

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
27 January 2011 (27.01.2011)

PCT

(10) International Publication Number
WO 2011/011667 A1

- (51) **International Patent Classification:**
C03C 3/085 (2006.01) C03C 3/091 (2006.01)
C03C 3/087 (2006.01)
- (21) **International Application Number:**
PCT/US2010/043027
- (22) **International Filing Date:**
23 July 2010 (23.07.2010)
- (25) **Filing Language:** English
- (26) **Publication Language:** English
- (30) **Priority Data:**
61/228,290 24 July 2009 (24.07.2009) US
61/263,930 24 November 2009 (24.11.2009) US
61/347,589 24 May 2010 (24.05.2010) US
12/840,754 21 July 2010 (21.07.2010) US
- (71) **Applicant (for all designated States except US): CORNING INCORPORATED** [US/US]; 1 Riverfront Plaza, Corning, New York 14831 (US).
- (72) **Inventors; and**
- (75) **Inventors/Applicants (for US only): AITKEN, Bruce G** [US/US]; 10235 Beaver Pond Lane, Corning, New York 14830 (US). **DICKINSON, James E Jr** [US/US]; 202 Wall Street, Corning, New York 14830 (US). **KICZENSKI, Timothy J** [US/US]; 361 Steege Hill Road, Corning, New York 14830 (US).
- (74) **Agent: THOMPSON, Tina N;** Corning Incorporated, Intellectual Property Department, SP-TI-3-1, Corning, New York 14831 (US).

- (81) **Designated States (unless otherwise indicated, for every kind of national protection available):** AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.
- (84) **Designated States (unless otherwise indicated, for every kind of regional protection available):** ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- with international search report (Art. 21(3))
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))

(54) **Title:** FUSION FORMABLE SILICA AND SODIUM CONTAINING GLASSES

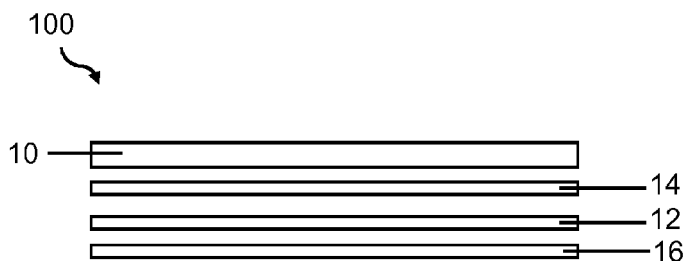


Figure 1

(57) **Abstract:** Sodium containing aluminosilicate and boroaluminosilicate glasses are described herein. The glasses can be used as substrates or superstrates for photovoltaic devices, for example, thin film photovoltaic devices such as CIGS photovoltaic devices. These glasses can be characterized as having strain points $\geq 535^{\circ}\text{C}$, for example, $\geq 570^{\circ}\text{C}$, thermal expansion coefficients of from 8 to 9 ppm/ $^{\circ}\text{C}$, as well as liquidus viscosities in excess of 50,000 poise. As such they are ideally suited for being formed into sheet by the fusion process.

WO 2011/011667 A1

FUSION FORMABLE SILICA AND SODIUM CONTAINING GLASSES**BACKGROUND**

[0001] This application claims the benefit of priority to US Provisional Patent Application No. 61/228,290 filed on July 24, 2009, to US Provisional Patent Application No. 61/263,930 filed on November 24, 2009, to US Provisional Patent Application No. 61/347,589 filed on May 24, 2010 and US Patent Application No. 12/840754 filed on July 21, 2010.

Field

[0002] Embodiments relate generally to sodium containing glasses and more particularly to fusion formable silica and sodium containing glasses which may be useful in photochromic, electrochromic, Organic Light Emitting Diode (OLED) lighting, or photovoltaic applications, for example, thin film photovoltaics.

Technical Background

[0003] Recent interest in the higher efficiencies offered by thin film photovoltaics has spawned considerable efforts into the development of new glass substrates and superstrates tailored to the needs of this new market. The thin film photovoltaics manufacturing processes typically require substrates capable of handling elevated temperatures for extended periods of time without warping, making glasses particularly well suited for these applications.

Additionally, some thin film photovoltaic processes (such as CIGS) desire sodium to diffuse from the glass into the deposited layers, making sodium-containing glasses even more desirable for particular applications.

[0004] Existing glasses (such as soda lime or display compositions) have been used to demonstrate extremely high efficiencies in this field but the use of any glasses designed for other applications is wrought with problems. For example,

soda lime glass offers a cheap, readily available sodium-containing substrate but its low strain point drastically inhibits its use in the higher temperature process that allow thin film photovoltaic processes to reach their highest efficiencies.

[0005] The use of glasses designed for display applications provides the required high strain point but the coefficient of thermal expansion (CTE) of these glasses is often too low to allow the reliable construction of large photovoltaic panels due to CTE mismatch with the photovoltaic films.

Additionally, many glasses designed for display applications are intentionally alkali-free, making them less useful for those thin film photovoltaic applications desiring sodium diffusion from the glass.

[0006] In some thin film photovoltaic applications, it would be advantageous to have a sodium-containing glass sheet with a high strain point and a high CTE. Further, it would be advantageous to have a sodium-containing glass with a high strain point and high CTE that is fusion formable to allow processing into a flat sheet with optimal surface characteristics.

SUMMARY

[0007] A compositional range of fusion-formable, high strain point sodium-containing aluminosilicate and boroaluminosilicate glasses useful, for example, for thin-film photovoltaic applications are described herein. More specifically, these glasses are advantageous materials to be used in copper indium gallium diselenide (CIGS) photovoltaic modules where the sodium required to optimize cell efficiency is to be derived from the substrate glass. Current CIGS module substrates are typically made from soda-lime glass sheet that has been manufactured by the float process.

However, use of higher strain point glass substrates can enable higher temperature CIGS processing, which is expected to translate into desirable improvements in cell efficiency. Moreover, it may be that the smoother surface of fusion-formed glass sheets yields additional benefits, such as improved film adhesion, etc.

[0008] Accordingly, the sodium-containing glasses described herein can be characterized by strain points $\geq 540^{\circ}\text{C}$, for example, $\geq 570^{\circ}\text{C}$ so as to provide advantage with respect to soda-lime glass and/or liquidus viscosity $\geq 50,000$ poise to allow manufacture via the fusion process, for example, a liquidus viscosity of 130,000 poise or greater. In order to avoid thermal expansion mismatch between the substrate and CIGS layer, the inventive glasses, according to some embodiments, are further characterized by a thermal expansion coefficient in the range of from 8 to 9 ppm/ $^{\circ}\text{C}$.

[0009] One embodiment is a glass comprising, in weight percent:

- 50 to 72 percent SiO_2 ;
- greater than 15 to 25 percent Al_2O_3 ;
- 0 to 10 percent B_2O_3 ;
- 10 to 25 percent total M_2O ; and
- greater than 0 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0010] Another embodiment is a glass comprising, in weight percent:

- 50 to 72 percent SiO_2 ;
- 10 to 25 percent Al_2O_3 ;
- 0 to 10 percent B_2O_3 ;
- 10 to 25 percent total M_2O ; and

0.5 to less than 14 percent RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0011] Another embodiment is a photovoltaic device comprising, a glass comprising, in weight percent:

50 to 72 percent SiO₂;

10 to 25 percent Al₂O₃;

0 to 10 percent B₂O₃;

10 to 25 percent total M₂O; and

greater than 0 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0012] Additional features and advantages of the invention will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from the description or recognized by practicing the invention as described in the written description and claims hereof, as well as the appended drawings.

[0013] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary of the invention, and are intended to provide an overview or framework to understanding the nature and character of the invention as it is claimed.

[0014] The accompanying drawings are included to provide a further understanding of the invention, and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s) of the invention and

together with the description serve to explain the principles and operation of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0015] The invention can be understood from the following detailed description either alone or together with the accompanying drawings.

[0016] **Figure 1** is an illustration of features of a photovoltaic device according to one embodiment.

DETAILED DESCRIPTION

[0017] Reference will now be made in detail to various embodiments of the invention.

[0018] As used herein, the term "substrate" can be used to describe either a substrate or a superstrate depending on the configuration of the photovoltaic cell. For example, the substrate is a superstrate, if when assembled into a photovoltaic cell, it is on the light incident side of a photovoltaic cell. The superstrate can provide protection for the photovoltaic materials from impact and environmental degradation while allowing transmission of the appropriate wavelengths of the solar spectrum. Further, multiple photovoltaic cells can be arranged into a photovoltaic module. Photovoltaic device can describe either a cell, a module, or both.

[0019] As used herein, the term "adjacent" can be defined as being in close proximity. Adjacent structures may or may not be in physical contact with each other. Adjacent structures can have other layers and/or structures disposed between them.

[0020] One embodiment is a glass comprising, in weight percent:

50 to 72 percent SiO_2 ;

greater than 15 to 25 percent Al_2O_3 ;

0 to 10 percent B_2O_3 ;

10 to 25 percent total M_2O ; and
greater than 0 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0021] Another embodiment is a glass comprising, in weight percent:

50 to 72 percent SiO_2 ;
10 to 25 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
0.5 to less than 14 percent RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0022] Another embodiment is a photovoltaic device comprising, a glass comprising, in weight percent:

50 to 72 percent SiO_2 ;
10 to 25 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
greater than 0 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0023] In another embodiment, the photovoltaic device comprises a glass consisting essentially of, in weight percent:

50 to 72 percent SiO_2 ;
10 to 25 percent Al_2O_3 ;

0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
greater than 0 to 25 percent total RO ;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0024] The photovoltaic device can comprise any of the described embodiments of the disclosed glasses. The glass can be in the form of a sheet and be either the substrate or superstrate or both of the photovoltaic device.

[0025] In another embodiment, the glass comprises, in weight percent:

50 to 72 percent SiO_2 ;
10 to 25 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
greater than 0 to 25 percent total RO ;

wherein, M is an alkali metal selected from Na, Li, Rb, and Cs wherein the glass comprises substantially no K_2O and wherein the glass comprises 9 to 17 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0026] In another embodiment, the glass consists essentially of, in weight percent:

50 to 72 percent SiO_2 ;
10 to 25 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
greater than 0 to 25 percent total RO ;

wherein, M is an alkali metal selected from Na, Li, Rb, and Cs wherein the glass comprises substantially no K_2O and

wherein the glass comprises 9 to 17 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0027] In one embodiment, the glass comprises, in weight percent:

- 50 to 59 percent SiO_2 ;
- 10 to 25 percent Al_2O_3 ;
- 0 to 10 percent B_2O_3 ;
- 10 to 25 percent total M_2O ; and
- 2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0028] In another embodiment, the glass comprises, in weight percent:

- 54 to 59 percent SiO_2 ;
- 10 to 21 percent Al_2O_3 ;
- 0 to 10 percent B_2O_3 ;
- 10 to 25 percent total M_2O ; and
- 2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0029] According to another embodiment, the glass comprises, in weight percent:

- 54 to 59 percent SiO_2 ;
- 17 to 21 percent Al_2O_3 ;
- 0 to 10 percent B_2O_3 ;
- 10 to 25 percent total M_2O ; and
- 2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0030] According to another embodiment, the glass comprises, in weight percent:

52 to 59 percent SiO_2 ;
20 to 25 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0031] In another embodiment, the glass consists essentially of, in weight percent:

54 to 59 percent SiO_2 ;
17 to 21 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na_2O ; and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0032] In a further embodiment, the glass comprises, in weight percent:

56 to 58 percent SiO_2 ;
17 to 21 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and

2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0033] In another embodiment, the glass consists essentially of, in weight percent:

50 to 59 percent SiO₂;

10 to 25 percent Al₂O₃;

0 to 10 percent B₂O₃;

10 to 25 percent total M₂O; and

2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0034] In another embodiment, the glass consists essentially of, in weight percent:

52 to 59 percent SiO₂;

20 to 25 percent Al₂O₃;

0 to 10 percent B₂O₃;

10 to 25 percent total M₂O; and

2 to 25 percent total RO;

wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

[0035] In yet another embodiment, the glass consists essentially of, in weight percent:

56 to 58 percent SiO₂;

17 to 21 percent Al₂O₃;

0 to 10 percent B₂O₃;

10 to 25 percent total M_2O ; and
2 to 25 percent total RO ;

wherein, M is an alkali metal selected from Na , K , Li , Rb , and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg , Ca , Ba , and Sr .

[0036] In one embodiment, the glass consists essentially of, in weight percent:

54 to 59 percent SiO_2 ;
10 to 21 percent Al_2O_3 ;
0 to 10 percent B_2O_3 ;
10 to 25 percent total M_2O ; and
2 to 25 percent total RO ;

wherein, M is an alkali metal selected from Na , K , Li , Rb , and Cs and wherein the glass comprises at least 9 weight percent Na_2O , and wherein, R is an alkaline earth metal selected from Mg , Ca , Ba , and Sr .

[0037] According to one embodiment, the glass comprises 55 to 72 weight percent SiO_2 , for example, 51 to 72 weight percent SiO_2 , for example, 52 to 72 weight percent SiO_2 , for example, 53 to 72 weight percent SiO_2 , for example, 54 to 72 weight percent SiO_2 , for example, 55 to 72 weight percent SiO_2 , for example, 56 to 72 weight percent SiO_2 , for example, 57 to 72 weight percent SiO_2 , for example, 58 to 72 weight percent SiO_2 , for example, 59 to 72 weight percent SiO_2 , for example, 60 to 72 weight percent SiO_2 . In one embodiment, the glass comprises 55 to 72 weight percent SiO_2 and comprises greater than 15 to 25 weight percent Al_2O_3 .

[0038] The glass, in one embodiment, is rollable. The glass, in one embodiment, is down-drawable. The glass can be slot drawn or fusion drawn, for example. According to another embodiment the glass can be float formed.

[0039] The glass, according to one embodiment, comprises less than 8 weight percent K_2O , for example, less than 7 weight percent K_2O , for example, less than 6 weight percent K_2O , less than 5 weight percent K_2O , less than 4 weight percent K_2O , for example, less than 3 weight percent K_2O . The glass, according to some embodiments, comprises substantially no K_2O , for example, is substantially K_2O free.

[0040] According to one embodiment, the glass comprises less than 4 weight percent K_2O , and the glass has a strain point of $535^\circ C$ or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and has a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0041] The glass, according to one embodiment, comprises less than 4 weight percent K_2O and less than 2.5 weight percent MgO . In one embodiment, the glass comprises less than 4 weight percent K_2O and less than 2.5 weight percent MgO and has a strain point of $535^\circ C$ or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0042] Some embodiments of the disclosed glasses have the advantage of a high Na_2O content, making them capable of delivering more Na to a deposited CIGS layer during fabrication of photovoltaic cells - which in turn is expected to lead to higher CIGS cell efficiency. Finally, as Na outdiffusion during CIGS deposition/crystallization may possibly be impeded by the presence of another alkali, the fact that some examples are K-free or have substantially reduced K_2O content may provide yet another advantage.

[0043] The glass can further comprise 3 weight percent or less, for example, 0 to 3 weight percent, for example, greater than 0 to 3 weight percent, for example, 1 to 3 weight percent of TiO_2 , MnO , ZnO , Nb_2O_5 , MoO_3 , Ta_2O_5 , WO_3 , ZrO_2 , Y_2O_3 , La_2O_3 , HfO_2 , CdO , SnO_2 , Fe_2O_3 , CeO_2 , As_2O_3 , Sb_2O_3 , Cl , Br , or combinations thereof. The glass, in one embodiment, comprises 3 weight percent or less, for example, 0 to 3 weight percent, for example, greater than 0 to 3 weight percent, for example, 1 to 3 weight percent of TiO_2 or ZrO_2 .

[0044] As mentioned above, the glasses, according some embodiments, comprise 0 to 10 weight percent, for example, 1 to 8 weight percent or for example, greater than 0 to 10 weight percent B_2O_3 , for example, 0.5 to 10 weight percent B_2O_3 , for example 1 to 10 weight percent B_2O_3 . B_2O_3 is added to the glass to reduce melting temperature, to decrease liquidus temperature, to increase liquidus viscosity, and to improve mechanical durability relative to a glass containing no B_2O_3 . In one embodiment, the glass is substantially B_2O_3 free.

[0045] The glass, according to one embodiment, comprises greater than 0 to 25 percent RO, for example, 0.5 to 25 percent RO, for example, 1 to 25 percent RO wherein, R is an alkaline earth metal. The glass, according to one embodiment, comprises less than 14 percent RO, for example, 13 or less, for example, 12 or less, for example, 11 or less, for example, 10 or less, for example, 9 or less, for example, 8 or less. In one embodiment, the glass comprises 0.5 to less than 14 percent RO, for example, 0.5 to 13 percent RO. The glass, according to one embodiment, comprises greater than 2 to 25 percent RO, for example, wherein R is an alkaline earth metal.

[0046] According to one embodiment, the glass comprises 0.5 to less than 14 percent RO, and the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of $50 \times$

10^{-7} or greater, and has a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0047] The glass, according to some embodiments, comprises less than 4.0 weight percent MgO, for example, less than 3.0 weight percent MgO, for example, less than 2.5 weight percent MgO, less than 2.0 weight percent MgO. The glass can comprise, for example, 0 to 4 weight percent MgO, for example, greater than 0 to 4 weight percent MgO, for example, greater than 0 to 3 weight percent MgO, for example, greater than 0 to 2.5 weight percent MgO, for example, 0.2 to 4 weight percent MgO, for example, 0.2 to 3 weight percent MgO, for example, 0.2 to 2.5 weight percent MgO. According to another embodiment, the glass comprises, for example, 1 to 3 weight percent MgO. MgO can be added to the glass to reduce melting temperature and to increase strain point. It can disadvantageously lower CTE relative to other alkaline earths (e.g., CaO, SrO, BaO), and so other adjustments may be made to keep the CTE within the desired range. Examples of suitable adjustments include increase SrO at the expense of CaO, increasing alkali oxide concentration, and replacing a smaller alkali oxide (e.g., Na₂O) in part with a larger alkali oxide (e.g., K₂O).

[0048] According to one embodiment, the glass comprises less than 2.5 weight percent MgO, and the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and has a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0049] According to another embodiment, the glass is substantially free of BaO. For example, the content of BaO

can be 0.05 weight percent or less, for example, zero weight percent.

[0050] In some embodiments, the glass is substantially free of Sb_2O_3 , As_2O_3 , or combinations thereof, for example, the glass comprises 0.05 weight percent or less of Sb_2O_3 or As_2O_3 or a combination thereof. For example, the glass can comprise zero weight percent of Sb_2O_3 or As_2O_3 or a combination thereof.

[0051] The glasses, in some embodiments, comprise 2 to 4 weight percent CaO. Relative to alkali oxides or SrO, CaO contributes to higher strain point, lower density, and lower melting temperature. It is a primary component of certain possible devitrification phases, particularly anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), and this phase has complete solid solution with an analogous sodium phase, albite ($\text{NaAlSi}_3\text{O}_8$). High Na and Ca contents taken alone can cause liquidus temperatures to be unacceptably high. However, the chemical sources for CaO include limestone, a very inexpensive material, so to the extent that high volume and low cost are factors, it is typically useful to make the CaO content as high as can be reasonably achieved relative to other alkaline earth oxides.

[0052] The glasses can comprise, in some embodiments, 0.2 to 4 weight percent SrO, for example, 0.5 to 4 weight percent, for example 1 to 4, for example, 2 to 4 weight percent SrO. In certain embodiments, the glass contains no deliberately batched SrO, though it may of course be present as a contaminant in other batch materials. SrO contributes to higher coefficient of thermal expansion, and the relative proportion of SrO and CaO can be manipulated to improve liquidus temperature, and thus liquidus viscosity. SrO is not as effective as CaO or MgO for improving strain point, and replacing either of these with SrO tends to cause the melting temperature to increase.

[0053] Also as mentioned above, the glasses, according to some embodiments, include 10 to 25 percent M_2O , wherein M is one of the alkali cations Li, Na, K, Rb and Cs. The alkali cations raise the CTE steeply, but also lower the strain point and, depending upon how they are added, increase melting temperatures. The least effective alkali oxide for CTE is Li_2O , and the most effective alkali oxide is Cs_2O . As noted above, sodium can participate in one of the possible devitrification phases of the inventive glasses, and while adjustments in other components can be used to counteract this, e.g., changing the $CaO/(CaO+SrO)$ ratio, this tendency may make it advantageous to replace sodium with other alkalis, or to use a mix of alkalis instead of sodium alone. If high volume and low cost are important, then it is desirable to as much as possible confine the alkali oxides to Na_2O and K_2O or combinations thereof.

[0054] According to some embodiments, the glass comprises 9 to 17 percent Na_2O , for example, 10 to 16 percent Na_2O . In one embodiment, the glass comprises 9 weight percent or more Na_2O , for example, 9 to 12 weight percent Na_2O .

[0055] The glass, according to some embodiments, is down-drawable; that is, the glass is capable of being formed into sheets using down-draw methods such as, but not limited to, fusion draw and slot draw methods that are known to those skilled in the glass fabrication arts. Such down-draw processes are used in the large-scale manufacture of ion-exchangeable flat glass.

[0056] The glass, according to one embodiment, comprises 10 to 30 weight percent $Al_2O_3 + B_2O_3$.

[0057] The glass, according to one embodiment, comprises 20 to 30 weight percent $Al_2O_3 + B_2O_3$.

[0058] The glass, according to one embodiment, comprises 21 to 25 weight percent Al_2O_3 .

[0059] The glass, according to one embodiment, comprises 10 to 21 weight percent $\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$.

[0060] The glass, according to one embodiment, comprises 17 to 21 weight percent $\text{Al}_2\text{O}_3 + \text{B}_2\text{O}_3$.

[0061] The glass, according to one embodiment, comprises greater than 15 to 25 weight percent Al_2O_3 , for example, 16 or greater to 25 weight percent, for example, 16 to 24 weight percent Al_2O_3 or, for example, 17 to 25 weight percent Al_2O_3 , for example, 17 to 21 weight percent Al_2O_3 .

[0062] According to one embodiment, the glass comprises greater than 15 to 25 weight percent Al_2O_3 , has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0063] The glass, according to one embodiment, comprises greater than 15 to 25 percent Al_2O_3 and comprises 0.5 to less than 14 percent RO. In one embodiment, the glass comprises greater than 15 to 25 percent Al_2O_3 , 0.5 to less than 14 percent RO, has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater, for example, 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0064] The glass, according to one embodiment, comprises:

- 9 to 12 percent Na_2O ;
- 2 to 8 percent K_2O ;
- 2 to 8 percent CaO ;
- 2 to 4 percent SrO ; and

1 to 3 percent MgO.

[0065] The fusion draw process uses a drawing tank that has a channel for accepting molten glass raw material. The channel has weirs that are open at the top along the length of the channel on both sides of the channel. When the channel fills with molten material, the molten glass overflows the weirs. Due to gravity, the molten glass flows down the outside surfaces of the drawing tank. These outside surfaces extend down and inwardly so that they join at an edge below the drawing tank. The two flowing glass surfaces join at this edge to fuse and form a single flowing sheet. The fusion draw method offers the advantage that, since the two glass films flowing over the channel fuse together, neither outside surface of the resulting glass sheet comes in contact with any part of the apparatus. Thus, the surface properties are not affected by such contact.

[0066] The slot draw method is distinct from the fusion draw method. Here the molten raw material glass is provided to a drawing tank. The bottom of the drawing tank has an open slot with a nozzle that extends the length of the slot. The molten glass flows through the slot/nozzle and is drawn downward as a continuous sheet therethrough and into an annealing region. Compared to the fusion draw process, the slot draw process provides a thinner sheet, as only a single sheet is drawn through the slot, rather than two sheets being fused together, as in the fusion down-draw process.

[0067] In order to be compatible with down-draw processes, the aluminoborosilicate glass described herein has a high liquidus viscosity. In one embodiment, the glass has a liquidus viscosity of 50,000 poise or greater, for example, 150,000 poise or greater, for example, 200,000 poise or greater, for example, 250,000 poise or greater, for example, 300,000 poise

or greater, for example, 350,000 poise or greater, for example, 400,000 poise or greater, for example, greater than or equal to 500,000 poise. The liquidus viscosities of some exemplary glasses could be closely correlated with the difference between the liquidus temperature and the softening point.

[0068] In one embodiment, the glass has a strain point of 535°C or greater, for example, 540°C or greater, for example, a strain point of 560°C or greater, for example, a strain point of 570°C or greater, for example, 580°C or greater. In some embodiments, the glass has a coefficient of thermal expansion of 50×10^{-7} or greater, for example, 60×10^{-7} or greater, for example, 70×10^{-7} or greater, for example, 80×10^{-7} or greater. In one embodiment, the glass has a coefficient of thermal expansion of from 50×10^{-7} to 90×10^{-7} .

[0069] In one embodiment, the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and has a liquidus viscosity of 150,000 poise or greater. The glass having these properties, in one embodiment, is fusion formable.

[0070] In one embodiment, the glass has a coefficient of thermal expansion of 50×10^{-7} or greater and a strain point of 535°C or greater. In one embodiment, the glass has a coefficient of thermal expansion of 50×10^{-7} or greater and a strain point of 540°C or greater. In one embodiment, the glass has a coefficient of thermal expansion of 60×10^{-7} or greater and a strain point of 560°C or greater. In one embodiment, the glass has a coefficient of thermal expansion of 60×10^{-7} or greater and a strain point of 580°C or greater. In one embodiment, the glass has a coefficient of thermal expansion of 50×10^{-7} or greater and a strain point of 570°C or greater. In one embodiment, the glass has a coefficient of

thermal expansion of 70×10^{-7} or greater and a strain point of 570°C or greater. Embodiments of the described glasses can have several combinations of properties within the disclosed ranges. It should be appreciated that all of the possible combinations are not listed herein.

[0071] According to one embodiment, the glass is ion exchanged in a salt bath comprising one or more salts of alkali ions. The glass can be ion exchanged to change its mechanical properties. For example, smaller alkali ions, such as lithium or sodium, can be ion-exchanged in a molten salt containing one or more larger alkali ions, such as sodium, potassium, rubidium or cesium. If performed at a temperature well below the strain point for sufficient time, a diffusion profile will form in which the larger alkali moves into the glass surface from the salt bath, and the smaller ion is moved from the interior of the glass into the salt bath. When the sample is removed, the surface will go under compression, producing enhanced toughness against damage. Such toughness may be desirable in instances where the glass will be exposed to adverse environmental conditions, such as photovoltaic grids exposed to hail. A large alkali already in the glass can also be exchanged for a smaller alkali in a salt bath. If this is performed at temperatures close to the strain point, and if the glass is removed and its surface rapidly reheated to high temperature and rapidly cooled, the surface of the glass will show considerable compressive stress introduced by thermal tempering. This will also provide protection against adverse environmental conditions. It will be clear to one skilled in the art that any monovalent cation can be exchanged for alkalis already in the glass, including copper, silver, thallium, etc., and these also provide attributes of potential

value to end uses, such as introducing color for lighting or a layer of elevated refractive index for light trapping.

[0072] According to another embodiment, the glass can be float formed as known in the art of float forming glass.

[0073] In one embodiment, the glass is in the form of a sheet. The glass in the form of a sheet can be thermally tempered.

[0074] In one embodiment, an Organic Light Emitting Diode device comprises the glass in the form of a sheet.

[0075] The glass, according to one embodiment, is transparent. The glass sheet, according to one embodiment, is transparent.

[0076] **Figure 1** is an illustration of features **100** of a photovoltaic device according to one embodiment. In one embodiment, a photovoltaic device comprises the glass in the form of a sheet. The photovoltaic device can comprise more than one of the glass sheets, for example, as a substrate and/or as a superstrate. In one embodiment, the photovoltaic device comprises the glass sheet **10** as a substrate and/or superstrate, a conductive material **12** located adjacent to the substrate, and an active photovoltaic medium **16** adjacent to the conductive material. In one embodiment, the active photovoltaic medium comprises a copper indium gallium diselenide (CIGS) layer. In one embodiment, the active photovoltaic medium comprises a cadmium telluride (CdTe) layer. In one embodiment, the active photovoltaic medium is a CIGS layer. In one embodiment, the active photovoltaic medium is a cadmium telluride (CdTe) layer.

[0077] The photovoltaic device, according to one embodiment, further comprises a barrier layer **14** disposed between the superstrate or substrate and the active photovoltaic medium. In one embodiment, the photovoltaic device further comprises a barrier layer disposed between or adjacent to the superstrate or substrate and a transparent conductive oxide (TCO) layer,

wherein the TCO layer is disposed between or adjacent to the active photovoltaic medium and the barrier layer. A TCO may be present in a photovoltaic device comprising a CdTe functional layer. In one embodiment, the barrier layer is disposed directly on the glass. The barrier layer can effect the migration of alkali ions from the glass into other layers of the device, for example, the active photovoltaic medium, for example, increase, decrease, or meter the migration.

[0078] In one embodiment, the glass sheet is transparent. In one embodiment, the glass sheet as the substrate and/or superstrate is transparent.

[0079] According to some embodiments, the glass sheet has a thickness of 4.0mm or less, for example, 3.5mm or less, for example, 3.2mm or less, for example, 3.0mm or less, for example, 2.5mm or less, for example, 2.0mm or less, for example, 1.9mm or less, for example, 1.8mm or less, for example, 1.5mm or less, for example, 1.1mm or less, for example, 0.5mm to 2.0mm, for example, 0.5mm to 1.1mm, for example, 0.7mm to 1.1mm. Although these are exemplary thicknesses, the glass sheet can have a thickness of any numerical value including decimal places in the range of from 0.1mm up to and including 4.0mm.

[0080] In one embodiment, an electrochromic device comprises the glass in the form of a sheet. The electrochromic device can be, for example, an electrochromic window. In one embodiment, the electrochromic window comprises one or more of the glass sheets, such as in a single, double, or triple pane window.

[0081] The fusion formable glasses of this invention, by virtue of their relatively high strain point, represent advantaged substrate materials for CIGS photovoltaic modules. When manufactured by the fusion process, their superior surface

quality relative to that of float glass may also result in further improvements to the photovoltaic module making process. Advantageous embodiments of this invention are characterized by liquidus viscosity in excess of 400,000 poise, thereby enabling the fabrication of the relatively thick glass sheets that may be advantageous for some module manufacturers.

Examples

[0082] The following is an example of how to fabricate a sample of an exemplary glass, according to one embodiment of the invention, as shown in Table 1. This composition corresponds to Example number 1 shown in Table 3.

oxide	mol%
SiO ₂	63.64
Al ₂ O ₃	13.00
MgO	3.14
CaO	3.15
SrO	1.56
Na ₂ O	11.32
K ₂ O	4.09
SnO ₂	0.10

Table 1.

In some embodiments, the total does not add up to 100%, since certain tramp elements are present at non-negligible concentrations.

[0083] Batch materials, as shown in Table 2 were weighed and added to a 4 liter plastic container:

Batch Components	batch weight
sand	1322.67
alumina	473.03
Magnesia	45.22
Limestone	115.32
Strontium carbonate	83.32
Soda ash	425.20
Potassium carbonate	202.74

10% SnO ₂ and 90% sand	52.8
-----------------------------------	------

Table 2.

[0084] It should be appreciated that in the batch, limestone, depending on the source can contain tramp elements and/or vary amounts of one or more oxides, for example, MgO and/or BaO. The sand is advantageously beneficiated so that at least 80% by mass passes 60 mesh, for example 80 mesh, for example 100 mesh. The SnO₂ added, in this example, was pre-mixed with sand at a level of 10% by weight so as to ensure homogeneous mixing with the other components. The bottle containing the batch materials was mounted to a tumbler and the batch materials were mixed so as to make a homogeneous batch and to break up soft agglomerates. The mixed batch was transferred to a 1800cc platinum crucible and placed into a high-temperature ceramic backer. The platinum in its backer was loaded into a glo-bar furnace idling at a temperature of 1630°C. After 16 hours, the crucible+backer was removed and the glass melt was poured onto a cold surface, such as a steel plate, to form a patty, and then transferred to an annealer held at a temperature of 640°C. The glass patty was held at the annealer temperature for 2 hours, then cooled at a rate of 1°C per minute to room temperature.

[0085] Table 3, Table 4, Table 5, Table 6, Table 7, Table 8, Table 9, Table 10, Table 11, and Table 12 show exemplary glasses, according to embodiments of the invention, and made according to the above example. Properties data for some exemplary glasses are also shown in Table 3, Table 4, Table 5, Table 6, Table 7, Table 8, Table 9, Table 10, Table 11, and Table 12. In the Tables T_{str} (°C) is the strain point which is the temperature when the viscosity is equal to $10^{14.7}$ P as measured by beam bending or fiber elongation. T_{ann} (°C) is the annealing point which is the temperature when the viscosity is

equal to $10^{13.18}$ P as measured by beam bending or fiber elongation. $T_s(^{\circ}\text{C})$ is the softening point which is the temperature when the viscosity is equal to $10^{7.6}$ P as measured by beam bending or fiber elongation. $\alpha(10^{-7}/^{\circ}\text{C})$ or $a(10^{-7}/^{\circ}\text{C})$ in the Tables is the coefficient of thermal expansion (CTE) which is the amount of dimensional change from either 0 to 300°C or 25 to 300°C depending on the measurement. CTE is typically measured by dilatometry. $\rho(\text{g}/\text{cc})$ is the density which is measured with the Archimedes method (ASTM C693). $T_{200}(^{\circ}\text{C})$ is the two-hundred Poise (P) temperature. This is the temperature when the viscosity of the melt is 200P as measured by HTV (high temperature viscosity) measurement which uses concentric cylinder viscometry. $T_{\text{liq}}(^{\circ}\text{C})$ is the liquidus temperature. This is the temperature where the first crystal is observed in a standard gradient boat liquidus measurement (ASTM C829-81). Generally this test is 72 hours but can be as short as 24 hours to increase throughput at the expense of accuracy (shorter tests could underestimate the liquidus temperature). $\eta_{\text{liq}}(^{\circ}\text{C})$ is the liquidus viscosity. This is the viscosity of the melt corresponding to the liquidus temperature.

Example	1	2	3	4	5	6
Composition (mol%)						
Na ₂ O	11.32	10.30	12.30	11.32	11.32	11.32
K ₂ O	4.09	5.11	3.11	3.09	2.09	4.09
MgO	3.14	3.14	3.14	3.54	3.94	3.94
CaO	3.14	3.14	3.14	3.54	3.94	3.94
SrO	1.57	1.57	1.57	1.77	1.97	1.97
Al ₂ O ₃	13.00	13.00	13.00	13.00	13.00	12.00
SiO ₂	63.63	63.63	63.63	63.63	63.63	62.63
SnO ₂	0.10	0.10	0.10	0.10	0.10	0.10
Composition (wt%)						
Na ₂ O	10.40	9.43	11.40	10.50	10.50	10.50
K ₂ O	5.74	7.13	4.38	4.36	2.96	5.78

MgO	1.89	1.88	1.89	2.14	2.39	2.38
CaO	2.63	2.62	2.64	2.98	3.33	3.32
SrO	2.42	2.41	2.43	2.75	3.07	3.06
Al ₂ O ₃	19.70	19.60	19.80	19.80	19.90	18.30
SiO ₂	56.90	56.60	57.20	57.20	57.50	56.40
SnO ₂	0.22	0.22	0.23	0.23	0.23	0.23
T _{str} (°C)	595	591	583	593	603	570
T _{ann} (°C)	644	642	635	646	656	621
α (10 ⁻⁷ /°C)	87.9	90.2	88.2	83.6	80.5	89.8
ρ (gm/cc)	2.513	2.509	2.512	2.519	2.527	2.534
T ₂₀₀ (°C)	1630					
T _{liq} (°C)	1025	1045	1025	1055	1090	1040
η_{liq} (kp)	546					

Table 3.

Example	7	8	9	10	11
Composition (mol%)					
Na ₂ O	11.32	11.32	11.32	11.09	10.87
K ₂ O	4.09	4.09	4.09	4.01	3.93
MgO	3.14	3.14	3.14	3.08	3.01
CaO	3.15	3.15	3.15	3.09	3.02
SrO	1.56	1.56	1.56	1.53	1.5
Al ₂ O ₃	11.00	9.00	7.00	12.74	12.48
SiO ₂	63.63	63.63	63.63	62.36	61.09
SnO ₂	0.10	0.10	0.10	0.10	0.10
B ₂ O ₃	2.00	4.00	6.00	2.00	4.00
(RO+R ₂ O)/Al ₂ O ₃	2.11	2.58	3.32	1.79	1.79
R ₂ O/RO	1.96	1.96	1.96	1.96	1.97
(RO+R ₂ O)/Al ₂ O ₃ +B ₂ O ₃	1.79	1.79	1.79	1.55	1.35
R ₂ O/Al ₂ O ₃ +B ₂ O ₃	1.19	1.19	1.19	1.02	0.90
Composition (wt%)					
Na ₂ O	10.51	10.61	10.72	10.19	9.98
K ₂ O	5.79	5.85	5.91	5.62	5.51
MgO	1.90	1.92	1.94	1.85	1.80
CaO	2.66	2.68	2.71	2.58	2.52
SrO	2.43	2.45	2.48	2.36	2.31
Al ₂ O ₃	16.86	13.93	10.94	19.32	18.91
SiO ₂	57.47	58.04	58.61	55.73	54.55
SnO ₂	0.23	0.23	0.23	0.22	0.22
B ₂ O ₃	2.09	4.23	6.41	2.07	4.14
T _{str} (°C)	550	539	537	566	550
T _{ann} (°C)	595	582	579	614	595
α (10 ⁻⁷ /°C)	90.4	87.7	83.6	90.2	87.5
ρ (gm/cc)	2.503	2.500	2.494	2.507	2.494

T_{200} (°C)	1574			1583	
T_{liq} (°C)					
η_{liq} (kP)	389			323	

Table 4.

Example	12	13	14	15	16	17	18	19
Composition (mol%)								
Na ₂ O	10.93	11.06	11.19	11.19	11.06	10.93	10.93	10.93
K ₂ O	3.95	3.99	4.04	4.04	3.99	3.95	3.95	3.95
MgO	0	0	0	3.11	3.07	3.03	0	0
CaO	7.59	7.68	7.77	3.11	3.07	3.04	7.59	7.59
SrO	0	0	0	1.55	1.54	1.52	0	0
B ₂ O ₃	0	0	0	0	0	0	1.00	2.00
Al ₂ O ₃	16.00	15.00	14.00	14.00	15.00	16.00	16.00	16.00
SiO ₂	61.43	62.17	62.9	62.9	62.17	61.43	60.43	59.43
SnO ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Composition (wt%)								
Na ₂ O	9.92	10.10	10.30	10.20	10.10	9.88	9.90	9.89
K ₂ O	5.46	5.55	5.66	5.63	5.53	5.44	5.46	5.45
MgO	0	0	0	1.86	1.82	1.79	0	0
CaO	6.25	6.36	6.47	2.58	2.53	2.49	6.24	6.23
SrO	0	0	0	2.38	2.35	2.30	0	0
B ₂ O ₃	0	0	0	0	0	0	1.02	2.04
Al ₂ O ₃	23.90	22.60	21.20	21.10	22.50	23.90	23.90	23.90
SiO ₂	54.20	55.20	56.10	55.90	55.00	54.00	53.20	52.30
SnO ₂	0.22	0.22	0.22	0.22	0.22	0.22	0.22	0.22
T_{str} (°C)	630	618	604	602	615	628	607	588
T_{ann} (°C)	684	669	655	653	669	683	659	639
α (10 ⁻⁷ /°C)	85.9	87.9	89	86.7	85.5	85.2	86.2	86.7
ρ (gm/cc)	2.502	2.505	2.504	2.513	2.513	2.515	2.496	2.499
T_{200} (°C)	1622	1622		1646	1645	1659	1613	1604
T_{liq} (°C)	1055	1085		1035	1075	1120	1035	1025
η_{liq} (kP)	448	194		729	339	237	539	427

Table 5.

Example	20	21	22	23	24	25	26	27
Composition (mol%)								
Na ₂ O	14.80	12.20	14.80	14.80	14.80	14.80	14.00	14.00
K ₂ O	0.90	2.90	0	0	0.50	0	0	0

MgO	3.60	1.30	4.50	3.60	3.60	3.60	0	0
CaO	1.90	5.70	1.90	2.80	1.90	1.90	8.00	5.00
SrO	0	0	0	0	0.40	0.90	0	0
ZnO	0	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	0	0	0	0
Al ₂ O ₃	10.80	14.20	10.80	10.80	10.80	10.80	10.00	11.00
TiO ₂	0	0	0	0	0	0	0	0
ZrO ₂	0	0	0	0	0	0	0	0
SiO ₂	67.90	63.60	67.90	67.90	67.90	67.90	67.90	69.90
SnO ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Composition (wt%)								
Na ₂ O	14.20	11.30	14.30	14.30	14.20	14.20	13.50	13.30
K ₂ O	1.32	4.09	0	0	0.73	0	0	0
MgO	2.25	0.78	2.83	2.26	2.25	2.25	0	0
CaO	1.65	4.78	1.67	2.45	1.65	1.65	6.98	4.33
SrO	0	0	0	0	0.64	1.44	0	0
ZnO	0	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	0	0	0	0
Al ₂ O ₃	17.10	21.70	17.20	17.20	17.10	17.10	15.90	17.30
TiO ₂	0	0	0	0	0	0	0	0
ZrO ₂	0	0	0	0	0	0	0	0
SiO ₂	63.30	57.20	63.70	63.60	63.20	63.20	63.50	64.80
SnO ₂	0.23	0.23	0.24	0.23	0.23	0.23	0.23	0.23
T _{str} (°C)	582	604	586	581	579	578	573	583
T _{ann} (°C)	632	658	639	632	629	629	622	636
T _s								
α (10 ⁻⁷ /°C)	84.6	86.6	82.3	83	80.1	83.8	81	78.9
ρ (gm/cc)	2.451	2.489	2.45	2.452	2.461	2.469	2.489	2.455
T ₂₀₀ (°C)	1652	1646	1633	1623	1631	1635		1656
T _{liq} (°C)	990	1025	1040	1040	985	1010	1130	1070
h _{liq} (kP)	765	771	360	261	558	552		157

Table 6.

Example	28	29	30	31	32	33	34	35
Composition (mol%)								
Na ₂ O	14.00	14.80	14.00	14.00	11.50	12.50	14.80	14.00
K ₂ O	0	0	0	0	3.9	3.9	0	0
MgO	2.00	2.75	0	2.00	0	0	3.60	0
CaO	2.00	1.45	4.00	2.00	7.60	7.60	1.90	0
SrO	1.00	0.70	0	1.00	0	0	0.90	5.00

ZnO	0	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	0	0	0	0
Al ₂ O ₃	11.00	12.30	12.00	11.00	16.00	16.00	10.80	11.00
TiO ₂	0	0	0	2.00	0	0	0	0
ZrO ₂	0	0	0	0	0	0	1.50	0
SiO ₂	69.90	67.90	69.90	67.90	60.90	59.90	66.40	69.90
SnO ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Composition (wt%)								
Na ₂ O	13.30	14.00	13.30	13.20	10.40	11.30	14.00	12.90
K ₂ O	0	0	0	0	5.39	5.39	0	0
MgO	1.24	1.70	0	1.23	0	0	2.22	0
CaO	1.73	1.25	3.44	1.72	6.26	6.26	1.63	0
SrO	1.59	1.11	0	1.58	0	0	1.42	7.70
ZnO	0	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	0	0	0	0
Al ₂ O ₃	17.30	19.20	18.70	17.20	24.00	23.90	16.80	16.70
TiO ₂	0	0	0	2.44	0	0	0	0
ZrO ₂	0	0	0	0	0	0	2.82	0
SiO ₂	64.60	62.50	64.30	62.40	53.70	52.80	60.90	62.40
SnO ₂	0.23	0.23	0.23	0.23	0.22	0.22	0.22	0.22
T _{str} (°C)	585	602	599	595	626	624	614	570
T _{ann} (°C)	639	656	654	641	678	669	662	618
T _s								
α (10 ⁻⁷ /°C)	77.6	79.6	77.8	78.4	88.9	91.4	79	79.1
ρ (gm/cc)	2.458	2.455	2.44	2.479	2.51	2.516	2.516	2.536
T ₂₀₀ (°C)	1681	1682	1725				1605	
T _{liq} (°C)	1030	1040	1040	1035	1080	1110	1010	1060
η_{liq} (kP)	536	790	848				910	

Table 7.

Example	36	37	38	39	40	41	42	43
Composition (mol%)								
Na ₂ O	14.00	16.00	14.00	13.00	13.00	13.00	13.00	13.00
K ₂ O	0	0	0	0	0	0	0	0
MgO	0	5.00	4.50	4.00	3.50	3.50	3.00	5.90
CaO	0	0	0	4.00	3.50	3.50	3.00	0
SrO	0	0	0	0	0	0	0	0
ZnO	5.00	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	1.00	0	0	0
Al ₂ O ₃	11.00	9.00	8.20	10.00	9.00	10.00	9.00	8.08

TiO ₂	0	0	0	0	0	0	0	0
ZrO ₂	0	0	0	0	0	0	0	0
SiO ₂	69.90	70.00	73.50	69.00	70.00	70.00	72.00	73.00
SnO ₂	0.10	0.10	0.10	0.10	0.10	0.10	0.10	0.10
Composition (wt%)								
Na ₂ O	13.10	15.61	13.70	12.60	12.64	12.58	12.64	12.81
K ₂ O	0	0	0	0	0	0	0	0
MgO	0	3.18	2.87	2.53	2.22	2.21	1.9	3.81
CaO	0	0	0	3.52	3.09	3.08	2.65	0
SrO	0	0	0	0	0	0	0	0
ZnO	6.16	0	0	0	0	0	0	0
B ₂ O ₃	0	0	0	0	1.11	0	0	0
Al ₂ O ₃	17.00	14.49	13.24	16.00	14.44	15.97	14.44	13.14
TiO ₂	0	0	0	0	0	0	0	0
ZrO ₂	0	0	0	0	0	0	0	0
SiO ₂	63.50	66.43	69.92	65.06	66.22	65.87	68.08	69.95
SnO ₂	0.23	0.24	0.24	0.24	0.24	0.24	0.24	0.24
T _{str} (°C)	617	570	580	600	572	594	578	592
T _{ann} (°C)	671	621	634	650	620	646	631	650
T _s		854	886	880	851	888	878	915
α (10 ⁻⁷ /°C)		82.9	76.6	74.3	75.8	74.1	73	71.5
ρ (gm/cc)	2.497	2.429	2.392	2.457	2.443	2.445	2.432	2.404
T ₂₀₀ (°C)		1641	1731	1641	1637	1664	1678	1687
T _{liq} (°C)	1010	970	985	1105	1050	1090	1050	1030
η _{liq} (kP)		1223	2127	104	177	178	338	668

Table 8.

Example	44	45	46
Composition (mol%)			
Na ₂ O	15.00	15.34	11.90
K ₂ O	0	0	0
MgO	0	0	5.00
CaO	3.40	0.59	0
SrO	0	0	0
ZnO	0	0	0
B ₂ O ₃	0	5.00	2.00
Al ₂ O ₃	11.50	16.03	9.00
TiO ₂	0	0	0
ZrO ₂	0	0	0
SiO ₂	70.00	62.94	72.00

SnO ₂	0.10	0.10	0.10
Composition (wt%)			
Na ₂ O	14.23	14.02	11.6
K ₂ O	0	0	0
MgO	0	0	3.18
CaO	2.93	0.49	0
SrO	0	0	0
ZnO	0	0	0
B ₂ O ₃	0	5.15	2.20
Al ₂ O ₃	18.00	24.17	14.48
TiO ₂	0	0	0
ZrO ₂	0	0	0
SiO ₂	64.57	55.92	68.26
SnO ₂	0.23	0.23	0.23
T _{str} (°C)	589	609	591
T _{ann} (°C)	638	668	645
T _s	876	954	918
α (10 ⁻⁷ /°C)	80	80.7	68.1
ρ (gm/cc)	2.445	2.405	2.395
T ₂₀₀ (°C)			
T _{liq} (°C)	1010	none	1110
h _{liq} (kP)			

Table 9.

Example	47	48	49	50	51	52
Composition (mol%)						
Na ₂ O	14.80	14.85	14.88	14.80	14.80	14.80
MgO	3.60	1.38	0.69	3.85	3.60	3.30
CaO	1.90	3.73	4.86	2.05	1.90	1.75
SrO	0.90	0.35	0.18	1.00	0.90	0.85
Al ₂ O ₃	10.80	13.15	13.58	12.30	12.80	13.30
ZrO ₂	1.00	0	0	0	0	0
SiO ₂	66.90	66.44	65.71	65.90	65.90	65.90
SnO ₂	0.10	0.10	0	0.10	0.10	0.10
Composition (wt%)						
Na ₂ O	14.00	14.00	14.00	14.00	14.00	13.90
MgO	2.23	0.85	0.42	2.38	2.22	2.03
CaO	1.63	3.19	4.14	1.76	1.63	1.49
SrO	1.43	0.55	0.28	1.59	1.43	1.34
Al ₂ O ₃	16.90	20.40	21.00	19.20	20.00	20.70
ZrO ₂	1.89	0	0	0	0	0

SiO ₂	61.60	60.80	59.90	60.70	60.50	60.30
SnO ₂	0.23	0.23	0.23	0.23	0.23	0.23
T _{str} (°C)	607	612	616	606	621	623
T _{ann} (°C)	654	663	666	657	670	675
T _s						
α (10 ⁻⁷ /°C)	79.8	80.5	81.3	79.4	78.8	79.6
ρ (gm/cc)	2.501	2.474	2.479	2.482	2.476	2.474
T ₂₀₀ (°C)	1628			1641		1668
T _{liq} (°C)	1015	1050	1045	1060	1070	1080
η_{liq} (kp)	817			358		475

Table 10.

Example	53	54	55	56	57	58
Composition (mol%)						
Na ₂ O	13.50	14.90	13.19	14.90	15.58	16.93
K ₂ O	0	0	0.98	0	0	0
MgO	0	0	5.68	0	0	0
CaO	4.50	6.00	1.17	2.00	4.92	1.60
SrO	0	0	0.38	0	0	0
ZnO	0	0	0	4.00	0	0
Al ₂ O ₃	12.00	14.00	9.50	14.00	15.34	18.57
ZrO ₂	0	0	0	0	0	0
SiO ₂	70.00	65.00	67.31	65.00	64.09	58.80
SnO ₂	0.10	0	0.10	0.10	0.10	0.01
Composition (wt%)						
Na ₂ O	12.77	13.93	12.87	13.73	14.42	15.25
K ₂ O	0	0	1.46	0	0	0
MgO	0	0	3.62	0	0	0
CaO	3.86	5.09	1.04	1.67	4.14	1.31
SrO	0	0	0.62	0	0	0
ZnO	0	0	0	4.85	0	0
Al ₂ O ₃	18.72	21.60	15.29	21.28	23.44	27.6
ZrO ₂	0	0		0	0	0
SiO ₂	64.38	59.10	63.87	58.23	57.67	51.5
SnO ₂	0.23	0.23	0.23	0.23	0.23	0.23
T _{str} (°C)	613	619	588	623	636	617
T _{ann} (°C)	666	669	637	675	686	675
T _s	911	899	872	924	919	937
α (10 ⁻⁷ /°C)	75.6	81.6	80.1	79.4	82.4	83.1
ρ (gm/cc)	2.449	2.484	2.549	2.519	2.482	2.442
T ₂₀₀ (°C)	1744	1641			1679	1634
T _{liq} (°C)	1040	1050	1000	1035	1040	1050

η_{liq} (kp)	985	521			1927	1279
-------------------	-----	-----	--	--	------	------

Table 11.

Example	59	60	61	62	63	64
Composition (mol%)						
Na ₂ O	12.57	12.27	10.77	11.07	10.82	11.58
K ₂ O	2.30	2.24	2.24	3.44	2.79	2.30
MgO	4.81	4.69	4.69	3.39	3.64	6.20
CaO	2.60	2.00	3.00	3.15	3.15	0.60
SrO	0	1.00	1.50	1.56	1.56	0
ZnO	0	0	0	0	0	0
Al ₂ O ₃	8.70	10.44	10.44	12.15	11.30	7.61
ZrO ₂	0	0	0	0	0	0
SiO ₂	68.82	67.16	67.16	65.13	66.63	71.51
SnO ₂	0.20	0.20	0.20	0.10	0.10	0.20
Composition (wt%)						
Na ₂ O	12.17	11.65	10.20	10.28	10.14	11.32
K ₂ O	3.39	3.24	3.24	4.87	3.99	3.43
MgO	3.04	2.91	2.90	2.05	2.23	3.96
CaO	2.28	1.72	2.58	2.66	2.68	0.53
SrO	0	1.59	2.38	2.43	2.45	0
ZnO	0	0	0	0	0	0
Al ₂ O ₃	13.88	16.36	16.32	18.62	17.48	12.27
ZrO ₂	0	0	0	0	0	0
SiO ₂	64.73	62.01	61.86	58.80	60.74	67.97
SnO ₂	0.47	0.46	0.46	0.23	0.23	0.48
T _{str} (°C)	560	584	598	592	593	571
T _{ann} (°C)	610	634	648	642	644	622
T _s	837.6	866.1	876.6	871.8	876.8	866.8
α (10 ⁻⁷ /°C)	86.5	85.2	81.2	88.3	84.9	82.4
ρ (gm/cc)	2.459	2.483	2.498	2.507	2.500	2.428
T ₂₀₀ (°C)	1629	1641	1650	1630	1663	1677
T _{liq} (°C)	1005	1040	1090	1040	1070	915
η_{liq} (kp)	370	384	143	338	282	4800

Table 12.

[0086] It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit or scope of the invention. Thus, it is intended that the present invention cover the modifications and variations of this

invention provided they come within the scope of the appended claims and their equivalents.

CLAIMS

What is claimed is:

1. A glass comprising, in weight percent:
50 to 72 percent SiO₂;
greater than 15 to 25 percent Al₂O₃;
0 to 10 percent B₂O₃;
10 to 25 percent total M₂O; and
greater than 0 to 25 percent total RO;
wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.
2. The glass according to claim 1, wherein the glass comprises less than 2.5 weight percent MgO.
3. The glass according to claim 2, wherein the glass comprises less than 4 weight percent K₂O.
4. The glass according to claim 2, wherein the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater.
5. The glass according to claim 4, wherein the glass comprises less than 4 weight percent K₂O.
6. The glass according to claim 1, wherein the glass comprises less than 4 weight percent K₂O.
7. The glass according to claim 1, wherein the glass comprises 0.5 to less than 14 weight percent RO.

8. The glass according to claim 7, wherein the glass comprises less than 2.5 weight percent MgO.
9. The glass according to claim 8, wherein the glass comprises less than 4 weight percent K₂O.
10. The glass according to claim 8, wherein the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater.
11. The glass according to claim 10, wherein the glass comprises less than 4 weight percent K₂O.
12. The glass according to claim 7, wherein the glass comprises less than 4 weight percent K₂O.
13. A photovoltaic device comprising the glass according to claim 1.
14. A glass comprising, in weight percent:
 - 50 to 72 percent SiO₂;
 - 10 to 25 percent Al₂O₃;
 - 0 to 10 percent B₂O₃;
 - 10 to 25 percent total M₂O; and
 - 0.5 to less than 14 percent RO;wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

15. The glass according to claim 14, wherein the glass comprises less than 2.5 weight percent MgO.
16. The glass according to claim 15, wherein the glass comprises less than 4 weight percent K₂O.
17. The glass according to claim 15, wherein the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater.
18. The glass according to claim 17, wherein the glass comprises less than 4 weight percent K₂O.
19. The glass according to claim 14, wherein the glass comprises less than 4 weight percent K₂O.
20. A photovoltaic device comprising the glass according to claim 14.
21. A photovoltaic device comprising, a glass comprising, in weight percent:
50 to 72 percent SiO₂;
10 to 25 percent Al₂O₃;
0 to 10 percent B₂O₃;
10 to 25 percent total M₂O; and
greater than 0 to 25 percent total RO;
wherein, M is an alkali metal selected from Na, K, Li, Rb, and Cs and wherein the glass comprises at least 9 weight percent Na₂O, and wherein, R is an alkaline earth metal selected from Mg, Ca, Ba, and Sr.

22. The photovoltaic device according to claim 21, wherein the glass has a strain point of 535°C or greater, a coefficient of thermal expansion of 50×10^{-7} or greater, and a liquidus viscosity of 130,000 poise or greater.
23. The photovoltaic device according to claim 21, wherein the glass comprises greater than 15 to 25 weight percent Al_2O_3 .
24. The photovoltaic device according to claim 21, wherein the glass comprises 55 to 72 weight percent SiO_2 .
25. The photovoltaic device according to claim 24, wherein the glass comprises greater than 15 to 25 weight percent Al_2O_3 .
26. The photovoltaic device according to claim 21, wherein the glass comprises 9 to 17 weight percent Na_2O .
27. The photovoltaic device according to claim 21, wherein the glass comprises 0.5 to less than 14 weight percent RO.
28. The photovoltaic device according to claim 21, wherein the glass comprises greater than 15 to 25 percent Al_2O_3 and comprising 0.5 to less than 14 percent RO.
29. The photovoltaic device according to claim 21, wherein the glass is in the form of a sheet.
30. The photovoltaic device according to claim 29, wherein the glass is in the form of a sheet and is a substrate or a superstrate.

31. The photovoltaic device according to claim 30, comprising an active photovoltaic medium comprising copper indium gallium diselenide or cadmium telluride adjacent to the substrate or superstrate.

32. The photovoltaic device according to claim 31, comprising a barrier layer between the active photovoltaic medium and the substrate or superstrate.

33. The photovoltaic device according to claim 21, wherein the glass comprises less than 2.5 weight percent MgO.

34. The photovoltaic device according to claim 21, wherein the glass comprises less than 4 weight percent K₂O.

35. The photovoltaic device according to claim 21, wherein the glass comprises less than 2.5 weight percent MgO, and less than 4 weight percent K₂O.

1/1

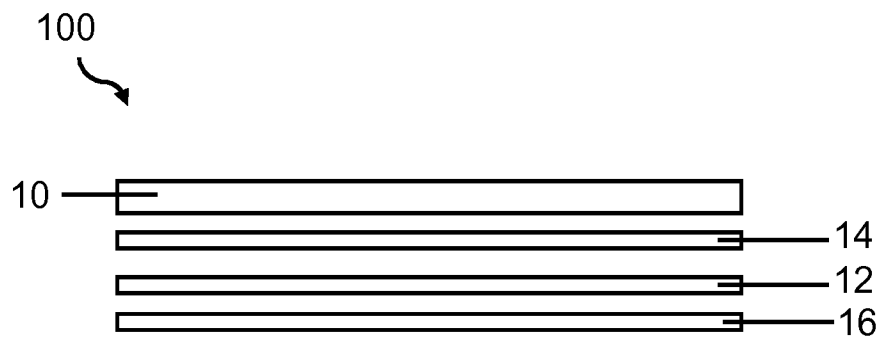


Figure 1

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2010/043027

A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C3/085 C03C3/087 C03C3/091
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2009/019965 A1 (NIPPON ELECTRIC GLASS CO [JP]; MURATA TAKASHI [JP]) 12 February 2009 (2009-02-12) examples	1-35
X,P	& US 2009/197088 A1 (MURATA TAKASHI [JP]) 6 August 2009 (2009-08-06) paragraph [0011] - paragraph [0014] paragraph [0029] - paragraph [0031] paragraph [0082] - paragraph [0083] paragraph [0086] paragraph [0092] paragraph [0095] - paragraph [0097] examples	1-35
X	WO 2008/149858 A1 (NIPPON ELECTRIC GLASS CO [JP]; MURATA TAKASHI [JP]; YAMAZAKI HIROKI [J]) 11 December 2008 (2008-12-11) example 9 ----- -/--	1-35

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

2 November 2010

Date of mailing of the international search report

30/11/2010

Name and mailing address of the ISA/

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040,
Fax: (+31-70) 340-3016

Authorized officer

Somann, Karsten

INTERNATIONAL SEARCH REPORT

International application No

PCT/US2010/043027

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	& US 2010/087307 A1 (MURATA TAKASHI [JP] ET AL) 8 April 2010 (2010-04-08) example 9	1-35
X	JP 2001 226137 A (NIPPON SHEET GLASS CO LTD) 21 August 2001 (2001-08-21) paragraph [0003] examples	1-35
X	JP 2002 003241 A (CENTRAL GLASS CO LTD) 9 January 2002 (2002-01-09) example 5 comparative example 3	1-35
X	US 4 298 389 A (JOHNSON LAUREN K ET AL) 3 November 1981 (1981-11-03) example 7 example As glass	1-35
X	JP 2004 131314 A (ASAHI GLASS CO LTD) 30 April 2004 (2004-04-30) example 9 paragraph [0002] paragraph [0035]	1-35
X	DE 100 05 088 C1 (SCHOTT GLAS [DE]) 15 March 2001 (2001-03-15) the whole document	1-35
X	JP 11 135819 A (MATSUSHITA ELECTRIC IND CO LTD) 21 May 1999 (1999-05-21) the whole document	1-35
X,P	WO 2009/154314 A1 (NIPPON ELECTRIC GLASS CO [JP]; SAWADA MASAHIRO [JP]; NAGAKANE TOMOHIRO) 23 December 2009 (2009-12-23) examples 1,8 the whole document	1-35
X,P	US 2009/325776 A1 (MURATA TAKASHI [JP]) 31 December 2009 (2009-12-31) examples	1-32,34, 35

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2010/043027

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2009019965	A1	12-02-2009	NONE
WO 2008149858	A1	11-12-2008	CN 101679105 A 24-03-2010 JP 2009013052 A 22-01-2009 KR 20100019480 A 18-02-2010 US 2010087307 A1 08-04-2010
JP 2001226137	A	21-08-2001	JP 3702360 B2 05-10-2005
JP 2002003241	A	09-01-2002	NONE
US 4298389	A	03-11-1981	NONE
JP 2004131314	A	30-04-2004	NONE
DE 10005088	C1	15-03-2001	AU 2852401 A 14-08-2001 WO 0156941 A1 09-08-2001 JP 2003525830 T 02-09-2003 US 2003087746 A1 08-05-2003
JP 11135819	A	21-05-1999	NONE
WO 2009154314	A1	23-12-2009	NONE
US 2009325776	A1	31-12-2009	WO 2009157297 A1 30-12-2009 JP 2010030876 A 12-02-2010