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PATENTS ACT 1990

PATENT REQUEST : STANDARD PATENT

I/We being the person(s) identified below as the Applicant(s), request the grant of a patent to the person(s) identified below as the Nominated Person(s), for an invention described in the accompanying standard complete specification.

Full application details follow:

[71/70] Applicant(s)/Nominated Person(s):

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of

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[54] Invention Title:

Glass having low solar radiation and ultaviolet ray transmittance

[72] Name(s) of actual inventor(s):

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Basic Convention Application(s) Details:

[31] Application Number	[33] Country	Code	[32] Date of Application
262866/1994	Japan	JP	26 October 1994

DATED this TWENTY FOURTH day of OCTOBER 1995

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a member of the firm of DAVIES COLLISON CAVE for and on behalf of the applicant(s)

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NOTICE OF ENTITLEMENT

We, **Asahi Glass Company Ltd.**, the applicant/Nominated Person named in the accompanying Patent Request state the following:-

The Nominated Person is entitled to the grant of the patent because the Nominated Person would, on the grant of a patent for the invention to the inventors, be entitled to have the patent assigned to the Nominated Person.

The Nominated Person is entitled to claim priority from the basic application listed on the patent request because the Nominated Person made the basic application.

DATED this TWENTY FOURTH day of OCTOBER 1995

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a member of the firm of
DAVIES COLLISON CAVE
for and on behalf of the
applicant(s)

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GLASS HAVING LOW SOLAR RADIATION AND ULTRAVIOLET RAY TRANSMITTANCE

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(56) Prior Art Documents
JP 4-310539
US 5385872
US 5362689

(57) Claim

1. A glass having a low solar radiation and ultraviolet ray transmittance and having a dominant wavelength of from 500 to 540 nm for transmittance, which comprises a soda lime-silica type glass containing from 0.52 to 0.64 wt% of total iron calculated as Fe_2O_3, from 0.2 to 0.6 wt% of TiO_2 and from 0.9 to 2.0 wt% of total cerium calculated as CeO_2, wherein the weight of FeO calculated as Fe_2O_3 is from 28 to 38% of the weight of the total iron calculated as Fe_2O_3, the visible light transmittance by light source A is at least 70%, the ultraviolet ray transmittance is at most 15%, and the transmittance of light having a wavelength of 370 nm is at most 30%.

Our Ref.: AA-778 (F95-4)

GLASS HAVING LOW SOLAR RADIATION AND ULTRAVIOLET RAY TRANSMITTANCE

The present invention relates to glass having low transmittance of solar radiation and ultraviolet ray.

As glass for vehicles having reduced solar radiation transmittance (see JIS R3106) and ultraviolet ray transmittance (see ISO 9050), US Patent 4,792,536 discloses soda lime-silica type glass wherein the weight of FeO calculated as Fe_2O_3 is made at least 45% of the weight of the total iron calculated as Fe_2O_3. This glass has a bluish color.

With this glass, Glauber's salt used as a refining agent does not provide a refining function, since the weight of FeO calculated as Fe_2O_3 is at least 45% of the weight of the total iron calculated as Fe_2O_3. Accordingly, molten glass is required to be maintained under reduced pressure for fining, which makes the melting step of glass cumbersome.

Further, soda lime-silica type glass containing at least 0.51 wt% of Fe_2O_3, is known. This glass has a

greenish color.

As such glass, for example, the following glass is disclosed in US Patent 5,077,133. Namely, it has a thickness of 3 mm and contains from 0.68 to 0.92 wt% of total iron, from 0.5 to 1.2 wt% of CeO_2 and from 0.02 to 0.85 wt% of TiO_2, wherein the amount of bivalent iron in the total iron is from 23 to 29 wt%. Another one has a thickness of 4 mm and contains from 0.61 to 0.86 wt% of total iron, from 0.3 to 0.75 wt% of CeO_2 and from 0.02 to 0.45 wt% of TiO_2, wherein the amount of bivalent iron in the total iron is from 23 to 29 wt%.

Japanese Unexamined Patent Publication No. 56466/1994 discloses glass having low solar radiation and ultraviolet ray transmittance, which consists essentially of a soda lime-silica type matrix glass containing from 0.53 to 0.70 wt% of total iron calculated as Fe_2O_3, from 0.2 to 0.4 wt% of TiO_2 and from 0.4 to 0.8 wt% of total cerium calculated as CeO_2, wherein the weight of FeO calculated as Fe_2O_3 is from 30 to 40% of the weight of the total iron calculated as Fe_2O_3.

In recent years, there has been an increasing demand for glass having the ultraviolet ray absorption further improved, particularly for automotive use. The present invention is to satisfy such a demand.

We have now found a glass having a visible light transmittance of at least 70% and low solar radiation transmittance and having

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substantially reduce ultraviolet ray transmittance, particularly transmittance at a wavelength of 370 nm.

According to the present invention there is provided a glass having a low solar radiation and ultraviolet ray transmittance and having a dominant wavelength of from 500 to 540 nm for transmittance, which comprises a soda lime-silica type glass containing from 0.52 to 0.64 wt% of total iron calculated as Fe_2O_3, from 0.2 to 0.6 wt% of TiO_2 and from 0.9 to 2.0 wt% of total cerium calculated as CeO_2, wherein the weight of FeO calculated as Fe_2O_3 is from 28 to 38% of the weight of the total iron calculated as Fe_2O_3, the visible light transmittance by light source A is at least 70%, the ultraviolet ray transmittance is at most 15%, and the transmittance of light having a wavelength of 370 nm is at most 30%.

It will be understood that the term "the visible light transmittance by light source A" it is meant the visible light transmittance Y calculated according to JIS Z8722 by the following formula:

$$Y = K \sum_{380\ nm}^{780\ nm} S(\lambda)\, \bar{y}(\lambda)\, \tau(\lambda)$$

λ is wavelength (nm)

$S(\lambda)\, \bar{y}(\lambda)$ according to Table 2 extracted from JIS Z8722

$\tau(\lambda)$ is spectral transmittance

$$K = 100 / \sum_{380\ nm}^{780\ nm} S(\lambda)\, \bar{y}(\lambda)$$

where "light source A" is "CIE standard light source A" defined in accordance with JIS Z8720.

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Throughout this specification and the claims which follow, unless the context requires otherwise, the word "comprise", and variations such as "comprises" and "comprising", will be understood to imply the inclusion of a stated integer or step or group of integers or steps but not the exclusion of any other integer or step or group of integers or steps.

If the content of the total iron calculated as Fe_2O_3 is small, the solar radiation transmittance and the ultraviolet ray transmittance tend to be too high, and if it is large, the visible light transmittance tends to be too small. The content of the total iron is preferably at most 0.64 wt%, more preferably at most 0.63 wt%. If the amount of bivalent iron in this total iron is small, the solar radiation transmittance tends to be too high, and if it is large, the melting step of glass tends to be cumbersome, and the glass tends to have a bluish color.

If the CeO_2 content is too large, the costs for the raw material will be high, and it will require a long time to change the composition at the time of producing glass, whereby the productivity will be low. Further, the glass tends to have a yellowish color.

If the TiO_2 content is too small, the ultraviolet ray transmittance tends to be too high, and if it is large,

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the visible light transmittance tends to be too small, and the glass tends to have a yellowish color.

To keep the ultraviolet ray transmittance at a low level, in the second embodiment of the present invention, $CeO_2 + TiO_2$ is preferably from 1.2 to 2.3 wt%.

CoO is not an essential component. However, by incorporating it in a very small amount, the color of glass which tends to be yellowish by CeO_2 and TiO_2, can be adjusted to a green color. It is preferably contained in an amount of at least 0.0002 wt%.

If its content is too large, the visible light transmittance will be too small.

Among various components, the contents of the total iron and CeO_2 are preferably adjusted as follows depending upon the thickness of the glass. Namely, when the thickness is from 1.7 to 4.3 mm, the content of the total iron calculated as Fe_2O_3 is preferably from 0.59 to 0.64 wt%, and at the same time, the content of CeO_2 is preferably from 1.2 to 2.0 wt%. Further, when the thickness is from 1.7 to 4.4 mm, the content of the total iron calculated as Fe_2O_3 is particularly from 0.60 to 0.64 wt%, the content of TiO_2 is particularly from 0.3 to 0.5 wt%, the content of the total cerium calculated as CeO_2 is particularly from 1.4 to 1.7 wt%, and the weight of FeO calculated as Fe_2O_3 is from 30 to 35% of the weight of the total iron calculated as Fe_2O_3. Likewise, when the thickness is from 4.4 to 5.5 mm, the content of

the total iron calculated as Fe_2O_3 is preferably from 0.52 to 0.63 wt%, and at the same time, the content of CeO_2 is preferably from 0.9 to 1.2 wt%. Further, when the thickness is from 4.4 to 7.0 mm, the content of the total iron calculated as Fe_2O_3 is particularly from 0.57 to 0.62 wt%, the content of TiO_2 is particularly from 0.2 to 0.4 wt%, the content of the total cerium calculated as CeO_2 is particularly from 0.9 to 1.4 wt%, and the weight of FeO calculated as Fe_2O_3 is from 30 to 35% of the weight of the total iron calculated as Fe_2O_3.

The soda lime-silica type glass can be commonly used for vehicles or architectural use. Thus, one of preferred glass compositions of the present invention comprises:

SiO_2	68 - 74 wt%
Al_2O_3	0.5 - 3 wt%
MgO	3 - 6 wt%
CaO	6 - 10 wt%
$Na_2O + K_2O$	10 - 16 wt%
SO_3	0.05 - 1 wt%
Total iron calculated as Fe_2O_3	0.52 - 0.67 wt%
Fe_2O_3	0.35 - 0.50 wt%
FeO	0.16 - 0.24 wt%
TiO_2	0.2 - 0.6 wt%
Total cerium calculated as CeO_2	0.9 - 2 wt%

If the SiO_2 content is small, the weathering resistance tends to be low, and if it is large,

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devitrification is likely to result. If the Al_2O_3 content is small, the water resistance tends to be low, and if it is large, the meltability tends to be low.

Na_2O and K_2O are components which serve to promote melting of raw materials. If their total amount is small, such an effect tends to be small, and if it is large, the weathering resistance tends to be poor.

CaO and MgO are components which serve to promote meltability of the raw materials and improve the weathering resistance. If their content is small, such effects tend to be small, and if it is large, devitrification is likely to occur.

If the content of the SO_3 is small, the refining effect tends to be low.

Also in the present invention, the specific gravity of the glass is adjusted preferably to a level of from 2.49 to 2.53, more preferably from 2.51 to 2.52, in conformity with usual soda lime-silica type glass, with a view to improving the efficiency for the change of the composition.

The specific gravity can be adjusted in the same manner as in the first embodiment by controlling the composition of the matrix glass. Specifically, the weight ratio of $SiO_2/(MgO + CaO)$ is adjusted to a level of from 5.0 to 7.0, preferably from 5.4 to 6.6, more preferably from 6.0 to 6.6, most preferably from 6.2 to 6.6.

The glass of the present invention has a dominant wavelength of from 500 to 540 nm, particularly from 515 to 535 nm, for transmittance, and is usually employed in a thickness of from 1.7 to 7 mm. It is characterized by a solar radiation transmittance of from 45 to 52%, a visible light transmittance (by light source A) of at least 70%, an ultraviolet ray transmittance of not higher than 15%, particularly not higher than 10%, a transmittance of light having a wavelength of 370 nm of not higher than 30%, and an excitation purity of from 2 to 3%.

The glass of the present invention having low solar radiation and ultraviolet ray transmittance can be used as single sheet glass, laminated glass or double glazing unit panes. In the case of laminated glass or double glazing unit, glass sheets of the present invention may be used for the both sides of the laminated glass or the double glazing unit. Otherwise, the glass of the present invention may be used in combination with other kinds of glass to form the laminated glass or the double glazing unit.

The glass of the present invention having low solar radiation and ultraviolet ray transmittance can be prepared, for example, as follows. Namely, various raw materials are mixed so that the desired glass composition would be obtained. With respect to the raw materials useful for this purpose, iron powder or red iron oxide

may, for example, be used as the FeO and Fe_2O_3 source; cerium oxide, cerium carbonate or cerium hydroxide may, for example, be used as the cerium source; and titanium oxide may, for example, be used as the titanium source. As the raw materials for the matrix glass, those commonly used may be employed. Further, it is preferred to add a reducing agent such as carbon to these raw materials, so that iron in the molten glass is prevented from being oxidized to Fe_2O_3, and FeO will be contained in a predetermined amount.

The glass batch thus adjusted is continuously supplied to a melting furnace, and heated and melted at a temperature of about 1,500°C by e.g. heavy oil for vitrification. Then, this molten glass is refined and formed into a sheet glass having a predetermined thickness by e.g. a float process. Then, this sheet glass is cut into a predetermined shape to obtain the glass of the present invention having low solar radiation and ultraviolet ray transmittance. Further, the cut glass may be subjected to toughening, laminating or composing into double glazing unit.

Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

EXAMPLES 1 to 9

Soda lime-silica glass having the total iron

calculated as Fe_2O_3, CeO_2, TiO_2 and CoO incorporated in the amounts identified in the upper section of Table 1 as optical property-improving components to a matrix composition comprising 71 parts (parts by weight, the same applies hereinafter) of SiO_2, 1.7 parts of Al_2O_3, 12.3 parts of Na_2O, 0.5 part of K_2O, 8 parts of CaO, 3.5 parts of MgO and 0.6 part of SO_3, was prepared. The ratio of bivalent iron (in Table 1, referred simply as Fe^{II}) to the total iron was also identified in the same section.

In the preparation of the glass, the preliminarily formulated glass batch was put into a platinum pot of 300 cubic centimeters, and heated and melted in an electric furnace for vitrification. Then, the molten glass was cast on a stainless steel plate, and both sides of the formed sheet were polished to obtain a sheet glass having a thickness of 3.5 mm (5.0 mm in Examples 6, 7 and 9).

With respect to these sheets, the solar radiation transmittance T_e, the visible light transmittance (by light source A) T_{Va}, the ultraviolet ray transmittance T_{UV}, the transmittance of wavelength at 370 nm T_{370}, the dominant wavelength D_W and the excitation purity P_E were obtained, and the results are shown in the lower section of Table 1. Also with respect to the glass of Comparative Example (Example 8), such properties were obtained in the same manner, and they are shown also in Table 1.

The solar radiation transmittance and the visible light transmittance were determined by JIS R3106, the ultraviolet ray transmittance was determined by ISO 9050, and the dominant wavelength and the excitation purity were determined by JIS Z8722.

As is evident from Table 1, the glass of the present invention has a green color and has high visible light transmittance, low solar radiation transmittance and particularly low ultraviolet ray transmittance.

Table 1

Examples		1	2	3	4	5	6	7	8	9
Fe_2O_3	parts	0.62	0.59	0.62	0.61	0.61	0.53	0.54	0.64	0.60
Fe^{II}	wt%	31	34	32	33	32	33	32	35	35
CeO_2	parts	1.27	1.5	1.55	1.3	1.4	1.20	0.90	0.54	1.23
TiO_2	parts	0.4	0.45	0.35	0.4	0.4	0.40	0.40	0.32	0.31
CoO	parts	0.0009	0.0015	0.0017	-	0.0012	-	-	-	-
T_e	%	48.2	46.8	47.2	47.8	47.9	42.1	43.4	46.7	45.5
T_{Va}	%	73.0	72.0	73.3	74.4	73.4	71.4	72.9	73.8	72.8
T_{UV}	%	9.8	8.1	7.9	9.8	9.0	7.2	8.8	16.3	7.9
T_{370}	%	28.2	24.5	24.3	28.1	26.4	21.5	26.4	41.5	24.0
D_W	nm	521	519	525	528	525	519	519	506	519
P_e	%	2.3	2.3	2.4	2.6	2.4	2.8	2.7	2.6	2.4

TABLE TWO

Wavelength λ nm,	$S(\lambda)\bar{x}(\lambda)$	$S(\lambda)\bar{y}(\lambda)$	$S(\lambda)z(\lambda)$	Wavelength λ (nm)	$S(\lambda)\bar{x}(\lambda)$	$S(\lambda)\bar{y}(\lambda)$	$S(\lambda)z/\lambda$
380	0.01	0.00	0.06	580	104.86	99.56	0.19
385	0.02	0.00	0.11	585	115.33	96.39	0.17
390	0.05	0.00	0.24	590	124.93	92.15	0.13
395	0.10	0.00	0.48	595	132.50	87.13	0.13
400	0.21	0.01	1.00	600	137.07	81.42	0.10
405	0.37	0.01	1.78	605	138.75	75.21	0.08
410	0.77	0.02	3.67	610	136.70	68.58	0.05
415	1.50	0.04	7.16	615	131.37	61.76	0.03
420	2.82	0.08	13.55	620	122.72	54.72	0.03
425	4.89	0.17	23.68	625	110.64	47.26	0.01
430	7.00	0.29	34.18	630	96.90	39.97	0.01
435	8.75	0.45	43.24	635	83.68	33.51	0.00
440	10.00	0.66	50.14	640	70.76	27.65	0.00
445	10.74	0.92	54.99	645	58.28	22.32	0.00
450	11.12	1.26	58.64	650	46.79	17.66	0.00
455	11.29	1.70	61.76	655	36.85	13.75	0.00
460	11.00	2.27	63.11	660	28.36	10.49	0.00
465	10.12	2.98	61.58	665	21.26	7.82	0.00
470	8.38	3.90	55.20	670	15.62	5.72	0.00
475	6.47	5.13	47.43	675	11.58	4.23	0.00
480	4.61	6.71	39.22	680	8.67	3.15	0.00

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Wavelength λ nm,	$S(\lambda)\bar{x}(\lambda)$	$S(\lambda)\bar{y}(\lambda)$	$S(\lambda)z(\lambda)$	Wavelength λ (nm)	$S(\lambda)\bar{x}(\lambda)$	$S(\lambda)\bar{y}(\lambda)$	$S(\lambda)z/\lambda$
485	2.96	8.64	31.45	685	6.21	2.25	0.00
490	1.73	11.21	25.08	690	4.36	1.58	0.00
495	0.84	14.70	20.09	695	3.09	1.12	0.00
500	0.29	19.33	16.28	700	2.25	0.81	0.00
505	0.15	25.63	13.36	705	1.63	0.59	0.00
510	0.61	33.23	10.45	710	1.18	0.43	0.00
515	2.02	42.12	7.74	715	0.85	0.31	0.00
520	4.59	51.48	5.67	720	0.61	0.22	0.00
525	8.31	60.12	4.34	725	0.44	0.16	0.00
530	13.10	68.21	3.34	730	0.31	0.11	0.00
535	18.63	75.49	2.46	735	0.22	0.08	0.00
540	24.96	82.00	1.74	740	0.15	0.06	0.00
545	32.16	87.65	1.20	745	0.11	0.04	0.00
550	40.27	92.44	0.81	750	0.08	0.03	0.00
555	49.38	96.44	0.55	755	0.05	0.02	0.00
560	59.45	99.50	0.39	760	0.04	0.01	0.00
565	70.27	101.36	0.28	765	0.03	0.01	0.00
570	81.68	102.04	0.23	770	0.02	0.01	0.00
575	93.35	101.43	0.20	775	0.01	0.01	0.00
				780	0.01	0.00	0.00
10 nm			X Y Z x y z		1185.04 0.4476	1078.97 0.4075	383.51 0.1449
5 nm			X Y Z x y z		2370.46 0.4476	2157.92 0.4074	767.81 0.1450

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According to the present invention, glass having a green color and having high visible light transmittance and low ultraviolet ray transmittance, particularly low transmittance of the wavelength of 370 nm, can be provided. Such glass is particularly suitable for windshield glass for automobiles.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A glass having a low solar radiation and ultraviolet ray transmittance and having a dominant wavelength of from 500 to 540 nm for transmittance, which comprises a soda lime-silica type glass containing from 0.52 to 0.64 wt% of total iron calculated as Fe_2O_3, from 0.2 to 0.6 wt% of TiO_2 and from 0.9 to 2.0 wt% of total cerium calculated as CeO_2, wherein the weight of FeO calculated as Fe_2O_3 is from 28 to 38% of the weight of the total iron calculated as Fe_2O_3, the visible light transmittance by light source A is at least 70%, the ultraviolet ray transmittance is at most 15%, and the transmittance of light having a wavelength of 370 nm is at most 30%.

2. A glass according to Claim 1, which comprises:

SiO_2	68 - 74 wt%
Al_2O_3	0.5 - 3 wt%
MgO	3 - 6 wt%
CaO	6 - 10 wt%
$Na_2O + K_2O$	10 - 16 wt%
SO_3	0.05 - 1 wt%
Total iron calculated as Fe_2O_3	0.52 - 0.64 wt%
Fe_2O_3	0.35 - 0.50 wt%
FeO	0.16 - 0.24 wt%
TiO_2	0.2 - 0.6 wt%
Total cerium calculated as CeO_2	0.9 - 2 wt%

3. A glass according to either Claim 1, or Claim 2, which has a dominant wavelength of from 515 to 535 nm for transmittance.

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4. A glass according to any one of claims 1 to 3, which has a specific gravity of from 2.49 to 2.53.

5. A glass according to any one of claims 1 to 4, which has a thickness of from 1.7 to 4.3 mm, and wherein the total iron calculated as Fe_2O_3 is from 0.59 to 0.64 wt%, and CeO_2 is from 1.2 to 2.0 wt%.

6. A glass according to any one of claims 1 to 4, which has a thickness of from 4.4 to 5.5 mm, and wherein the total iron calculated as Fe_2O_3 is from 0.52 to 0.63 wt%, and CeO_2 is from 0.9 to 1.2 wt%.

7. A glass according to any one of claims 1 to 4, which has a thickness of from 1.7 to 4.4 mm, and wherein the total iron calculated as Fe_2O_3 is from 0.60 to 0.64 wt%, TiO_2 is from 0.3 to 0.5 wt%, the total cerium calculated as CeO_2 is from 1.4 to 1.7 wt%, and the weight of FeO calculated as Fe_2O_3 is from 30 to 35 % of the weight of the total iron calculated as Fe_2O_3.

8. A glass according to any one of claims 1 to 4, which has a thickness of from 4.4 to 7.0 mm, and wherein the total iron calculated as Fe_2O_3 is from 0.57 to 0.62 wt%, TiO_2 is from 0.2 to 0.4 wt%, the total cerium calculated as CeO_2 is from 0.9 to 1.4 wt%, and the weight of FeO calculated as Fe_2O_3 is from 30 to 35% of the weight of the total iron calculated as Fe_2O_3.

9. A glass substantially as hereinbefore described with reference to the Examples.

DATED this 28th day of JULY, 1998.
Asahi Glass Company Ltd.
by DAVIES COLLISON CAVE
Patent Attorneys for the Applicant(s)

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ABSTRACT

A glass having low solar radiation and ultraviolet ray transmittance, which consists essentially of a soda lime-silica type glass containing from 0.52 to 0.67 wt% of total iron calculated as Fe_2O_3, from 0.2 to 0.6 wt% of TiO_2 and from 0.9 to 2.0 wt% of total cerium calculated as CeO_2, wherein the weight of FeO calculated as Fe_2O_3 is from 28 to 38% of the weight of the total iron calculated as Fe_2O_3, the visible light transmittance (by light source A) is at least 70%, the ultraviolet ray transmittance is at most 15%, and the transmittance of light having a wavelength of 370 nm is at most 30%.