an amount equivalent to the iron oxide content of the conventional soda-lime glass sheet, in order to lower the ratio of $\text{Fe}^{2+} / \text{Fe}^{3+}$, it is required that the oxidizing agent be used in a relatively large amount, thereby causing an increase in manufacturing cost of the glass sheet.

[0016] Moreover, since the absorption at a wavelength in the vicinity of 400 nm is increased as described above, when used as a substrate for a solar cell, which includes a photoelectric conversion layer of amorphous silicon having the highest sensitivity of energy conversion at a wavelength in the vicinity of 500 to 600 nm, the efficiency of the energy conversion is decreased.

[0017] In the glass composition disclosed in JP 8(1996)-40742 A, by changing the base composition of the glass, the soda-lime glass having an iron oxide content equivalent to that of the conventional glass is increased in transmittance.

[0018] However, the method disclosed in this publication merely can provide the effect of shifting the absorption of FeO to the longer wavelength side, which is insufficient for use for buildings in which no coloration is desired and applications requiring high transmittance.

[0019] Furthermore, in the composition disclosed in this publication, MgO and MgO + CaO are contained in insufficient amounts, respectively, and a resultant inconvenience related to melting is compensated by containing Na_2O in a larger amount than in a conventional case. As a result, water resistance and weather resistance are deteriorated, and thus browning becomes more likely to be caused. Further, this composition is not suitable for mass production from the viewpoint of cost effectiveness.

[0020] Furthermore, although the effect disclosed in the publication can be enhanced by adding components such as F, BaO and the like, the addition of these components leads to a cost increase, shortening of a furnace life attributable to the volatilization of F, and release of harmful substances into the air.

[0021] DE 29819347 discloses a soda-lime-silicate glass composition which contains CoO as a colouring component.

DISCLOSURE OF THE INVENTION

[0022] In order to solve the afore-mentioned problems in the conventional technique, the present invention is to provide a high transmittance glass sheet that is different from conventional glass sheets. Furthermore, it is another object of the present invention to provide a high transmittance glass sheet that emits fluorescence in the visible region efficiently under ultraviolet irradiation. Moreover, it is still another object of the present invention to provide methods of manufacturing these glass sheets.

[0023] That is, one embodiment of a glass sheet according to the present invention (hereinafter, referred to as a glass sheet according to the present invention) is formed of a composition comprising A high transmittance glass sheet formed of a composition comprising as base glass components, expressed in wt. %:

65 to 80% of SiO_2 ,
 0 to 5% of Al_2O_3 ,
 0 to 7% of MgO,
 5 to 15% of CaO,
 10 to 18% of Na_2O ,
 0 to 5% of K_2O ,
 7 to 17% of MgO + CaO (exclusive of 7%),
 10 to 20% of $\text{Na}_2\text{O} + \text{K}_2\text{O}$, and
 0.05 to 0.3% of SO_3 ; and

as colouring components, expressed in wt. %:

more than 0 to less than 0.2% TiO_2 .
 not less than 0.005% to less than 0.02% of total iron oxide in terms of Fe_2O_3 (T- Fe_2O_3);
 less than 0.008% of FeO, and
 not more than 0.005% of cerium oxide and not more than 0.03% of manganese oxide,
 wherein the composition has a ratio (FeO ratio) of FeO in terms of Fe_2O_3 to T- Fe_2O_3 of lower than 40%.

[0024] This glass sheet exhibits as optical properties, on a 4.0 mm thickness basis, a solar radiation transmittance of 87.5% or higher, a visible light transmittance of 90.0% or higher, a dominant wavelength of 540 to 580 nm, and an excitation purity of 0.36% or lower, where the visible light transmittance, the dominant wavelength and the excitation purity are measured with the illuminant C.

[0025] Additionally, this glass sheet is free from colouring components other than titanium dioxide, iron oxide, cerium oxide and manganese oxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0026]

5 FIG. 1 is a graph showing a relationship between a fluorescence intensity ratio and a cerium oxide content with respect to each of glass sheets that vary in T- Fe_2O_3 content.
 FIG. 2 is a graph showing spectral transmittance curves obtained before and after performing ultraviolet irradiation at a wavelength of not more than 400 nm with respect to a glass sheet having a low iron content, to which cerium oxide is added (0.10 wt. %) and a glass sheet having a low iron content, to which cerium oxide is not added (0 wt. %).
 10 FIG. 3 is a graph showing a relationship between a transmittance at a wavelength of 1,000 nm and a cerium oxide content with respect to each of glass sheets having a low iron content, where the transmittance is measured before and after ultraviolet irradiation at a wavelength of not more than 400 nm.

EMBODIMENTS OF THE INVENTION

15 **[0027]** Hereinafter, the present invention will be described by way of preferred embodiments. In the following description, a content of each component is expressed in % that represents wt. %. Further, the values of a visible light transmittance, a dominant wavelength and an excitation purity are based on measurements performed on a 4.0 mm thickness basis using the CIE standard illuminant C. Furthermore, the values of a solar radiation transmittance are also based on
 20 measurements performed on the 4.0 mm thickness basis.

[0028] Description is directed first to the glass sheet according to the present invention.

[0029] One preferred embodiment of the glass sheet has, in addition to the above-mentioned optical properties (solar radiation transmittance: 87.5% or higher, visible light transmittance: 90.0% or higher, dominant wavelength: 540 to 580 nm, excitation purity: 0.36% or lower), a composition containing not more than 0.005% of cerium oxide and having a
 25 FeO ratio of 22% or higher, and exhibits an excitation purity of 0.25% or lower. This allows a high transmittance glass sheet that achieves a higher degree of colorlessness to be obtained. Preferably, this high transmittance glass sheet is substantially free from cerium oxide.

[0030] Another embodiment of the glass sheet has, in addition to the above-mentioned optical properties, a composition having a FeO ratio of lower than 22%, and exhibits a solar radiation transmittance of 90.0% or higher and a visible light
 30 transmittance of 90.5% or higher. This allows a high transmittance glass sheet that exhibits high transmittance, particularly in a region ranging from the visible region to the near-infrared region.

[0031] When cerium oxide or the like that acts as an oxidizing agent is added, the transmittance in a region ranging from a longer wavelength side of the visible region to the infrared region is improved, and a high solar radiation transmittance and a high visible light transmittance can be attained. However, the inventors of the present invention have
 35 found that when a glass sheet having a T- Fe_2O_3 content as low as that described above, to which an oxidizing agent is added, is subjected to ultraviolet irradiation, the transmittance in a region ranging from a longer wavelength side of the visible region to the infrared region is lowered. FIG. 2 shows an example of this phenomenon. As typically shown in the figure, when a glass sheet to which cerium oxide is added is subjected to ultraviolet irradiation, particularly, the transmittance in a region ranging from a longer wavelength side of the visible region to the infrared region may be lowered
 40 considerably.

[0032] As shown in FIG. 2, as for a glass sheet to which cerium oxide is not added, by ultraviolet irradiation, the transmittance in a region ranging from a longer wavelength side of the visible region to the near-infrared region is increased, and the transmittance in a region ranging from a shorter wavelength side of the visible region to the ultraviolet
 45 region is lowered slightly. By using this phenomenon, a spectral transmittance property of a glass sheet can be controlled easily by ultraviolet irradiation.

[0033] As confirmed by the inventors of the present invention, for the observation of this phenomenon, preferably, cerium oxide and manganese oxide that act as oxidizing agents are not contained substantially. These compounds, however, may be contained as long as their respective amounts are at impurity levels. As for cerium oxide, for example, as shown in FIG. 3, in order to attain an increase in the transmittance in the near-infrared region (transmittance at a
 50 wavelength of 1,000 nm is shown in FIG. 3) by ultraviolet irradiation, the content of the cerium oxide is limited to not more than 0.005%. Similarly, the content of manganese oxide is not more than 0.03%.

[0034] When a glass sheet having limited contents of components acting as oxidizing agents and a T- Fe_2O_3 content reduced to not more than 0.02% is subjected to ultraviolet irradiation at a wavelength of not more than 400 nm, the transmittance at a wavelength of 1,000 nm can be improved by not less than 0.1%, in some cases, by not less than
 55 0.3%. Although not entirely clarified, conceivably, lowering of a FeO ratio contributes to the improvement in the transmittance in the near-infrared region, which have been confirmed by Examples (Examples 19 to 30) that will be described later. For example, even when a glass sheet has a FeO ratio of 22% or higher, ultraviolet irradiation allows the FeO ratio to be decreased to lower than 22%. In each of the Examples that will be described later, by ultraviolet irradiation, a FeO

ratio could be decreased by at least 3% to 5% or more, to be lower than 22%.

[0035] Here, the variations in the transmittance and the FeO ratio are expressed by differences between values expressed in % obtained before and after variation (a 0.1% increase in transmittance is defined by a +0.1 point difference between transmittance values expressed in %).

[0036] The transmittance of the above-mentioned glass sheet in a region ranging from the visible region to the near-infrared region can be improved by the ultraviolet irradiation. Thus, the glass sheet is suitable particularly for use for a substrate for a solar cell panel, a cover glass plate for a solar cell panel or the like because the glass sheet has an advantage in maintaining power generation efficiency for a long period of time.

[0037] As is apparent from the foregoing description, one aspect of the present invention resides in a method of manufacturing a high transmittance glass sheet. In the method, the above-mentioned composition of the first glass sheet contains cerium oxide and manganese oxide in their limited amounts of not more than 0.005% and not more than 0.03% respectively, and the glass sheet is subjected to ultraviolet irradiation at a wavelength of not more than 400nm. Thus, for example, the transmittance at a wavelength of 1,000 nm can be increased by not less than 0.1%. Further, for example, a FeO ratio of 22% or higher also can be decreased to lower than 22%. There is no particular limit to a light source used for the ultraviolet irradiation, and natural light may be used. However, when subjected to irradiation in advance at the time of shipment using an artificial light source such as an ultraviolet lamp, the glass sheet can be used in a state of having a high transmittance from the beginning.

[0038] The following description is directed to base glass components or the like as common features to the embodiments described above.

[0039] Preferably, the base glass components are 65 to 80% of SiO₂, 0 to 5% of Al₂O₃, 0 to 7% of MgO, 5 to 15% of CaO, 10 to 18% of Na₂O, 0 to 5% of K₂O, 7 to 17% of MgO + CaO (exclusive of 7%), 10 to 20% of Na₂O + K₂O, and 0.05 to 0.3% of SO₃. Further, it is preferable that more than 10% of MgO + CaO and more than 0.1% of SO₃ are contained. Further, it is preferable that more than 0.5% of MgO is contained from the viewpoint of improving meltability and formability. Further, it is preferable that more than 0.5% of Al₂O₃ is contained from the viewpoint of improving water resistance.

[0040] Preferably, the above composition is substantially free from fluorine, boron oxide, barium oxide and strontium oxide. This is because the absence of these components allows the generation of harmful substances to be prevented, and thus deterioration of a melting furnace can be suppressed. Further, the above composition is free from coloring components other than titanium dioxide, iron oxide, cerium oxide and manganese oxide.

[0041] As described above, still another aspect of the present invention resides in use of the high transmittance glass sheet according to the present invention or a method of using the same for any one application selected from the group consisting of an interior glass, a showcase, a display case, a high transmittance window glass, a high transmittance mirror, a glass substrate for a solar cell panel, a cover glass plate for a solar cell panel, a solar water heater, a solar-heat transmittance window glass, and a flat-panel display substrate glass. This allows the high transmittance glass sheet according to the present invention to give considerable effects in terms of high transmittance, colorlessness, a wavelength conversion property and the like.

[0042] Although not particularly limited thereto, preferably, the non-colored high transmittance glass sheet according to the present invention is obtained in such a manner that a batch material for the glass sheet is melted in a top-heating tank-type melting furnace and further is refined. When melting and refining are performed in one tank, the glass sheet can be manufactured at a reduced cost.

[0043] Hereinafter, the composition of the high transmittance glass sheet according to the present invention will be described.

[0044] In glass, iron oxide is present in a form of Fe₂O₃ or FeO. Fe₂O₃ serves to enhance an ultraviolet-absorbing ability, and FeO serves to enhance a heat-absorbing ability. In order to attain substantial colorlessness and high transmittance, the contents of T- Fe₂O₃ and FeO are required to be not more than 0.02% and less than 0.008%, respectively, and a FeO ratio is required to be lower than 40%. When the contents of T- Fe₂O₃ and FeO and the FeO ratio reach and become greater than their respective upper limits, the visible light transmittance becomes too low, and a blue tone of FeO is intensified.

[0045] When the content of T- Fe₂O₃ is less than 0.005%, it is necessary to use high purity materials having low iron contents. This leads to a substantial cost increase. Thus, preferably, T- Fe₂O₃ is contained in an amount of not less than 0.005%.

[0046] When used for a solar cell having a photoelectric conversion layer using amorphous silicon, a glass sheet preferably has a high transmittance at a wavelength in the vicinity of 500 to 600 nm and exhibits moderate solar radiation absorption. In this case, preferably, when the content of T- Fe₂O₃ is in the above-mentioned range, the content of FeO is more than 0.003%, and the FeO ratio is 22% or higher.

[0047] When used for a solar cell having a photoelectric conversion layer using crystalline silicon or the like, preferably, a glass sheet has a high transmittance at a wavelength in the vicinity of 1,000 nm. In this case, preferably, when the content of T- Fe₂O₃ is in the above-mentioned range, the content of FeO is less than 0.004%, and the FeO ratio is lower than 22%.

[0048] Cerium oxide is effective in regulating the content of FeO and a FeO ratio. Particularly, in order to attain a low FeO content and a low FeO ratio required when high transmittance at a wavelength in the vicinity of 1,000 nm is desired, generally, cerium oxide should be added in an amount of less than 0.005%. In this case, however, in some applications, consideration should be given to variations in transmittance caused by ultraviolet radiation as shown in FIG. 2.

[0049] SiO₂ is a main component forming a skeleton of a glass. When the content of SiO₂ is less than 65%, the durability of the glass is decreased, and when the content of SiO₂ is more than 80%, melting of the glass is hindered.

[0050] Al₂O₃ serves to improve the durability and the water resistance of the glass. However, when the content of Al₂O₃ is more than 5%, melting of the glass is hindered. In order to improve the durability and the water resistance, preferably, the content of Al₂O₃ is more than 0.5%. More preferably, the content of Al₂O₃ is in the range of 1.0 to 2.5%.

[0051] Both MgO and CaO serve to improve the durability of the glass and are used to regulate the liquidus temperature and the viscosity of the glass in a forming process. When the content of MgO exceeds 7%, the liquidus temperature is increased excessively. MgO allows a low liquidus temperature to be maintained when contained in a moderate amount. Thus, the content of MgO is preferably more than 0.5%, and more preferably not less than 2%. On the other hand, when the content of CaO is less than 5%, the meltability is degraded. Further, when the content of CaO exceeds 15%, the liquidus temperature is increased. Thus, preferably, the content of CaO is less than 13%. When a total content of MgO and CaO is not more than 7%, the durability of the glass is decreased. Conversely, when the total content exceeds 17%, the liquidus temperature is increased. Thus, preferably, the total content is not more than 15%. In the case where the total content of MgO and CaO is as small as, for example, not more than 10%, it is required that the content of Na₂O be increased so that the degradation of the meltability and an increase in viscosity of a melt are compensated. This leads to a cost increase and a decrease in chemical durability of the glass. Thus, preferably, the total content of MgO and CaO is more than 10%.

[0052] Both Na₂O and K₂O are used as melting accelerators of the glass. When the content of Na₂O is less than 10% or when a total content of Na₂O and K₂O is less than 10%, only a poor effect of accelerating glass melting can be obtained. It is not preferable that the content of Na₂O exceeds 18% or the total content of Na₂O and K₂O exceeds 20% since this results in a decrease in durability of the glass. In applications where water resistance is required particularly, the content of Na₂O is preferably not more than 15%, and more preferably not more than 14.5%. Since a material cost of K₂O is high compared with Na₂O, it is not preferable that the content of K₂O exceeds 5%.

[0053] SO₃ serves to accelerate refining of the glass. When the content of SO₃ is less than 0.05%, a sufficient refining effect cannot be attained by a regular melting method. Thus, preferably, the content of SO₃ is more than 0.1%. Conversely, when the content of SO₃ exceeds 0.3%, SO₂ produced as a result of decomposition of SO₃ remains in the glass in the form of a bubble, and SO₃ that has been dissolved becomes more likely to produce bubbles by reboiling.

[0054] TiO₂ is added in a proper amount for the purpose of enhancing an ultraviolet-absorbing ability or the like as long as the amount is in the range that allows the optical properties that are the intended properties of the present invention not to be impaired. When an excessive amount of TiO₂ is contained, the glass becomes more likely to become yellowish, and the transmittance at a wavelength in the vicinity of 500 to 600 nm is lowered. Thus, preferably, the content of TiO₂ is limited to a low level in the range of less than 0.2%.

[0055] As long as the objects of the present invention can be attained, fluorine, boron oxide, barium oxide, and strontium oxide may be contained. However, these components create adverse impacts such as a cost increase, shortening of a furnace life, release of harmful substances into the air or the like. Thus, preferably, these components are not contained substantially.

[0056] In the case where an oxidizing agent is added, it is preferable to use cerium oxide in an amount in the range defined above in view of the effect of cerium oxide and an ultraviolet-absorbing effect as another particular effect of cerium oxide. However, an oxidizing agent other than cerium oxide, for example manganese oxide, may be added in an amount in the range of not more than 1% in combination with cerium oxide or as a sole oxidizing agent.

[0057] Furthermore, SnO₂ may be added as a reducing agent in an amount in the range of not more than 1%.

EXAMPLE

[0058] Hereinafter, the present invention will be described in detail by way of examples. However, the present invention is not limited to the following Examples.

(Examples 1 to 18)

[0059] Glass batch materials having compositions shown in Tables 1 to 3, in which the respective contents are expressed in terms of oxide and in wt. %, were prepared by using low-iron alumina-containing silica sand, limestone, dolomite, soda ash, salt cake, magnesium oxide, cerium oxide, manganese dioxide, and a carbon-based reducing agent as required. Each batch of these materials was heated in an electric furnace to a temperature of 1,450°C to be melted. After four hours of melting, the batch was poured onto a stainless steel plate and annealed to room temperature, so that

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a glass having a thickness of about 10 mm was obtained. Then, this glass sheet was ground to a thickness of 4.0 mm.

[0060] With respect to each of the glass sheets thus obtained, measurements were performed using the illuminant C for optical properties that are a visible light transmittance, a dominant wavelength, and an excitation purity, and measurements of a solar radiation transmittance also were performed.

[0061] Furthermore, each of the glass sheets was subjected to ultraviolet irradiation at a wavelength of 335 nm for measurements of emission intensity at the respective wavelengths. The respective values of a fluorescence intensity ratio (fluorescence intensity at 395 nm / fluorescence intensity at 600 nm) are also shown in Tables 1 to 3. Further, water resistance was determined according to JIS (Japanese Industrial Standards) R3502-1995 (Section 3.1 "alkali elution test"). The water resistance of each of the glass sheets can be evaluated using an elution amount of alkali (Na_2O ; mg) obtained by this test.

[0062] Tables 1 to 3 show the results of these measurements.

(Table 1)

Example	1	2	3	4	5	6
SiO_2	71.1	70.4	69.8	69.8	68.0	71.6
Al_2O_3	1.8	2.0	2.9	4.8	2.5	0.2
MgO	4.4	2.1	3.9	2.1	5.9	4.8
CaO	9.0	11.2	7.8	8.9	8.1	7.2
Na_2O	12.6	12.9	14.6	13.2	14.3	15.1
K_2O	0.8	1.1	0.7	0.9	0.9	0.9
SO_3	0.23	0.22	0.28	0.22	0.27	0.19
T- Fe_2O_3	0.019	0.019	0.018	0.018	0.016	0.016
TiO_2	0.04	0.03	0.03	0.04	0.03	0.03
Cerium oxide	0	0	0	0	0	0
Manganese oxide	0	0	0	0	0	0
Total	100.0	100.0	100.0	100.0	100.0	100.0
FeO	0.005	0.007	0.006	0.005	0.004	0.006
FeO ratio	26	37	33	28	25	38
Visible light transmittance	91.4	90.8	91.1	91.4	91.5	90.9
Solar radiation transmittance	90.3	89.1	89.8	90.3	90.7	89.5
Dominant wavelength	558	552	553	557	562	552
Excitation purity	0.19	0.18	0.18	0.18	0.19	0.17
Fluorescence intensity ratio	0	0	0	0	0	0
Elution amount of Na_2O	0.59	0.80	0.50	0.15	0.76	1.69

(Table 2)

Example	7	8*	9*	10*	11*	12*
SiO_2	71.7	71.7	71.6	71.6	71.5	71.5
Al_2O_3	1.7	1.7	1.7	1.7	1.7	1.7
MgO	4.2	4.2	4.2	4.2	4.2	4.2
CaO	8.5	8.5	8.5	8.5	8.5	8.5
Na_2O	13.0	13.0	13.0	13.0	13.0	13.0
K_2O	0.7	0.7	0.7	0.7	0.7	0.7

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(continued)

Example	7	8*	9*	10*	11*	12*
SO ₃	0.12	0.12	0.12	0.12	0.12	0.12
T-Fe ₂ O ₃	0.015	0.015	0.015	0.015	0.015	0.015
TiO ₂	0.02	0.02	0.02	0.02	0.02	0.02
Cerium oxide	0	0.04	0.06	0.10	0.14	0.20
Manganese oxide	0	0	0	0	0	0
Total	100.0	100.0	100.0	100.0	100.0	100.0
FeO	0.004	0.003	0.003	0.002	0.002	0.001
FeO ratio	27	20	20	13	13	7
Visible light transmittance	91.2	91.6	91.6	91.7	91.6	91.6
Solar radiation transmittance	90.0	90.7	90.6	91.0	91.0	91.3
Dominant wavelength	554	565	565	570	571	573
Excitation purity	0.19	0.20	0.20	0.20	0.24	0.30
Fluorescence intensity ratio	2	21	31	28	16	11
Elution amount of Na ₂ O	0.58	0.58	0.58	0.58	0.59	0.59
* Reference Examples						

(Table 3)

Example	13*	14*	15*	16*	17*	18*
SiO ₂	71.0	71.7	71.6	72.0	71.1	71.1
Al ₂ O ₃	1.4	1.7	1.7	1.7	1.8	1.5
MgO	4.3	4.0	4.2	4.2	4.4	6.2
CaO	8.6	8.5	8.5	8.5	9.0	8.7
Na ₂ O	13.5	13.0	13.0	12.5	12.6	11.1
K ₂ O	0.7	0.7	0.7	0.7	0.7	1.0
SO ₃	0.22	0.23	0.20	0.21	0.23	0.23
T-Fe ₂ O ₃	0.019	0.019	0.011	0.011	0.013	0.013
TiO ₂	0.03	0.03	0.04	0.04	0.04	0.04
Cerium oxide	0.22	0.10	0.05	0.06	0.10	0.10
Manganese oxide	0	0.06	0	0.08	0	0
Total	100.0	100.0	100.0	100.0	100.0	100.0
FeO	0.001	0.002	0.002	0.001	0.002	0.002
FeO ratio	5	11	18	9	15	15
Visible light transmittance	91.6	91.6	91.7	91.8	91.7	91.7
Solar radiation transmittance	91.2	91.0	91.0	91.3	90.9	90.9
Dominant wavelength	573	570	567	570	568	568
Excitation purity	0.31	0.23	0.20	0.21	0.20	0.20
Fluorescence intensity ratio	9	26	27	27	28	28

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(continued)

Example	13*	14*	15*	16*	17*	18*
Elution amount of Na ₂ O	0.79	0.57	0.52	0.44	0.53	0.44
* Reference Examples						

[0063] In each of Examples 1 to 18, a solar radiation transmittance of 87.5% or higher (further to 89.0% or higher), a visible light transmittance of 90.0% or higher (further to 90.5% or higher), a dominant wavelength of 540 to 580 nm (further to 545 to 575 nm), and an excitation purity of 0.36% or lower (further to 0.33% or lower) are obtained. In each of the Examples 1 to 7, which is free from cerium oxide and exhibits a FeO ratio of 22% or higher, an excitation purity of 0.25% or lower is obtained, thereby attaining a more preferred color tone. In each of the Examples 8 to 18, which contains 0.02 to 0.25% of cerium oxide and exhibits a FeO ratio of lower than 22%, a solar radiation transmittance of 90.0% or higher and a visible light transmittance of 90.5% or higher are obtained, which indicates that a higher transmittance is likely to be attained. In each of the Examples 8 to 18 containing cerium oxide except for the Example 13 having a high content of cerium oxide, a fluorescence intensity ratio of 10% or higher is obtained.

[0064] In each of the Examples 1 to 5 and 7 to 18 containing more than 0.5% of Al₂O₃, a Na₂O elution amount of less than 1.0 mg is obtained, which indicates an excellent water resistance. Each of the Examples 1 to 18 has a composition that is substantially free from fluorine, barium oxide, and strontium oxide. The same applies to Examples and Reference Examples that will be described later.

(Comparative Examples 1 to 4)

[0065] Table 4 shows a composition and optical properties of each of Comparative Examples for the present invention. As in the foregoing description, compositions are expressed in wt. %.

(Table 4)

Comp. Example	1	2	3	4
SiO ₂	72.4	73.07	73.50	70.80
Al ₂ O ₃	1.42	1.80	0.90	1.90
MgO	4.1	0.08	-	3.70
CaO	8.0	10.11	9.00	8.90
SrO	-	0.21	-	-
Na ₂ O	13.1	14.63	15.80	13.50
K ₂ O	0.72	0.01	0.29	0.60
SO ₃	0.23	0.015	0.30	0.25
T- Fe ₂ O ₃	0.10	0.010	0.1	0.09
TiO ₂	0.03	-	0.04	-
Cerium oxide	-	-	-	0.20
ZrO ₂	-	0.28	-	-
Total	100.08	99.935	99.93	99.94
FeO	0.027	-	0.028	-
FeO ratio	30	60	31	-
Sheet thickness (mm)	3.20	5.66	3.85	-
Visible light transmittance	90.1	90.8	89.9*	-
Solar radiation transmittance	85.0	88.5	-	-
Ultraviolet transmittance	60.8	-	-	-
Dominant wavelength	502	490.5	541	-

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(continued)

Comp. Example	1	2	3	4
Excitation purity	0.34	0.27	0.30	-
Water resistance	0.51	0.68	1.14	-
* : The illuminant A was used as a light source.				

[0066] Comparative Example 1 represents a typical soda-lime glass sheet. Comparative Example 2 represents an example disclosed in the above-mentioned JP 7(1995)-29810 B. Comparative Example 3 represents an example disclosed in the above-mentioned JP 8(1996)-40742 A. Comparative Example 4 represents an example disclosed in JP 5(1993)-221683 A.

[0067] In the Comparative Example 1, compared with the glass sheet according to the present invention, the solar radiation transmittance is low, and the visible light transmittance also is not so high. In the Comparative Example 2, the properties other than the dominant wavelength are at equivalent levels to those of the glass sheet according to the present invention. However, the FeO ratio cannot be increased to 60% by using a conventional melting furnace, thereby creating a need to use a particular melting furnace, which is disadvantageous from the viewpoint of cost effectiveness. A presumption based on the visible light transmittance and the excitation purity of the Comparative Example 3 is that there is practically no difference between color tones of the Comparative Example 3 and the conventional soda-lime glass sheet. Further, because of a Na₂O content as high as 15.8%, the water resistance has a value exceeding 1.0, thereby being unsuitable for applications requiring water resistance. Although the optical properties of a glass of the Comparative Example 4 are not specifically shown, based on a spectral transmittance curve shown in the disclosure, the glass has a transmittance at 400 nm of about 83%, while a conventional soda-lime glass shown for comparison has that of about 87%. In the glass, the FeO content is lowered by the addition of cerium oxide, and thus the content of Fe₂O₃ is increased, so that the glass has a low transmittance at a wavelength on a shorter wavelength side of the visible region.

(Examples 19 to 30 / Reference Examples 1 to 6)

[0068] Glass sheets of 4 mm thickness were obtained in the same manner as in the cases of the Examples 1 to 18 except that batch materials were prepared by mixing materials so that compositions shown in Table 5 were obtained.

[0069] Each of the glass sheets thus obtained was subjected to ultraviolet irradiation according to the "light stability test" specified in JIS R3212-1998, Section 3.9 (cited also in JIS R3205-1998). In this test, in an ultraviolet irradiation device having a mercury lamp using vitreous silica or a light source equivalent thereto, each specimen was placed at a distance of 230 mm from the light source. While the temperature in the device is maintained at 45°C ± 5°C, the ultraviolet irradiation was performed with respect to each specimen for 100 hours.

[0070] Furthermore, in the same manner as in the cases of the Examples 1 to 18, measurements were performed for a visible light transmittance, a dominant wavelength, an excitation purity and a solar radiation transmittance as well as transmittance at predetermined wavelengths. These optical properties were measured before and after the ultraviolet irradiation. Further, with respect to each specimen, an amount of FeO was measured before and after the ultraviolet irradiation so that variations in a FeO ratio were determined. The results of the measurements are shown in Tables 5 to 9. As in the foregoing description, compositions are expressed in wt. %.

(Table 5)

Example	19		20		21		22		
SiO ₂	71.1		70.4		69.8		69.8		
Al ₂ O ₃	1.8		2.0		2.9		4.8		
MgO	4.4		2.1		3.9		2.1		
CaO	9.0		11.2		7.8		8.9		
Li ₂ O	0		0		0		0		
Na ₂ O	12.6		12.9		14.6		13.2		
K ₂ O	0.8		1.1		0.7		0.9		
SO ₃	0.2		0.2		0.3		0.2		
T- Fe ₂ O ₃	0.015		0.015		0.015		0.016		
TiO ₂	0.02		0.02		0.02		0.02		
Cerium oxide	0		0		0		0		
Vanadium oxide	0		0		0		0		
Manganese oxide	0		0		0		0		
Total	99.9		99.9		100.0		99.9		
Before/After test	Before	After	Before	After	Before	After	Before	After	
FeO	0.003	0.002	0.003	0.002	0.003	0.002	0.003	0.002	
FeO ratio	17	11	17	14	17	11	16	11	
Visible light transmittance	91.5	91.4	91.5	91.5	91.5	91.4	91.5	91.4	
Solar radiation transmittance	90.7	91.0	90.7	90.8	90.7	91.0	90.7	91.0	
Dominant wavelength	548	571	548	561	548	571	546	571	
Excitation purity	0.11	0.33	0.11	0.20	0.11	0.33	0.11	0.32	
Transmittance	1,000 nm	90.1	91.0	90.1	90.4	90.1	91.0	90.1	90.9
	800 nm	90.2	91.2	90.2	90.6	90.2	91.2	90.2	91.2
	600 nm	91.4	91.4	91.4	91.4	91.4	91.4	91.4	91.4
	400 nm	91.2	90.5	91.2	90.9	91.2	90.5	91.2	90.5

(Table 6)

Example	23		24		25		26		
SiO ₂	68.0		71.6		71.8		71.8		
Al ₂ O ₃	2.5		0.2		1.7		1.7		
MgO	5.9		4.8		4.2		4.2		
CaO	8.1		7.2		8.5		8.5		
Li ₂ O	0		0		0		0		
Na ₂ O	14.3		15.1		13.0		13.0		
K ₂ O	0.9		0.9		0.7		0.7		
SO ₃	0.3		0.2		0.1		0.1		
T- Fe ₂ O ₃	0.019		0.019		0.006		0.008		
TiO ₂	0.02		0.02		0.02		0.02		
Cerium oxide	0		0		0		0		
Vanadium oxide	0		0		0		0		
Manganese oxide	0		0		0		0		
Total	100.0		100.0		100.0		100.0		
Before/After test	Before	After	Before	After	Before	After	Before	After	
FeO	0.003	0.002	0.003	0.002	0.002	0.001	0.002	0.001	
FeO ratio	14	9	14	9	29	19	24	15	
Visible light transmittance	91.5	91.4	91.5	91.4	91.6	91.5	91.6	91.4	
Solar radiation transmittance	90.5	90.8	90.4	90.7	91.0	91.3	91.0	91.2	
Dominant wavelength	541	570	540	570	564	572	562	572	
Excitation purity	0.11	0.30	0.11	0.29	0.10	0.36	0.11	0.36	
Transmittance	1,000 nm	89.8	90.6	89.7	90.5	90.8	91.4	90.6	91.4
	800 nm	90.0	91.0	90.0	90.9	90.6	91.4	90.5	91.4
	600 nm	91.4	91.4	91.3	91.3	91.5	91.5	91.5	91.5
	400 nm	91.1	90.5	91.1	90.5	91.2	90.5	91.2	90.5

(Table 7)

Example	27		28		29		30		
SiO ₂	71.8		71.8		72.4		71.8		
Al ₂ O ₃	1.7		2.2		1.4		1.7		
MgO	4.2		4.2		4.1		4.2		
CaO	8.5		8.5		8.0		8.5		
Li ₂ O	0		2.0		0		0		
Na ₂ O	13.0		105		13.1		13.0		
K ₂ O	0.7		0.7		0.7		0.7		
SO ₃	0.1		0.1		0.2		0.1		
T- Fe ₂ O ₃	0.010		0.012		0.016		0.018		
TiO ₂	0.02		0.02		0.02		0.02		
Cerium oxide	0		0		0		0		
Vanadium oxide	0		0		0		0		
Manganese oxide	0		0		0		0		
Total	100.0		100.0		100.0		100.0		
Before/After test	Before	After	Before	After	Before	After	Before	After	
FeO	0.002	0.001	0.002	0.001	0.003	0.002	0.003	0.002	
FeO ratio	20	13	18	12	16	11	16	11	
Visible light transmittance	91.6	91.4	91.6	91.4	91.5	91.4	91.5	91.4	
Solar radiation transmittance	90.9	91.2	90.8	91.1	90.7	91.0	90.6	90.9	
Dominant wavelength	559	572	556	572	546	571	543	570	
Excitation purity	0.11	0.35	0.11	0.35	0.11	0.32	0.11	0.31	
Transmittance	1,000 nm	90.5	91.3	90.4	91.2	90.1	90.9	89.9	90.7
	800 nm	90.5	91.3	90.4	91.3	90.2	91.2	90.1	91.0
	600 nm	91.5	91.5	91.5	91.5	91.4	91.4	91.4	91.4
	400 nm	91.2	90.5	91.2	90.5	91.2	90.5	91.1	90.5

(Table 8)

Ref. Example	1		2		3		
SiO ₂	71.7		71.7		71.7		
Al ₂ O ₃	1.7		1.7		1.7		
MgO	4.2		4.2		4.2		
CaO	8.5		8.5		8.5		
Li ₂ O	0		0		0		
Na ₂ O	13.0		13.0		13.0		
K ₂ O	0.7		0.7		0.7		
SO ₃	0.1		0.1		0.1		
T- Fe ₂ O ₃	0.017		0.018		0.020		
TiO ₂	0.02		0.02		0.02		
Cerium oxide	0.10		0.10		0.10		
Vanadium oxide	0		0		0		
Manganese oxide	0		0		0		
Total	100.0		100.0		100.0		
Before/After test	Before	After	Before	After	Before	After	
FeO	0.001	0.006	0.001	0.007	0.001	0.002	
FeO ratio	3	37	4	36	5	8	
Visible light transmittance	91.7	91.1	91.7	91.1	91.5	90.9	
Solar radiation transmittance	91.1	88.3	91.0	88.3	90.7	88.9	
Dominant wavelength	569	569	569	569	570	572	
Excitation purity	0.20	0.40	0.22	0.42	0.33	0.30	
Transmittance	1,000 nm	91.7	87.4	91.6	87.3	91.1	88.3
	800 nm	91.9	89.7	91.8	89.9	91.5	90.3
	600 nm	91.7	91.1	91.7	91.2	91.5	91.0
	400 nm	90.9	85.6	90.8	85.2	90.6	88.1

(Table 9)

Ref. Example	4		5		6		
SiO ₂	71.6		71.7		71.6		
Al ₂ O ₃	1.7		1.7		1.7		
MgO	4.2		4.2		4.2		
CaO	8.5		8.5		8.5		
Li ₂ O	0		0		0		
Na ₂ O	13.0		13.0		13.0		
K ₂ O	0.7		0.7		0.7		
SO ₃	0.1		0.1		0.1		
T- Fe ₂ O ₃	0.020		0.016		0.020		
TiO ₂	0.02		0.02		0.02		
Cerium oxide	0.10		0.10		0.10		
Vanadium oxide	0		0.05		0.05		
Manganese oxide	0		0.05		0.05		
Total	100		100		100		
Before/After test	Before	After	Before	After	Before	After	
FeO	0.001	0.006	0.003	0.007	0.001	0.005	
FeO ratio	4	28	17	42	4	24	
Visible light transmittance	91.5	90.7	91.1	83.7	91.0	90.4	
Solar radiation transmittance	90.9	88.4	89.6	86.0	90.7	88.9	
Dominant wavelength	570	573	564	547	576	578	
Excitation purity	0.35	0.41	0.58	1.77	0.46	0.27	
Transmittance	1,000 nm	91.6	87.9	89.7	87.2	91.5	88.6
	800 nm	91.6	90.4	90.8	89.0	91.7	90.3
	600 nm	91.6	90.8	90.8	84.8	91.2	90.6
	400 nm	90.7	86.1	86.8	84.3	90.4	88.1

[0071] In each of Examples 19 to 30, which has a T- Fe₂O₃ content of not more than 0.02% and is free from a component acting as an oxidizing agent such as cerium oxide, the solar radiation transmittance is increased to 90.0% or higher

(further to 90.5% or higher) by the ultraviolet irradiation. Further, the transmittance at a wavelength of 1,000 nm is increased by not less than 0.3%. The visible light transmittance, although somewhat lowered in some cases, is maintained at a level of 90.5% or higher. In contrast to this, in each of Reference Examples 1 to 6, after performing ultraviolet irradiation under the conditions described above, the transmittance at a wavelength of 1,000 nm is decreased to lower than 90.0%.

[0072] The invention may be embodied in other forms without departing from the essential characteristics thereof. The embodiments disclosed in this application are to be considered in all respects as illustrative and not limiting. The scope of the invention is indicated by the appended claims rather than by the foregoing description, and all changes which come within the meaning and range of equivalency of the claims are intended to be embraced therein.

Claims

1. A high transmittance glass sheet formed of a composition comprising as base glass components, expressed in wt. %:

65 to 80% of SiO₂,
 0 to 5% of Al₂O₃,
 0 to 7% of MgO,
 5 to 15% of CaO,
 10 to 18% of Na₂O,
 0 to 5% of K₂O,
 7 to 17% of MgO + CaO (exclusive of 7%),
 10 to 20% of Na₂O + K₂O, and
 0.05 to 0.3% of SO₃; and

as colouring components, expressed in wt. %:

more than 0 to less than 0.2% TiO₂;
 not less than 0.005% to less than 0.02% of total iron oxide in terms of Fe₂O₃ (T- Fe₂O₃);
 less than 0.008% of FeO; and
 not more than 0.005% of cerium oxide and not more than 0.03% of manganese oxide,
 wherein the composition has a ratio (FeO ratio) of FeO in terms of Fe₂O₃ to T- Fe₂O₃ of lower than 40%.
 wherein the glass sheet is free from coloring components other than titanium dioxide, iron oxide, cerium oxide and manganese oxide; and
 the glass sheet has, on the 4.0 mm thickness basis, a solar radiation transmittance of 87.5% or higher, a visible light transmittance of 90.0% or higher, a dominant wavelength of 540 to 580 nm, and an excitation purity of 0.36% or lower, where the visible light transmittance, the dominant wavelength and the excitation purity are measured with illuminant C.

2. The high transmittance glass sheet according to claim 1, wherein the glass sheet has a FeO ratio of 22% or higher, and has an excitation purity of 0.25% or lower.

3. The high transmittance glass sheet according to claim 2, wherein the glass sheet is obtained by being irradiated with ultraviolet rays at a wavelength of not more than 400 nm; and the glass sheet has, on a 4.0 mm thickness basis, a light beam transmittance at a wavelength of 1,000 nm that is not less than 0.1% higher than that of the glass sheet before being irradiated with the ultraviolet rays.

4. The high transmittance glass sheet according to claim 2, wherein the glass sheet is obtained by being irradiated with ultraviolet rays at a wavelength of not more than 400 nm; and the glass sheet has a FeO ratio of lower than 22%.

5. The high transmittance glass sheet according to claim 2, wherein the glass sheet is obtained by being subjected to ultraviolet irradiation according to a light stability test specified in Japanese Industrial Standards, R3212; and the glass sheet has, on a 4.0 mm thickness basis, a light beam transmittance at a wavelength of 1,000 nm that is not less than 0.3% higher than that of the glass sheet before being subjected to the ultraviolet irradiation, a solar

radiation transmittance of 90.0% or higher, and a visible light transmittance of 90.5% or higher.

- 5
6. The high transmittance glass sheet according to claim 1, wherein the glass sheet contains more than 10% of MgO + CaO and more than 0.1% of SO₃.
7. The high transmittance glass sheet according to claim 1, wherein the glass sheet contains more than 0.5% of MgO.
- 10
8. The high transmittance glass sheet according to claim 1, wherein the glass sheet contains more than 0.5% of Al₂O₃.
9. The high transmittance glass sheet according to claim 1, wherein the glass sheet is substantially free from fluorine, boron oxide, barium oxide and strontium oxide.
- 15
10. Use of a high transmittance glass sheet, the glass sheet being a glass sheet as claimed in claim 1, in any one application selected from the group consisting of an interior glass, a showcase, a display case, a high transmittance window glass, a high transmittance mirror, a glass substrate for a solar cell panel, a cover glass plate for a solar cell panel, a solar water heater, a solar-heat transmittance window glass, and a flat-panel display substrate glass.
- 20
11. A method of manufacturing a high transmittance glass sheet, the glass sheet being a glass sheet as claimed in claim 1, wherein a batch material for the glass sheet is melted and refined in a top-heating tank-type melting furnace.
- 25
12. A method of manufacturing a high transmittance glass sheet, the glass sheet being a glass sheet as claimed in claim 2, wherein the glass sheet that has been formed is subjected to ultraviolet irradiation at a wavelength of not more than 400 nm.

Patentansprüche

- 30
1. Glasscheibe mit hoher Durchlässigkeit, die aus einer Zusammensetzung gebildet ist, die als Glasgrundkomponenten, ausgedrückt in Gew.-%, umfasst:

35

65 bis 80% SiO₂,
 0 bis 5% Al₂O₃,
 0 bis 7% MgO,
 5 bis 15% CaO,
 10 bis 18% Na₂O,
 0 bis 5% K₂O,
 7 bis 17% MgO + CaO (ausgenommen 7%),
 40

10 bis 20% Na₂O + K₂O, und
 0,05 bis 0,3% SO₃; und

als Einfärbungskomponenten, ausgedrückt in Gew.-%:

45

mehr als 0 bis weniger als 0,2% TiO₂;
 nicht weniger als 0,005% bis weniger als 0,02% Gesamteisenoxid, ausgedrückt als Fe₂O₃ (T - Fe₂O₃);
 weniger als 0,008% FeO; und
 nicht mehr als 0,005% Ceroxid und nicht mehr als 0,03% Manganoxid,
 wobei die Zusammensetzung ein Verhältnis (FeO-Verhältnis) von FeO, ausgedrückt als Fe₂O₃ zu T - Fe₂O₃,
 50

von niedriger als 40% aufweist;
 wobei die Glasscheibe frei von anderen Einfärbungskomponenten als Titandioxid, Eisenoxid, Ceroxid und Manganoxid ist; und
 die Glasscheibe auf der 4,0 mm-Dickenbasis eine Sonnenstrahlungsdurchlässigkeit von 87,5% oder höher,
 eine Durchlässigkeit von sichtbarem Licht von 90,0% oder höher, eine Hauptwellenlänge von 540 bis 580 nm,
 55

und eine Anregungsreinheit von 0,36% oder niedriger aufweist, wobei die Durchlässigkeit von sichtbarem Licht, die Hauptwellenlänge und die Anregungsreinheit mit Illuminant C gemessen sind.

2. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 1, bei der die Glasscheibe ein FeO-Verhältnis von 22%

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oder höher aufweist und eine Anregungsreinheit von 0,25% oder niedriger aufweist.

- 5 3. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 2, bei der die Glasscheibe gewonnen wird, indem sie mit ultravioletten Strahlen auf einer Wellenlänge von nicht mehr als 400 nm bestrahlt wird; und
die Glasscheibe auf einer 4,0mm-Dickenbasis eine Lichtstrahldurchlässigkeit auf einer Wellenlänge von 1000 nm aufweist, die nicht weniger als 0,1% höher als die der Glasscheibe, bevor sie mit den ultravioletten Strahlen bestrahlt wird, ist.
- 10 4. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 2, bei der die Glasscheibe gewonnen wird, indem sie mit ultravioletten Strahlen auf einer Wellenlänge von nicht mehr als 400 nm bestrahlt wird; und
die Glasscheibe ein FeO-Verhältnis von niedriger als 22% aufweist.
- 15 5. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 2, bei der die Glasscheibe gewonnen wird, indem sie Ultraviolettbestrahlung gemäß einem Lichtstabilitätstest, der in den japanischen Industriestandards, R3212, spezifiziert ist, ausgesetzt wird; und
die Glasscheibe auf einer 4,0 mm-Dickenbasis eine Lichtstrahldurchlässigkeit auf einer Wellenlänge von 1000 nm, die nicht weniger als 0,3% höher als die der Glasscheibe, bevor sie der Ultraviolettbestrahlung ausgesetzt wird, ist, eine Sonnenstrahlungsdurchlässigkeit von 90,0% oder höher, und eine Durchlässigkeit von sichtbarem Licht von
20 90,5% oder höher aufweist.
- 25 6. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 1, bei der die Glasscheibe mehr als 10% MgO + CaO und mehr als 0,1% SO₃ aufweist.
7. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 1, bei der die Glasscheibe mehr als 0,5% MgO enthält.
8. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 1, bei der die Glasscheibe mehr als 0,5% Al₂O₃ enthält.
- 30 9. Glasscheibe mit hoher Durchlässigkeit gemäß Anspruch 1, bei der die Glasscheibe im Wesentlichen frei von Fluor, Boroxid, Bariumoxid und Strontiumoxid ist.
- 35 10. Verwendung einer Glasscheibe mit hoher Durchlässigkeit, wobei die Glasscheibe eine Glasscheibe gemäß Anspruch 1 ist, in einer Anwendung ausgewählt aus der Gruppe bestehend aus einem Innenraumglas, einer Auslage, einer Vitrine, einem Fensterglas mit hoher Durchlässigkeit, einem Spiegel mit hoher Durchlässigkeit, einem Glassubstrat für ein Sonnenzellenpaneel, einer Abdeckglasplatte für eine Sonnenzellenpaneel, einem Sonnen-Wasserheizgerät, einem für Sonnenwärme durchlässigen Fensterglas und einem Flachbildschirmsubstratglas.
- 40 11. Verfahren zum Herstellen einer Glasscheibe mit hoher Durchlässigkeit, wobei die Glasscheibe eine Glasscheibe gemäß Anspruch 1 ist, wobei ein Batchmaterial für die Glasscheibe in einem von oben beheizenden tankartigen Schmelzofen geschmolzen und verfeinert wird.
- 45 12. Verfahren zum Herstellen einer Glasscheibe mit hoher Durchlässigkeit, wobei die Glasscheibe eine Glasscheibe gemäß Anspruch 2 ist, wobei die Glasscheibe, die gebildet worden ist, einer Ultraviolettbestrahlung auf einer Wellenlänge von nicht mehr als 400 nm ausgesetzt wird.

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Revendications

- 55 1. Plaque de verre à haute transmission formée d'une composition comprenant, comme composants de verre de base, les suivants exprimés en % en poids :
65 à 80 % de SiO₂,
0 à 5 % d'Al₂O₃,
0 à 7 % de MgO,

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5 à 15 % de CaO,
10 à 18 % de Na₂O,
0 à 5 % de K₂O,
7 à 17 % de MgO+CaO (à l'exclusion de 7 %),
10 à 20 % de Na₂O+K₂O et
0,05 à 0,3 % de SO₃ ; et,

comme composants colorants, les suivants exprimés en % en poids :

plus de 0 à moins de 0,2 % de TiO₂ ;
pas plus de 0,005 % à moins de 0,02 % d'oxyde de fer total en termes de Fe₂O₃(T-Fe₂O₃) ;
moins de 0,008 % de FeO ; et
pas plus de 0,005 % d'oxyde de cérium et pas plus de 0,03 % d'oxyde de manganèse,

dans laquelle la composition a un rapport (rapport FeO) de FeO en termes de Fe₂O₃ à T-Fe₂O₃ inférieur à 40 % ;
dans laquelle la plaque de verre est exempte de composants colorants autres que le dioxyde de titane, l'oxyde de fer, l'oxyde de cérium et l'oxyde de manganèse ; et

la plaque de verre a, sur la base d'une épaisseur de 4,0 mm, une transmission du rayonnement solaire de 87,5 % ou plus, une transmission de la lumière visible de 90,0 % ou plus, une longueur d'onde dominante de 540 à 580 nm et une pureté d'excitation de 0,36 % ou moins, où la transmission de la lumière visible, la longueur d'onde dominante et la pureté d'excitation sont mesurées avec l'illuminant C.

2. Plaque de verre à haute transmission selon la revendication 1,
dans laquelle la plaque de verre a un rapport FeO de 22 % ou plus et a une pureté d'excitation de 0,25 % ou moins.

3. Plaque de verre à haute transmission selon la revendication 2,
dans laquelle la plaque de verre est obtenue par irradiation avec des rayons ultraviolets à une longueur d'onde de pas plus de 400 nm ; et
la plaque de verre a, sur la base d'une épaisseur de 4,0 mm, une transmission de faisceau lumineux à une longueur d'onde de 1000 nm qui est supérieure de pas moins de 0,1 % à celle de la plaque de verre avant irradiation avec les rayons ultraviolets.

4. Plaque de verre à haute transmission selon la revendication 2,
dans laquelle la plaque de verre est obtenue par irradiation avec des rayons ultraviolets à une longueur d'onde de pas plus de 400 nm ; et
la plaque de verre a un rapport FeO inférieure à 22 %.

5. Plaque de verre à haute transmission selon la revendication 2,
dans laquelle la plaque de verre est obtenue par irradiation avec des rayons ultraviolets selon un test de stabilité à la lumière spécifié dans les Japanese Industrial Standards, R3212 ; et
la plaque de verre a, sur la base d'une épaisseur de 4,0 mm, une transmission de faisceau lumineux à une longueur d'onde de 1000 nm qui est supérieur de pas moins de 0,3 % à celle de la vitre de verre avant soumission au rayonnement ultraviolet, une transmission du rayonnement solaire de 90,0 % ou plus et une transmission de la lumière visible de 90,5 % ou plus.

6. Plaque de verre à haute transmission selon la revendication 1,
dans laquelle la plaque de verre contient plus de 10 % de MgO+CaO et plus de 0,1 % de SO₃.

7. Plaque de verre à haute transmission selon la revendication 1,
dans laquelle la plaque de verre contient plus de 0,5 % de MgO.

8. Plaque de verre à haute transmission selon la revendication 1,
dans laquelle la plaque de verre contient plus de 0,5 % d'Al₂O₃.

9. Plaque de verre à haute transmission selon la revendication 1,
dans laquelle la plaque de verre est sensiblement exempte de fluor, d'oxyde de bore, d'oxyde de baryum et d'oxyde de strontium.

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10. Utilisation d'une plaque de verre à haute transmission, la plaque de verre étant une plaque de verre selon la revendication 1, dans une application quelconque choisie dans le groupe constitué d'une vitre interne, d'une vitrine, d'une armoire d'affichage, d'une vitre de fenêtre à haute transmission, d'un miroir à haute transmission, d'un substrat de verre pour panneau solaire, d'une plaque de verre couvrante pour panneau solaire, d'un dispositif de chauffage d'eau solaire, d'une vitre de fenêtre à transmission de chaleur élevée et d'un verre de substrat d'affichage à panneau plat.
 11. Procédé de fabrication d'une plaque de verre à haute transmission, la plaque de verre étant une plaque de verre selon la revendication 1, dans lequel un matériau de charge pour la plaque de verre est fondu et raffiné dans un four de fusion du type à réservoir chauffé par le haut.
 12. Procédé de fabrication d'une plaque de verre à haute transmission, la plaque de verre étant une plaque de verre selon la revendication 2, dans lequel la plaque de verre qui a été formée est soumise à un rayonnement ultraviolet à une longueur d'onde de pas plus de 400 nm.

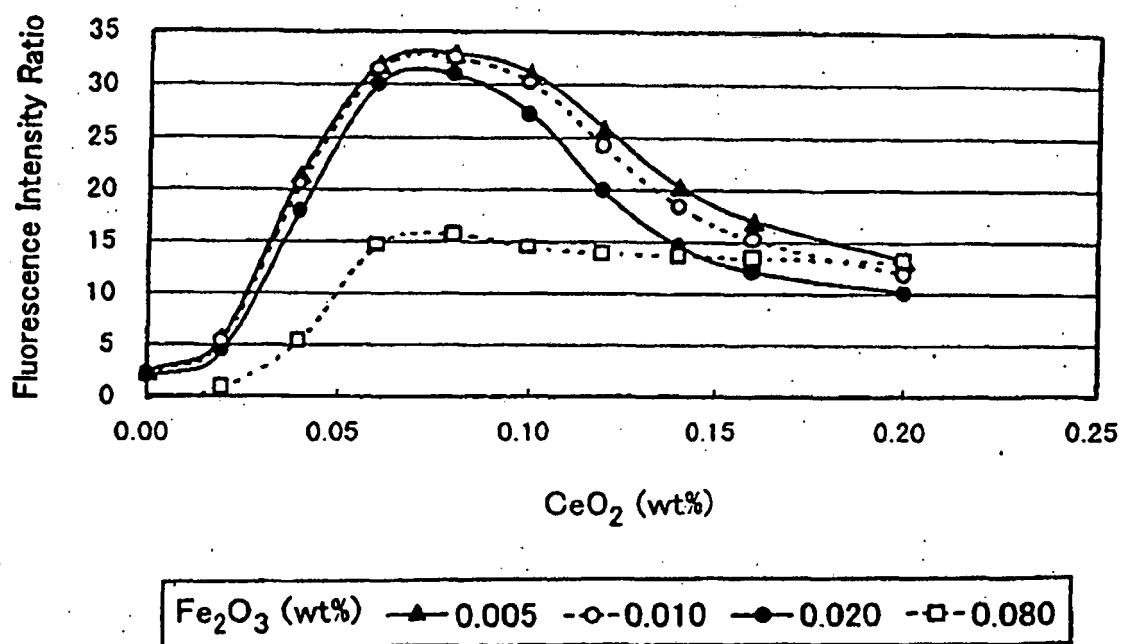


FIG. 1

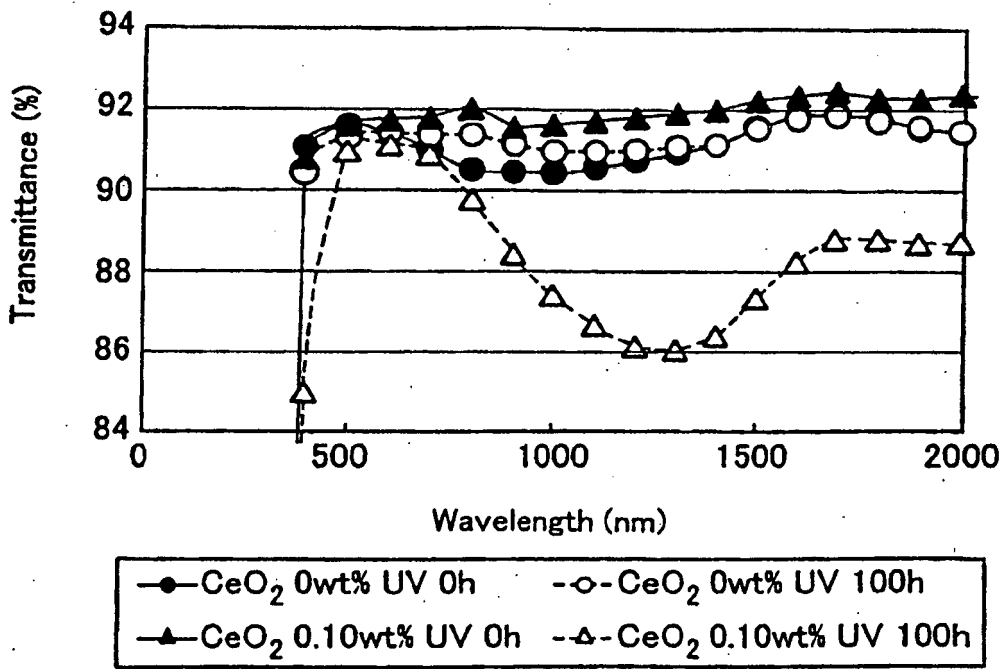


FIG. 2

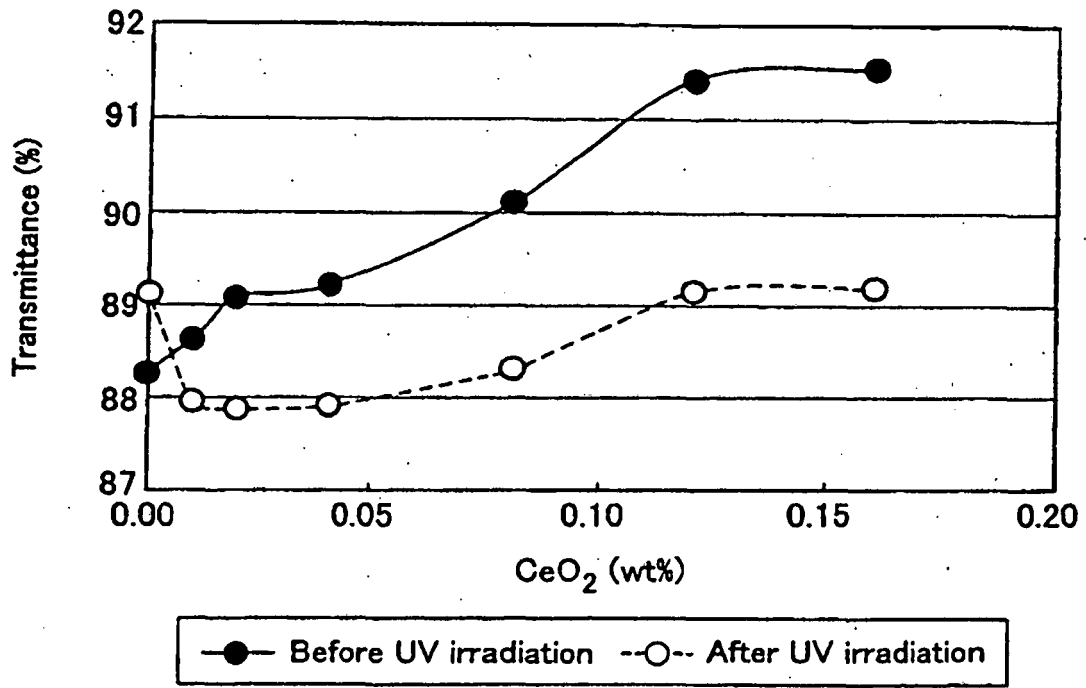


FIG. 3

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 7029810 B [0003] [0010] [0066]
- JP 8000715 B [0005] [0012]
- JP 5221683 A [0007] [0013] [0066]
- JP 8040742 A [0009] [0017] [0066]
- DE 29819347 [0021]