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(54) **PROCESS FOR PRODUCING HIGH SILICATE GLASS AND HIGH SILICATE GLASS**

VERFAHREN ZUR HERSTELLUNG VON SILIKATREICHEM GLAS UND SILIKATREICHES GLAS
VERRE HAUTEMENT SILICIQUE ET PROCEDE DE FABRICATION

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(73) Proprietor: **Japan Science and Technology Agency**
Kawaguchi-shi,
Saitama 332-0012 (JP)

(72) Inventors:
• **AKAI, Tomoko c/o National Institute of 563-8577 Osaka (JP)**
• **CHEN, Danping c/o National Institute of 563-8577 Osaka, (JP)**

(74) Representative: **Graf von Stosch, Andreas et al**
Graf von Stosch
Patentanwalts-gesellschaft mbH
Prinzregentenstrasse 22
80538 München (DE)

(56) References cited:

EP-A- 0 601 391 JP-A- 6 199 538
JP-A- 57 188 432 JP-A- 57 205 337
JP-A- 59 102 832 JP-A- 2003 313 050
US-A- 2 106 744 US-A- 3 113 855
US-A1- 2002 018 942

- **DATABASE WPI Derwent Publications Ltd., London, GB; AN 1983-10492K XP002475842 & JP 57 205337 A (HOYA CORP; HOYA DENSHI KK) 16 December 1982 (1982-12-16)**
- **BAMFORD C R: "COLOUR GENERATION AND CONTROL IN GLASS" CHAPTER 4: REDUCTION-OXIDATION EQUILIBRIA, 1977, pages 77-87, XP002474810 AMSTERDAM, ELSEVIER, NL**
- **TOOLEY F V ED - TOOLEY F V: "The Handbook of Glass Manufacture" HANDBOOK OF GLASS MANUFACTURE. BOOK OF REFERENCE FOR THE PLANT EXECUTIVE, TECHNOLOGIST AND ENGINEER, NEW YORK, ASHLEE PUBLISHING, US, vol. 2, 1984, pages 746-747, XP002474811**
- **EHRT D ET AL: "EINBAU UND VERTEILUNG VON FE2O3 AUF DIE MIKROPHASEN IN GRUNDGLAESERN DES SYSTEMS NA2O-B2O3-SIO2" SILIKATTECHNIK, VEB VERLAG FUER BAUWESEN. BERLIN, DE, vol. 27, no. 9, September 1976 (1976-09), pages 304-309, XP001220074**
- **LANGE: "Rohstoffe der Glasindustrie" 1993, DEUTSCHER VERLAG FÜR GRUNDSTOFFINDUSTRIE, LEIPZIG; STUTTGART, XP002476658 * page 182; table 2.84 ***

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for producing high silicate glass which has a high ultraviolet (UV) transmittance and which can be used as an excimer laser base material, a UV transmission filter, a UV utilization material, and the like. The present invention also relates to high silicate glass which has a high UV transmittance.

BACKGROUND ART

[0002] Conventionally, quartz glass has been widely used as a UV transmission material. Quartz glass is produced by using a CVD (chemical vapor deposition) process, a melting process, or other processes. However, these production processes have drawbacks such as extremely high cost and difficulty of upsizing. Particularly, the melting process has the drawback of requiring a very high temperature (1900°C or above). In recent years, a technique for producing a light source such as a UV region laser or a lamp has been established, and quartz glass has been used for various purposes other than infrared optical communications-use fiber, so that there has been an increasing demand for quartz glass in various ways. Therefore, there is a high demand for a method for producing quartz glass at lower cost.

[0003] Further, Patent Document 1 (United States Patent No. 2106744) discloses, as a method for mass-producing high silicate glass consisting mainly of silicic acid, a method including the steps of: separating alkaline borosilicate glass into an insoluble phase rich in SiO₂ and a soluble phase rich in B₂O₃ by subjecting the alkaline borosilicate glass to heat treatment; producing porous glass consisting mainly of SiO₂, by eluting the soluble phase with acid; and sintering the porous glass. This method is called a Vycor method.

[0004] However, the Vycor method causes Fe (iron) ions and water to remain in glass and thus has the problem that UV and IR transmittances cannot be sufficiently increased. For this reason, the Vycor method is not used as a method for producing quartz glass.

[0005] As described above, because Vycor glass (glass produced by the conventional Vycor method) contains a very small quantity of Fe ions highly absorptive of short-wavelength UV rays, the Vycor glass is known to have a lower UV transmittance than quartz glass (see Patent Document 2 (Japanese Unexamined Patent Publication No. 205337/1982 (Tokukaisho 57-205337; published on December 16, 1982))). In view of this, in order to increase a UV transmittance of high silicate glass, Patent Document 2 discloses a method for producing high silicate glass, the method including the steps of: subjecting porous glass to further acid treatment with acid containing ethylenediamine tetraacetic acid (EDTA) or a salt thereof; eluting as a water-soluble complex salt a very

small quantity of Fe ions contained in the porous glass; and sintering the porous glass.

[0006] However, glass produced by the method of Patent Document 2 has an absorption end of approximately 220 nm, and has a much lower UV transmittance than quartz glass, which has an absorption end of 160 nm. Therefore, it cannot be said that the method of Patent Document 2 has the effect of sufficiently removing Fe ions.

[0007] Beyond Patent documents 1 and 2, DATABASE WPI Derwent Publications Ltd., London; AN 1983-10492K XP002475842 & JP 57 205337 A discloses a method for producing high silicate glass, wherein borosilicate glass is produced by the method a one-melting-step in the presence of arsenic as Fe²⁺-oxidant.

[0008] The present invention has been made in view of the foregoing problems and has as an object to provide: a method for producing high silicate glass which has a low Fe concentration and can achieve a high UV transmittance while retaining advantages of Vycor glass that mass production at low cost is feasible and that complex formation with various photofunctional ions can be effected; and high silicate glass obtained by the method.

DISCLOSURE OF INVENTION

[0009] The inventors of the present application recognized that in alkaline borosilicate glass including imitation green glass and boric acid added thereto, the distribution of transition metal becomes uneven, and this causes metal ions to be concentrated in a borate phase, so that the metal ions leach by acid (see Non-patent Document 1 (T. Akai, D. Chen, H. Masui, H. Mitsuyoshi, and T. Yazawa, "A new way of recycling waste glass", Journal of Ecotechnology Research, p. 152-153; issued by International Association of Ecotechnology Research; published on December 5, 2002)). Further, the inventor supposed that heat treatment of the borosilicate glass causes low-valence Fe ions contained in the borosilicate glass to transform into high-valence Fe³⁺ ions so that the high-valence Fe³⁺ ions can be dispersed in the borate phase, and that the high-valence Fe³⁺ ions can be removed by further subjecting the borosilicate glass to acid treatment. Furthermore, the inventors found that Fe²⁺ ions contained in glass produced by using, as a raw material, borosilicate glass which contains a heavy metal or rare-earth element (preferably a high-valence heavy metal or rare-earth element) can be transformed into Fe³⁺ ions during melting. Based on this finding, the inventors have completed the present invention.

[0010] That is, a method of the present invention for producing high silicate glass is characterized by including: a phase-separating step of subjecting to heat treatment borosilicate glass containing any one element of manganese, cerium, chromium, cobalt, and copper, so as to phase-separate the borosilicate glass; an acid-treatment step of subjecting the phase-separated borosilicate glass to acid treatment so as to elute metalions;

and a sintering step of sintering the acid-treated borosilicate glass resulting in the high silicate glass, wherein the borosilicate glass is produced by carrying out first and second melting steps of melting a raw material by heating the raw material, wherein boric acid to be contained in the borosilicate glass is added in the second melting step.

[0011] The method for producing high silicate glass is an application of the Vycor method, and heat treatment of borosilicate glass makes it possible to phase-separate the borosilicate glass into an insoluble phase (silicate phase) consisting mainly of SiO_2 and a soluble phase (borate phase) consisting mainly of B_2O_3 . According to the producing method of the present invention, the borosilicate glass contains a heavy metal or rare-earth element such as manganese, cerium, chromium, cobalt, and copper so that in the phase-separating step, low-valence Fe ions (Fe^{2+} ions) can be transformed into Fe^{3+} ions.

[0012] According to the finding of the inventors, since high-valence metal ions are concentrated in a borate phase, the low-valence Fe ions which are contained in the borosilicate glass and which have been transformed into the Fe^{3+} ions are dispersed in the borate phase. In the method for producing high silicate glass, a metal can be eluted by the acid-treatment step, following the phase-separating step, so that the Fe^{3+} ions can be removed together with other metal ions. Moreover, sintering the borosilicate glass after the acid-treatment step makes it possible to obtain high silicate glass which has a low Fe concentration and a high UV transmittance.

[0013] That is, according to the method of the present invention for producing high silicate glass, high silicate glass which has a low Fe concentration and a high UV transmittance can be obtained. Moreover, since the method applies the same method as the conventional Vycor method, high silicate glass which has a high UV transmittance can be mass-produced at low cost.

[0014] The "heavy metal or rare-earth element" comes in various forms, such as simple chemical substance, compound, and ions, in which an element normally exists. However, in the method of the present invention for producing silicate glass, the heavy metal or rare-earth element preferably exists in the borosilicate glass in the form of a high-valence heavy metal or rare-earth element, such as manganese, cerium, chromium, cobalt, and copper, capable of serving as an oxidant. This makes it possible to more effectively oxidize low-valence Fe ions (Fe^{2+} ions) contained in borosilicate glass to Fe^{3+} ions.

[0015] In the method of the present invention for producing high silicate glass, the borosilicate glass contains any one element of manganese, cerium, chromium, cobalt, and copper.

[0016] According to the foregoing producing method, a Fe concentration of high silicate glass to be obtained can be further lowered, so that a UV transmittance can be further increased. Moreover, according to the foregoing producing method, since the same method as the conventional Vycor method is applied, high silicate glass

which has a high UV transmittance can be mass-produced at low cost.

[0017] Further, in the method of the present invention for producing high silicate glass, the borosilicate glass preferably contains 0.1 wt% to 2.0 wt% of oxide of the element (i.e., any one of manganese (Mn), cerium (Ce), chromium (Cr), cobalt (Co), and copper (Cu)).

[0018] According to the foregoing producing method, a Fe concentration of high silicate glass to be obtained can be much further lowered, so that a UV transmittance can be further increased. Moreover, according to the foregoing producing method, since the same method as the conventional Vycor method is applied, high silicate glass which has a high UV transmittance can be mass-produced at low cost.

[0019] In the method of the present invention for producing high silicate glass, the oxide containing the element is preferably a high-valence oxide of the element. This makes it possible to more effectively oxidize low-valence Fe ions (Fe^{2+} ions) contained in borosilicate glass to Fe^{3+} ions.

[0020] In the method of the present invention for producing high silicate glass, the borosilicate glass is produced by carrying out first and second melting steps of melting a glass consisting of a mixture of compounds serving as raw materials, by heating the glass.

[0021] According to the foregoing producing method, high silicate glass which has a higher UV transmittance can be produced as compared with high silicate glass produced without the second melting step.

[0022] In the method of the present invention for producing high silicate glass, boric acid to be contained in the borosilicate glass is added in the second melting step.

[0023] According to the foregoing producing method, high silicate glass which has a higher UV transmittance can be produced.

[0024] Preferably, the method of the present invention for producing high silicate glass is arranged such that when the borosilicate glass contains cerium or chromium, the borosilicate glass is subjected repeatedly to heat treatment and acid treatment between the acid-treatment step and the sintering step and is then subjected to further acid treatment by using acid containing ethylenediamine tetraacetic acid. More preferably, the method of the present invention for producing high silicate glass is arranged such that when the borosilicate glass contains cerium or chromium, the borosilicate glass is subjected repeatedly to heat treatment and acid treatment and using acid containing ethylenediamine tetraacetic acid for acid treatment before the sintering step.

[0025] According to the foregoing method, because ethylenediamine tetraacetic acid (EDTA) combines with a metal to form a complex salt, a Fe concentration of high silicate glass to be obtained can be further lowered.

[0026] Further, high silicate glass of the present invention is characterized by being produced according to any one of the foregoing arrangements of the method for producing high silicate glass.

[0027] Because the high silicate glass can be mass-produced at low cost compared with quartz glass which is produced by a melting process, a CVD process, or other processes, the high silicate glass can be upsized. Moreover, the high silicate glass has a higher UV transmittance than Vycor glass (glass produced by the conventional Vycor method) and has substantially the same UV transmittance as quartz glass. Therefore, the high silicate glass allows for formation of a complex compound by introducing UV emission photofunctional ions as dopants into the high silicate glass.

[0028] Because the high silicate glass of the present invention contains silica as porous as that contained in the Vycor glass (glass produced by the conventional Vycor method), the high silicate glass has the advantage of being translucent and having a large surface area. The advantage allows the high silicate glass to be used as a photocatalyst carrier and a complex glass base material for a novel photofunctional material. In this case, since the high silicate glass has a higher UV transmittance than the Vycor glass (glass produced by the conventional Vycor method), the high silicate glass can deal with Xe light (176 nm), which is used to shorten a wavelength of an exciter and which is used for a mercury-free lamp. Thus, the high silicate glass has the possibility of being widely used as various optical materials.

[0029] Further, in the method of the present invention for producing high silicate glass, pores of the silica may be impregnated with chemical substances such as rare-earth ions before the sintering step, so that the chemical substances are implanted into the pores in the sintering step.

[0030] Because the high silicate glass produced according to the foregoing method has substantially the same transmittance as quartz glass in a UV region, the high silicate glass can deal with Xe light (176 nm), which is used to shorten a wavelength of an exciter and which is used for a mercury-free lamp. Thus, the high silicate glass can be effectively used as a complex glass base material for a novel photofunctional material.

[0031] Furthermore, high silicate glass of the present invention is characterized by transmitting 30% or more of light at a wavelength of 200 nm when containing 10 ppm or more of boron and having a thickness of 1 mm.

[0032] The foregoing high silicate glass has a higher UV transmittance than the Vycor glass (glass produced by the conventional Vycor method). Therefore, the high silicate glass allows for formation of a complex compound by introducing UV emission photofunctional ions as dopants into the high silicate glass. Thus, the high silicate glass has the possibility of being widely used as various optical materials.

[0033] The high silicate glass is characterized by transmitting 30% or more of light at a wavelength of 200 nm when supposedly having a thickness of 1 mm. However, the thickness of the high silicate glass is not to be limited to 1 mm.

[0034] For a fuller understanding of the nature and ad-

vantages of the invention, reference should be made to the ensuing detailed description taken in conjunction with the accompanying drawings.

5 BRIEF DESCRIPTION OF DRAWINGS

[0035]

Fig. 1 is a graph showing results of measuring respective transmittances (%) of Glass 1 and Vycor glass with respect to light at each wavelength (nm). Note that Glass 1 is a type of high silicate glass which was produced from a MnO_2 -containing raw material in Example 1.

Fig. 2 is a graph showing results of measuring respective transmittances (%) of Glass 2 and Glass 3 with respect to light at each wavelength (nm). Note that Glass 2 is a type of high silicate glass which was produced by carrying out first and second melting steps, and Glass 3 is high silicate glass which was produced by carrying out without the second melting step.

Fig. 3 is a graph showing results of measuring transmittances (%) of types of high silicate glass produced in Example 3 with respect to light at each wavelength (nm).

Fig. 4 is a graph showing a result of measuring a transmittance of Glass 6 with respect to light at a short wavelength of 300 nm to 115 nm. Note that Glass 6 is a type of high silicate glass which was produced in Example 3 and which was subjected to acid treatment with EDTA.

BEST MODE FOR CARRYING OUT THE INVENTION

[0036] One embodiment of a method for producing high silicate glass and high silicate glass of the present invention will be described below. The present invention is not to be limited by this description.

[0037] High silicate glass according to the present invention consists mainly of silicon oxide (SiO_2), and the feature of its producing method brings the high silicate glass having a lower Fe concentration and a higher UV transmittance than the conventional high silicate glass produced for example by the Vycor method (see Patent Document 1).

In order to produce such high silicate glass, a producing method of the present invention includes: a phase-separating step of subjecting to heat treatment borosilicate glass containing any one element of manganese, cerium, chromium, cobalt, and copper, so as to phase-separate the borosilicate glass; an acid-treatment step of subjecting the phase-separated borosilicate glass to acid treatment so as to elute metal ions; and a sintering step of sintering the acid-treated borosilicate glass, wherein the borosilicate glass is produced by carrying out first and second melting steps of melting a raw material by heating the raw material, wherein boric acid to be contained in

the borosilicate glass is added in the second melting step.

[0038] In the present embodiment, such a case will be described that borosilicate glass whose glass composition contains 0.1 wt% to 2.0 wt% of oxide of any one element of manganese (Mn), cerium (Ce), chromium (Cr), cobalt (Co), and copper (Cu) is used as a raw material for high silicate glass in the foregoing method. The glass composition of the borosilicate glass serving as the raw material for the high silicate glass is not particularly limited, except for the foregoing condition. It is only necessary to copy the composition of normal borosilicate glass by using a compound used as a raw material for the normal borosilicate glass.

[0039] More specifically, the borosilicate glass only needs to appropriately contain compounds containing elements such as Si, O, B, Na, Al, and Ca, in addition to Mn, Ce, Cr, Co, or Cu, and include approximately 45 wt% to 60 wt% of SiO₂ and approximately 24 wt% to 36 wt% of B₂O₃. Preferably, Mn, Ce, Cr, Co, and Cu are included in the form of high-valence oxides such as MnO₂, CeO₂, Cr₂O₃, Co₂O₃, and CuO. A high-valence oxide of the element (any one of Mn, Ce, Cr, Co, and Cu) serves as an oxidant so as to cause iron contained in the borosilicate glass to be effectively transformed into Fe³⁺ ions.

[0040] The borosilicate glass can be produced in the following manner. First, the foregoing compounds are mixed in an appropriate proportion. Next, the mixture is melted for several hours at a temperature of 1350°C and 1450°C for example. Thereafter, the mixture is cooled down, thereby producing the borosilicate glass.

[0041] The borosilicate glass thus produced is subjected to heat treatment so as to be separated into an insoluble phase (silicate phase) consisting mainly of SiO₂ and a soluble phase (borate phase) consisting mainly of B₂O₃. The heat treatment is carried out for approximately 20 to 80 hours at a temperature of approximately 550°C to 650°C. In the present embodiment, this step is called a phase-separating step.

[0042] The borosilicate glass contains 0.1 wt% to 2.0 wt% of oxide (preferably a high-valence oxide) of any one of Mn, Ce, Cr, Co, and Cu, so that Fe ions contained in the borosilicate glass is transformed into Fe³⁺ ions and the Fe³⁺ can be dispersed in the borate phase in the phase-separating step.

[0043] In the method according to the present invention for producing high silicate glass, after the phase-separating step, an acid-treatment step is carried out. In the acid-treatment step, the phase-separated borosilicate glass is subjected to acid treatment so as to elute metal ions contained therein. This makes it possible to remove the iron ions dispersed in the borate phase, together with boron ions, sodium ions, calcium ions, and other ions, so that the borosilicate glass becomes porous glass with a low Fe content.

[0044] Thereafter, a sintering step of sintering the borosilicate glass (porous glass) is carried out, thereby producing high silicate glass which has a high UV transmittance. Preferably, the sintering step is carried out at

a temperature of approximately 1050°C to 1200°C. Further, the sintering step may be carried out in the air or in the reduction atmosphere.

[0045] The method of the present invention for producing high silicate glass is based on the Vycor method in that heat-treated borosilicate glass is subjected to acid treatment so as to elute a soluble phase and is further sintered. That is, the method according to the present invention for producing high silicate glass can be carried out in the same manner as the conventional Vycor method (see Patent Document 1) except that the borosilicate glass serving as a raw material contains 0.1 wt% to 2.0 wt% of oxide (preferably a high-valence oxide) of any one of Mn, Ce, Cr, Co, and Cu. Therefore, it can be said that the method of the present invention for producing high silicate glass is a method to which the Vycor method is applied.

[0046] The method of the present invention for producing high silicate glass produces high silicate glass which has a lower Fe concentration than that produced by the Vycor method. This makes it possible, as described in Example 1 later, to obtain high silicate glass capable of transmitting approximately 60% of UV rays at a wavelength of approximately 200 nm (see Fig. 1). Moreover, since the same method as the conventional Vycor method is applied, high silicate glass can be mass-produced at low cost.

[0047] The borosilicate glass is produced by carrying out a melting step of melting a raw material at a high temperature, the raw material being obtained by mixing in an appropriate proportion a plurality of compounds containing Si, O, B, Na, Al, other elements, and an oxide of any one of Mn, Ce, Cr, Co and Cu (preferably a high-valence oxide). The melting step is carried out twice, and boric acid (H₃BO₃) to be contained in the borosilicate glass is added in a second melting step of first and second melting steps. According to these arrangements, as described in Examples later, a UV transmittance of high silicate glass to be obtained can be further heightened.

[0048] Further, in the method of the present invention for producing high silicate glass, as described above, the sintering step may be carried out immediately after the acid-treatment step. Alternatively, heat treatment and acid treatment may be carried out repeatedly between the acid-treatment step and the sintering step.

Furthermore, in the method of the present invention for producing high silicate glass, when the borosilicate glass contains cerium (Ce) or chromium (Cr), it is preferable that the borosilicate glass be subjected repeatedly to heat treatment and acid treatment multiple times between the acid-treatment step and the sintering step and then be subjected to further acid treatment with acid containing ethylenediamine tetraacetic acid (EDTA). More preferably, the borosilicate glass is subjected repeatedly to heat treatment and acid treatment and using acid containing ethylenediamine tetraacetic acid for acid treatment before the sintering step.

[0049] According to this arrangement, because EDTA

combines with a metal contained in the borosilicate glass so as to form a complex salt, a Fe concentration of high silicate glass to be produced is further lowered. Further, high silicate glass of the present invention is produced according to the foregoing method for producing high silicate glass. That is, the high silicate glass of the present invention is produced by sintering a raw material after the phase-separating step and the acid-treatment step, the raw material being borosilicate glass which contains a heavy metal or rare-earth element. More specifically, the high silicate glass of the present invention is produced by using, as a raw material, borosilicate glass which contains 0.1 wt% to 2.0 wt% of oxide of any one of manganese, cerium, chromium, cobalt, and copper.

[0050] Since the high silicate glass is produced according to the producing method as described above, a very small quantity of Fe contained in the borosilicate glass is eluted by the acid-treatment step, thereby achieving a low Fe concentration. Thus, the high silicate glass can exhibit a high UV transmittance.

[0051] Therefore, the high silicate glass of the present invention has an advantage of being able to be excited by light at a shorter wavelength. For this reason, the high silicate glass allows for formation of a complex compound for example by introducing UV emission photofunctional ions as dopants into the high silicate glass. Thus, the high silicate glass of the present invention can be applied to the development of optical materials such as fluorescent materials.

[0052] The high silicate glass can be mass-produced at lower cost than quartz glass while retaining substantially the same UV transmittance as quartz glass.

[0053] Furthermore, the high silicate glass of the present invention can be shaped into various forms such as tubes, plates, and fibers by appropriately changing producing conditions. This extends the range of applications of the present invention. Specifically, the high silicate glass can be shaped into various forms for example by a method including the steps of: melting the borosilicate glass; placing the melted borosilicate glass in molds of various shapes; and cooling the melted borosilicate glass.

[0054] In the high silicate glass producing method described in the present embodiment, an example of the borosilicate glass that is a raw material of the high silicate glass is the borosilicate glass which contains 0.1 wt% to 2.0 wt% of oxide of any one of Mn, Ce, Cr, Co, and Cu. However, the borosilicate glass may contain another heavy metal or rare-earth element.

[0055] The present invention will be described more in detail by way of Examples in conjunction with the accompanying drawings. However, the present invention is not to be limited to the following Examples, and details thereof can be varied in many ways.

[Examples]

(Example 1)

[0056] In Example 1, glass was obtained in the following manner. Commercially available reagents (Na_2CO_3 , H_3BO_3 , SiO_2 , $\text{Al}(\text{OH})_3$, CaCO_3 , and MnO_2) were weighed and mixed so as to achieve a glass composition having Na_2O : 7.7 (wt%), CaO : 4.0 (wt%), Al_2O_3 : 2.7 (wt%), MnO_2 : 0.7 (wt%), B_2O_3 : 33.3 (wt%), and SiO_2 : 51.7 (wt%). The mixture was melted for four hours at 1400°C by using a platinum crucible.

[0057] The thus obtained glass was polished, was heated for 40 hours at 590°C in a heat-treating furnace, and was subjected to phase separation. Thereafter, the phase-separated glass was contained together with 1N nitric acid into an airtight container and was subjected to acid treatment for 24 to 72 hours at 90°C . The acid-treated glass was further sintered for two hours at 1100°C in the air, thereby producing high silicate glass (hereinafter referred to as "Glass 1"). Measurement was conducted on a transmittance of Glass 1 with a thickness of 1.0 mm.

[0058] As a comparative example of Example 1, high silicate glass was produced by the conventional Vycor method. Specifically, according to the conventional method, high silicate glass is produced in the same procedures as those of the foregoing method by using commercially available Vycor glass (manufactured by Iwaki Glass Co., Ltd) (High silicate glass produced by the conventional Vycor method is hereinafter referred to as "Vycor glass"). Measurement was conducted on a transmittance of the Vycor glass with a thickness of 1.0 mm.

[0059] The measurement results are shown in Fig. 1. Fig. 1 is a graph showing results of measuring respective transmittances (%) of the two types of high silicate glass with respect to light at each wavelength (nm). In Fig. 1, the solid line indicates a transmission spectrum of Glass 1, and the dotted line indicates a transmission spectrum of the Vycor glass.

[0060] As shown in Fig. 1, Glass 1 transmitted approximately 60% of UV rays having a wavelength of 200 nm. Meanwhile, the Vycor glass transmitted no UV rays at a wavelength of 200 nm or below.

(Example 2)

[0061] In Example 2, glass was obtained in the following manner. Commercially available reagents (Na_2CO_3 , H_3BO_3 , SiO_2 , $\text{Al}(\text{OH})_3$, and CaCO_3) were weighed and mixed so as to achieve a glass composition of SiO_2 : 77.5 (wt%), Na_2O : 11.5 (wt%), CaO : 6.0 (wt%), and Al_2O_3 : 5.0 (wt%). In a first melting step, the mixture was melted for four hours at 1500°C by using a platinum crucible. Thereafter, in a second melting step, H_3BO_3 was added to the mixture so as to achieve a glass composition having 50 parts by weight of H_3BO_3 per 100 parts by weight of the glass obtained after melting. Then, the mixture was subjected to second melting at 1400°C .

[0062] The thus obtained glass was polished, was heated for 40 hours at 590°C in a heat-treating furnace, and was subjected to phase-separation. The phase-separated glass was contained together with 1N nitric acid into an airtight container and was subjected to acid treatment for 24 to 72 hours at 90°C. The acid-treated glass was further sintered for two hours at 1100°C in the reduction atmosphere, thereby producing high silicate glass (hereinafter referred to as "Glass 2") with a thickness of 1.0 mm. Measurement was conducted on a transmittance of Glass 2.

[0063] As a comparative example of Example 2, high silicate glass was produced in the following manner. In a first melting step, H₃BO₃ was added in the same proportion as in Example 2, thereby producing high silicate glass (hereinafter referred to as "Glass 3") without a second melting step. Measurement was conducted on a transmittance of Glass 3 with a thickness of 1.0 mm. Glass 3 of the present comparative example was produced by the same method as Glass 2 of Example 2 except that the melting step was carried out once.

[0064] The measurements results are shown in Fig. 2. Fig. 2 is a graph showing results of measuring respective transmittances (%) of the two types of high silicate glass with respect to light at each wavelength (nm). In Fig. 2, the solid line indicates a transmittance spectrum of Glass 3, and the dotted line indicates a transmission spectrum of Glass 2.

[0065] As shown in Fig. 2, it was confirmed that Glass 2 had a higher transmittance with respect to UV rays having a wavelength of approximately 200 nm than Glass 3.

(Example 3)

[0066] In Example 3, which falls within the scope of claim 1, glass was obtained in the following manner. Commercially available reagents (Na₂CO₃, H₃BO₃, SiO₂, Al(OH)₃, CaCO₃, and CeO₂) were weighed and mixed so as to achieve a glass composition of SiO₂: 77.5 (wt%), Na₂O: 11.5 (wt%), CaO: 6.0 (wt%), Al₂O₃: 4.0 (wt%), and CeO₂: 1.0 (wt%). In a first melting step, the mixture was melted for four hours at 1500°C by using a platinum crucible. In a second melting step, H₃BO₃ was added to the mixture so as to achieve a glass composition having parts by weight of H₃BO₃ per 100 parts by weight of the glass obtained after melting. Then, the mixture was subjected to second melting at 1400°C.

[0067] The thus obtained glass was polished, was heated for 40 hours at 590°C in a heat-treating furnace, and was subjected to phase-separation. The phase-separated glass was contained together with 1N nitric acid into an airtight container and was subjected to acid treatment for 24 to 72 hours at 90°C, thereby obtaining porous glass.

[0068] The porous glass thus obtained by the acid treatment was further heated for 15 hours at 300°C. Thereafter, the porous glass was contained together with

3N nitric acid into an airtight container and was subjected to acid treatment for 24 hours at 90°C. The acid-treated glass was further sintered for two hours at 1100°C in the air, thereby producing high silicate glass (hereinafter referred to as "Glass 4"). Alternatively, the acid-treated glass was further sintered for two hours at 1100°C in the reduction atmosphere, thereby producing high silicate glass (hereinafter referred to as "Glass 5"). Thereafter, measurement was conducted on respective transmittances of Glass 4 and Glass 5 with a thickness of 1.0 mm.

[0069] In Example 3, another method was used to produce high silicate glass from the porous glass which had been subjected to acid treatment for 24 to 72 hours at 90°C. The method will be described below.

[0070] The porous glass which had been subjected to acid treatment for 24 to 72 hours at 90°C was heated for 15 hours at 300°C. Thereafter, the porous glass was contained together with 3N nitric acid into an airtight container and was subjected to acid treatment for 24 hours at 90°C. The acid-treated porous glass was further heated for 15 hours at 300°C. Thereafter, the porous glass was subjected to acid treatment for 24 hours at 90°C by using acid containing 1% of ethylenediamine tetraacetic acid (EDTA).

Thereafter, the resulting sample was sintered for two hours at 1100°C in the reduction atmosphere, thereby producing high silicate glass (hereinafter referred to as "Glass 6"). Measurement was conducted on a transmittance of Glass 6 with a thickness of 1.0 mm.

The measurement results are shown in Fig. 3. Fig. 3 is a graph showing results of measuring respective transmittances of the three types of high silicate glass with respect to light at each wavelength (nm). In Fig. 3, the solid line indicates a transmission spectrum of Glass 4. The dotted line indicates a transmission spectrum of Glass 5. The dashed line indicates a transmission spectrum of Glass 6.

As shown in Fig. 3, it was confirmed that Glass 5 (indicated by the dotted line) exhibited a higher UV transmittance than Glass 4 (indicated by the solid line). Further, it was confirmed that Glass 6 (indicated by the dashed line) exhibited a much higher UV transmittance. However, from a comparison between Examples 2 and 3, it is apparent that as to the types of high silicate glass produced without using EDTA (Glass 2, Glass 3, Glass 4, and Glass 5), Glass 4 and Glass 5, which were produced through heat treatment for 15 hours at 300°C and acid treatment, have substantially the same UV transmittances as Glass 2 and Glass 3, which were produced without heat treatment for 15 hours at 300°C and acid treatment. Further, EDTA had no effect on Glass 1.

Further, a transmittance of Glass 6 with respect to light at a shorter wavelength of 300 nm to 115 nm was measured by using a vacuum UV spectrophotometer (Test Model PUV-100; manufactured by JASCO Corporation). The measurement result is shown in Fig. 4. For comparison, measurement was similarly conducted on a transmittance of quartz glass with respect to light at the

short wavelength, the quartz glass being produced by a conventional method. In Fig. 4, the solid line indicates an absorption spectrum of Glass 6, and the dotted line indicates an absorption spectrum of the quartz glass.

[0075] As shown in Fig. 4, it was confirmed that Glass 6 exhibited a high UV transmittance, albeit slightly lower than the quartz glass, with respect to light at a short wavelength including the range from 300 nm to 115 nm.

INDUSTRIAL APPLICABILITY

[0076] As described above, a method of the present invention for producing high silicate glass is characterized by including: a phase-separating step of subjecting to heat treatment borosilicate glass containing a heavy metal or rare-earth element, so as to phase-separate the borosilicate glass; an acid-treatment step of subjecting the phase-separated borosilicate glass to acid treatment so as to elute a metal; and a sintering step of sintering the acid-treated borosilicate glass.

[0077] The foregoing method for producing high silicate glass brings about an effect of obtaining high silicate glass which has a low Fe concentration and a high UV transmittance. Further, since the method applies the same method as the conventional Vycor method, high silicate glass which has a high UV transmission can be mass-produced at low cost.

[0078] High silicate glass of the present invention is produced by using the method of the present invention for producing high silicate glass.

[0079] Because the high silicate glass can be mass-produced at low cost compared with quartz glass which is produced by a melting process, a CVD process, or other processes, the high silicate glass can be upsized. Moreover, the high silicate glass has a higher UV transmittance than Vycor glass (glass produced by the conventional Vycor method) and has substantially the same UV transmittance as quartz glass. Therefore, the high silicate glass allows for formation of a complex compound by introducing UV emission photofunctional ions as dopants into the high silicate glass.

[0080] Further, the high silicate glass of the present invention contains silica as porous as that contained in the Vycor glass (glass produced by the conventional Vycor method). This means the high silicate glass has the advantage of being translucent and having a large surface area. The advantage allows the high silicate glass to be used as a photocatalyst carrier and a complex glass base material for a novel photofunctional material. Thus, the high silicate glass is expected to be used for various purposes.

[0081] Furthermore, high silicate glass of the present invention is characterized by transmitting 30% or more of light at a wavelength of 200 nm when containing 10 ppm or more of boron and having a thickness of 1 mm.

[0082] The high silicate glass exhibits a higher UV transmittance than the Vycor glass (glass produced by the conventional Vycor method). Therefore, the high sil-

icate glass allows for formation of a complex compound by introducing UV emission photofunctional ions as dopants into the high silicate glass.

[0083] The high silicate glass of the present invention exhibits a high UV transmittance as described above. Therefore, the high silicate glass can be used as an excimer laser base material, a UV transmission filter, a UV utilization material, and the like.

Claims

1. A method for producing high silicate glass, the method comprising:

a phase-separating step of subjecting to heat treatment borosilicate glass containing any one element of manganese, cerium, chromium, cobalt, and copper, so as to phase-separate the borosilicate glass;

an acid-treatment step of subjecting the phase-separated borosilicate glass to acid treatment so as to elute metal ions; and

a sintering step of sintering the acid-treated borosilicate glass resulting in the high silicate glass,

wherein the borosilicate glass is produced by carrying out first and second melting steps of melting a raw material by heating the raw material, wherein boric acid to be contained in the borosilicate glass is added in the second melting step.

2. The method according to claim 1, wherein the borosilicate glass includes 0.1 wt% to 2.0 wt% of oxide of the element.

3. The method according to claims 1 or 2, wherein:

when the borosilicate glass contains cerium or chromium, the borosilicate glass is subjected repeatedly to heat treatment and acid treatment and using acid containing ethylenediamine tetraacetic acid for acid treatment before the sintering step.

Patentansprüche

1. Verfahren zur Herstellung von Hoch-Silikat-Glas, wobei das Verfahren umfasst:

einen Phasentrennungs-Schritt bei dem Borosilikat-Glas, das ein beliebiges Element aus Mangan, Cer, Chrom, Kobalt und Kupfer enthält, einer Wärmebehandlung unterworfen wird, um eine Phasentrennung des Borosilikat-Glases zu erreichen;

einen Säurebehandlungs-Schritt bei dem das phasengetrenten Borsilikat-Glas einer Säurebehandlung unterworfen wird, um Metallionen zu eluieren; und
einem Sinter-Schritt bei dem das säurebehandelte Borsilikat-Glas gesintert wird, was zum Hoch-Silikat-Glas führt,

wobei das Borsilikat-Glas durch die Durchführung eines ersten und zweiten Schmelz-Schrittes aus Schmelzen eines Rohstoffs durch Erhitzen des Rohstoffs hergestellt wird,
wobei die Borsäure, die im Borsilikat-Glas enthalten sein soll, im zweiten Schmelz-Schritt hinzugefügt wird.

2. Verfahren gemäß Anspruch 1, wobei das Borsilikat-Glas 0,1 Gew. % bis 2,0 Gew. % des Oxids des Elements enthält.

3. Verfahren gemäß den Ansprüchen 1 oder 2, wobei:

wenn das Borsilikat-Glas Cer oder Chrom enthält, das Borsilikat-Glas wiederholt der Wärmebehandlung und Säurebehandlung unterworfen wird und eine Säure, enthaltend Ethylendiamintetraessigsäure, für die Säurebehandlung vor dem Sinter-Schritt verwendet wird.

Revendications

1. Procédé pour produire un verre à haute teneur en silicate, le procédé comprenant :

une étape de séparation des phases d'exposition à un traitement thermique d'un verre de borosilicate contenant un élément quelconque parmi le manganèse, le cérium, le chrome, le cobalt et le cuivre, de manière à séparer les phases du verre de borosilicate ;

une étape de traitement à l'acide d'exposition du verre de borosilicate à phases séparées à un traitement à l'acide de manière à éluer les ions métalliques ; et

une étape de frittage de frittage du verre de borosilicate traité à l'acide conduisant au verre à haute teneur en silicate,

où le verre de borosilicate est produit par la mise en oeuvre d'une première et

d'une seconde étape de fusion de fusion d'une matière première par chauffage de la matière première,

où l'acide borique destiné à être contenu dans le verre de borosilicate est ajouté dans la seconde étape de fusion.

2. Procédé selon la revendication 1 où le verre de bo-

rosilicate inclut 0,1 % en poids à 2,0 % en poids d'oxyde de l'élément.

3. Procédé selon les revendications 1 ou 2 où :

quand le verre de borosilicate contient du cérium ou du chrome, le verre de borosilicate est soumis de manière répétée à un traitement thermique et un traitement à l'acide et un acide contenant de l'acide éthylendiaminetétraacétique est utilisé pour le traitement à l'acide avant l'étape de frittage.

FIG. 1

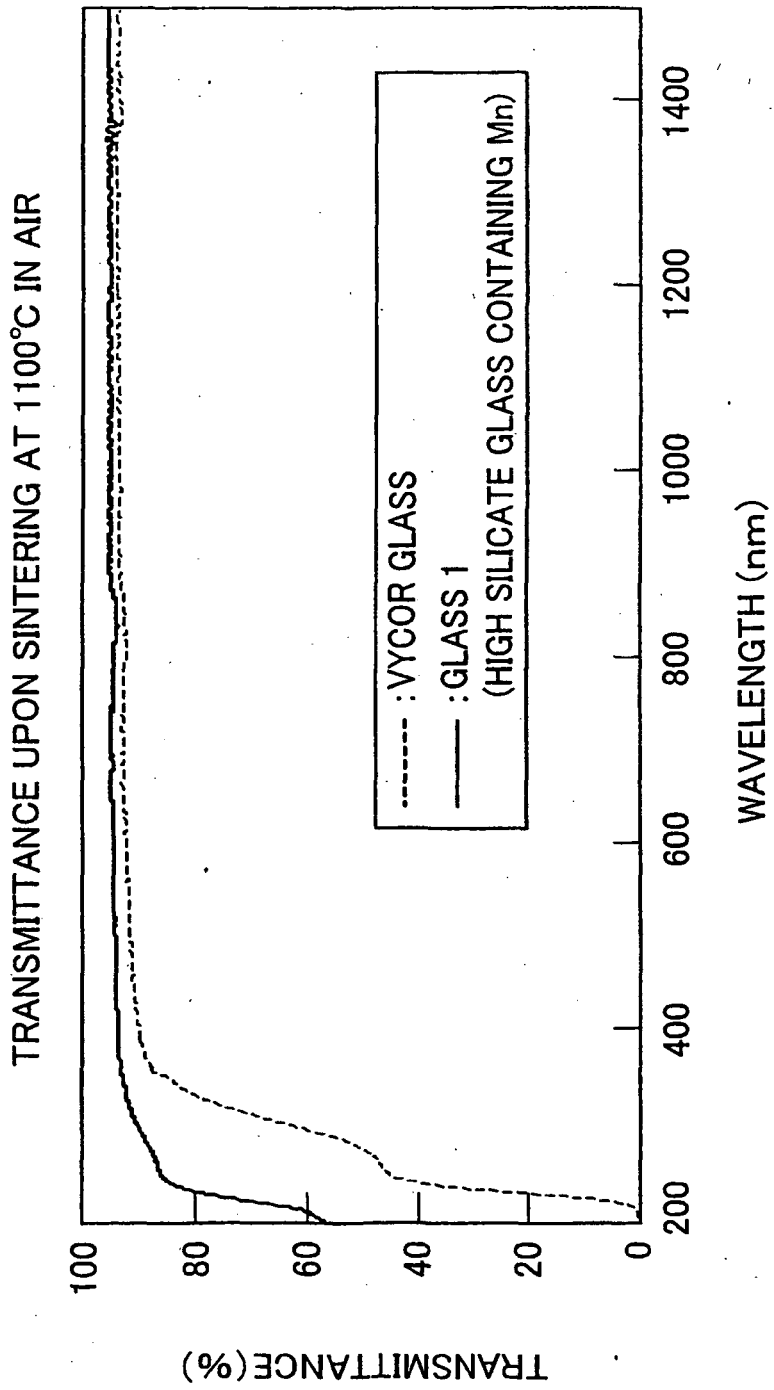


FIG. 2
TRANSMITTANCE UPON SINTERING
AT 1100°C IN REDUCTION ATMOSPHERE

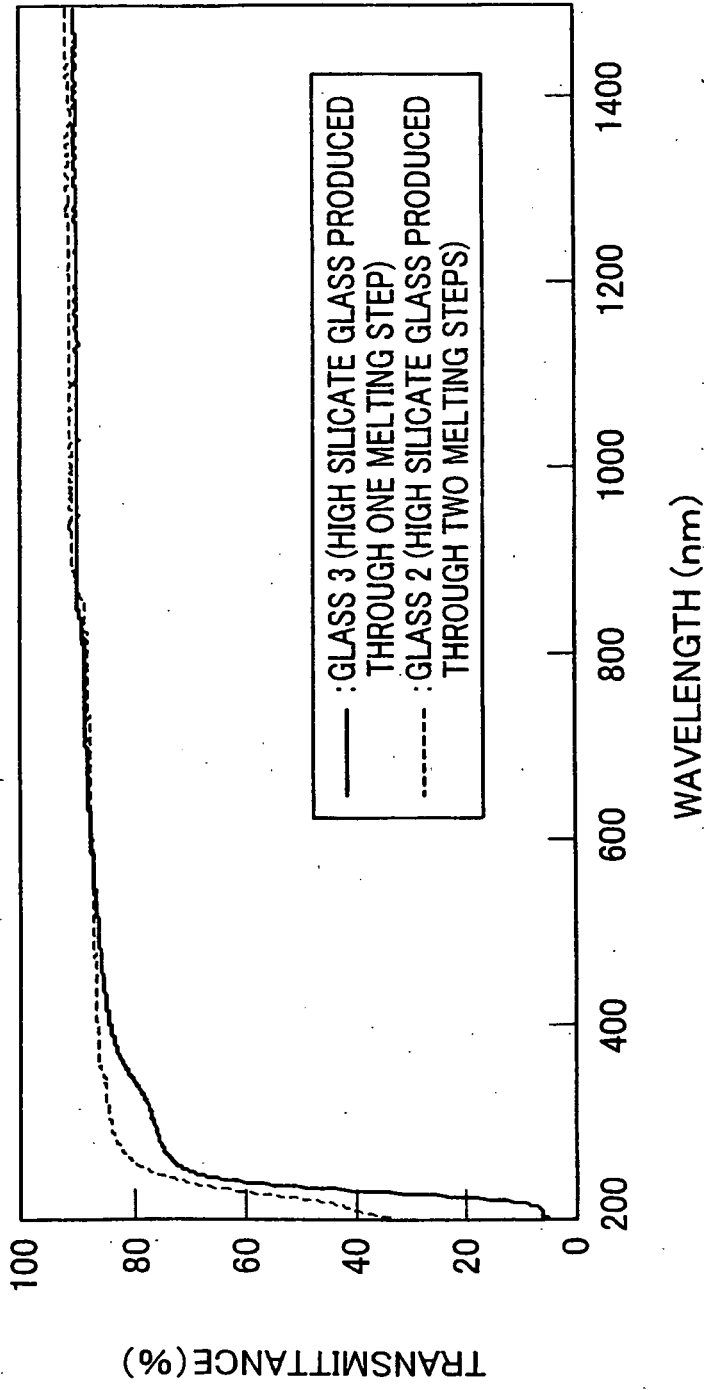
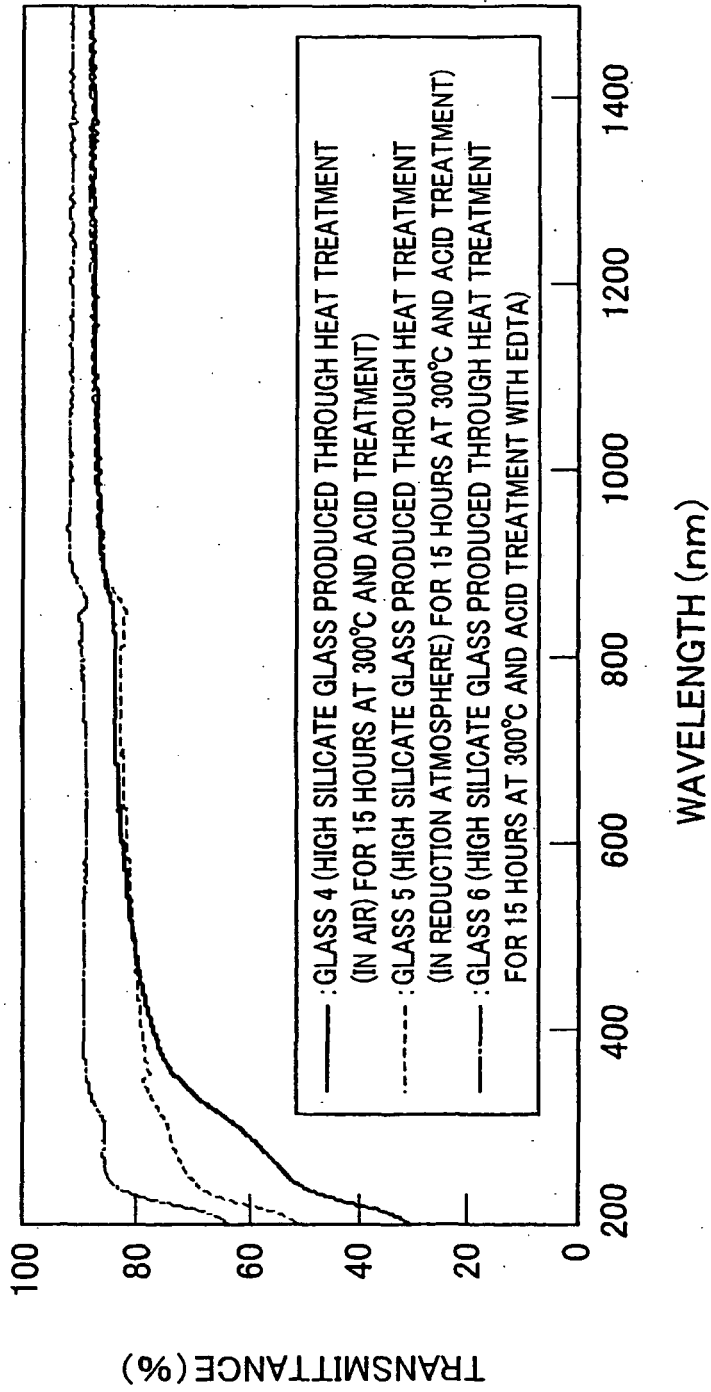


FIG. 3



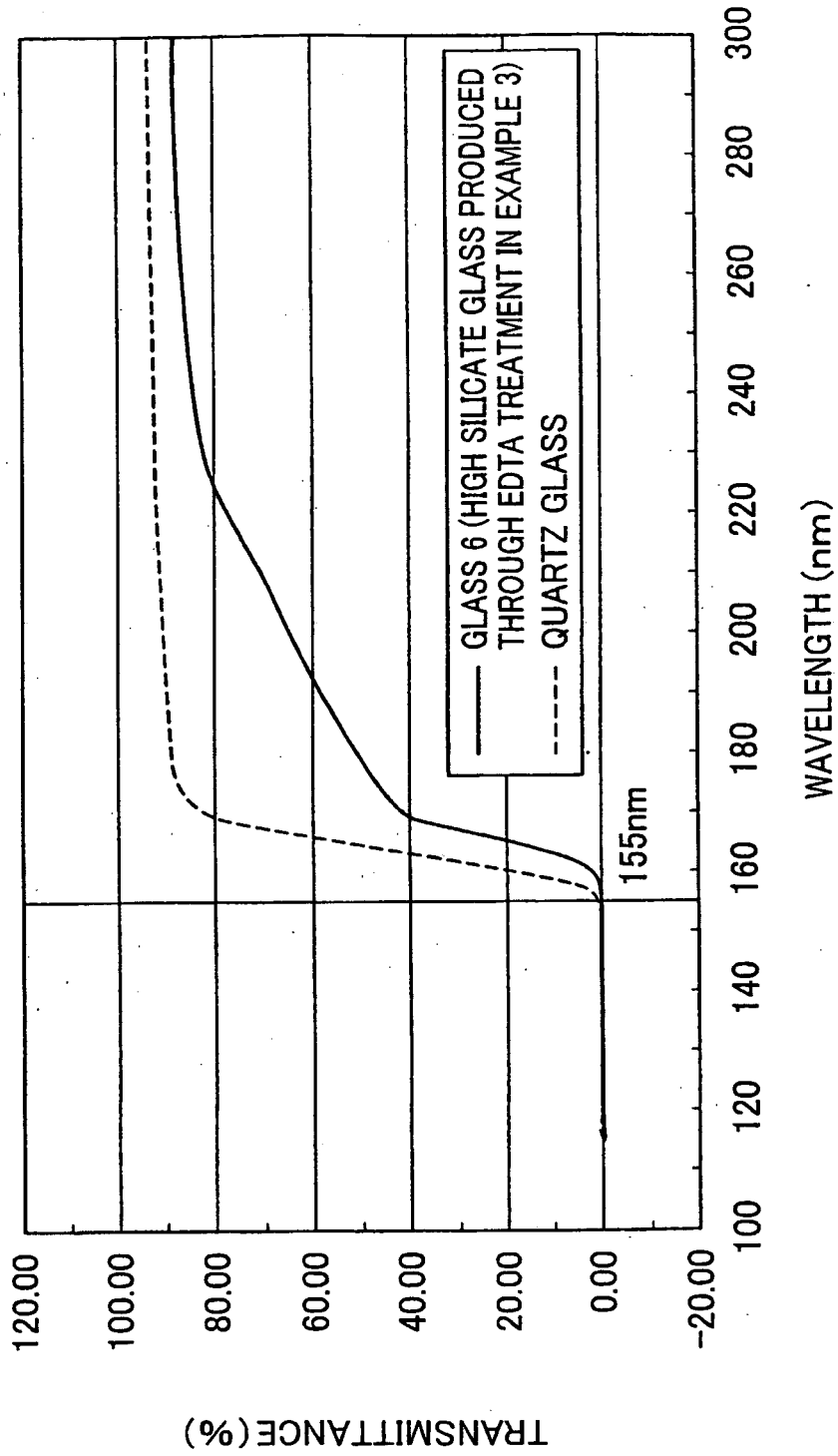


FIG. 4

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- US 2106744 A [0003]
- JP 57205337 A [0005] [0007]
- JP TOKUKAISHO57205337 B [0005]

Non-patent literature cited in the description

- A new way of recycling waste glass. **T. Akai ; D. Chen ; H. Masui ; H. Mitsuyoshi ; T. Yazawa.** Journal of Ecotechnology Research. International Association of Ecotechnology Research, 05 December 2002, 152-153 [0009]