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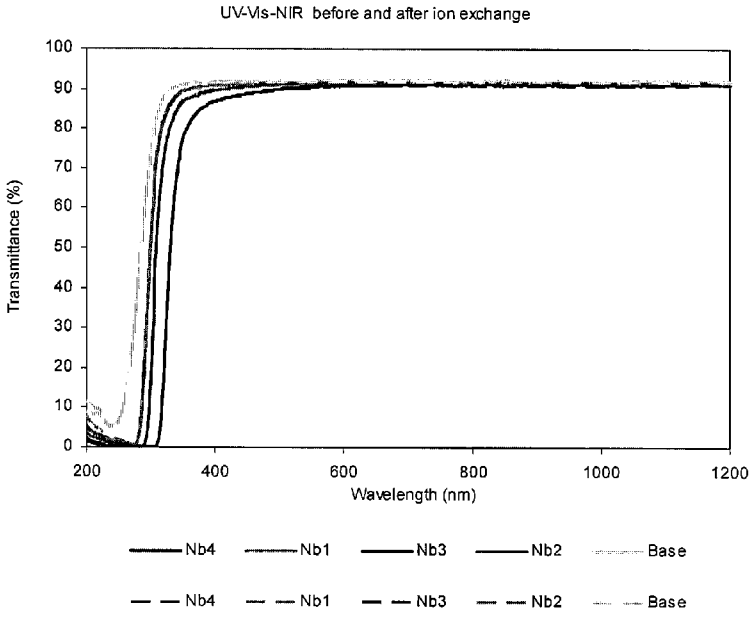
[Continued on next page]

(54) Title: ION EXCHANGEABLE TRANSITION METAL-CONTAINING GLASSES

(57) Abstract: Ion exchangeable glasses that comprise at least one of a transition metal oxide or a rare earth oxide and have compositions that simultaneously promote a surface layer having a high compressive stress and deep depth of layer or, alternatively, reduced ion exchange time.

FIG. 1a



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ION EXCHANGEABLE TRANSITION METAL-CONTAINING GLASSES

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of U.S. Provisional Application Serial No. 61/653,495 filed on May 31, 2012 the content of which is relied upon and incorporated herein by reference in its entirety.

BACKGROUND

[0002] The disclosure relates to ion exchangeable glasses. More particularly, the disclosure relates to ion exchangeable glasses that comprise either transition metals or rare earth metals.

[0001] In applications such as cover plates or windows for portable or mobile electronic communication and entertainment devices, glasses are typically strengthened by either chemical or thermal means.

SUMMARY

[0002] The present disclosure provides glasses that are ion exchangeable. The glasses comprise at least one of a transition metal oxide or a rare earth oxide and have compositions that simultaneously promote a surface layer having a high compressive stress and deep depth of layer or, alternatively, ion exchanged to a given compressive stress or depth of layer in a reduced ion exchange time.

[0003] Accordingly, one aspect of the disclosure is to provide an alkali aluminosilicate glass. The alkali aluminosilicate glass is ion exchangeable and comprises at least 50 mol% SiO_2, Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the at least one alkali metal oxide includes Na_2O, and wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%.

[0004] A second aspect of the disclosure is to provide an alkali aluminosilicate glass. The alkali aluminosilicate glass comprises at least 50 mol% SiO_2, Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the at least one alkali metal oxide includes Na_2O,

wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%. The alkali aluminosilicate glass is ion exchanged and has a surface and a layer under compressive stress extending from the surface to a depth of layer, wherein the compressive stress is at least about 1 GPa and the depth of layer is at least about 20 μm.

[0005] A third aspect of the disclosure is to provide a method of making an ion exchanged alkali aluminosilicate glass. The method comprises providing an alkali aluminosilicate glass, the alkali aluminosilicate glass comprising at least 50 mol% SiO_2, Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the alkali metal oxide includes Na_2O, and wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%; and ion exchanging the alkali aluminosilicate glass for a predetermined time to form a layer under a compressive stress of at least about 1 GPa, the layer extending from s surface of the alkali aluminosilicate glass to a depth of layer.

[0006] These and other aspects, advantages, and salient features will become apparent from the following detailed description, the accompanying drawings, and the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIGURES 1a-f are plots of transmission ultraviolet-visible-near infrared (UV-Vis-NIR) spectra of glasses described herein, measured before and after ion exchange;

[0008] FIGURES 2a-e are plots of temperature dependence of the sodium-potassium interdiffusion coefficient for glasses selected from Tables 1a-d;

[0009] FIGURES 3a-e are plots of depth of layer as a function of compressive stress for annealed samples ion exchanged at 410°C in technical grade KNO_3 for 4, 8, and 16 hours;

[0010] FIGURE 4 is a plot showing the effect of substituting Nb_2O_5 for MgO on compressive stress at a fixed depth of layer of 50 μm and the ion exchange time required to achieve a depth of layer of 50 μm;

[0011] FIGURES 5a and 5b are plots showing the effect of substituting different oxides for Al_2O_3 on the compressive stress at a fixed depth of layer of 50 μm and the ion exchange time required to achieve a depth of layer of 50 μm; and

[0012] FIGURE 6 is a plot showing the effect of adding approximately 1.5 mol% on top of the base glass composition on the compressive stress at a fixed depth of layer of 50 μm and the ion exchange time required to achieve a depth of layer of 50 μm.

DETAILED DESCRIPTION

[0013] In the following description, like reference characters designate like or corresponding parts throughout the several views shown in the figures. It is also understood that, unless otherwise specified, terms such as "top," "bottom," "outward," "inward," and the like are words of convenience and are not to be construed as limiting terms. In addition, whenever a group is described as comprising at least one of a group of elements and combinations thereof, it is understood that the group may comprise, consist essentially of, or consist of any number of those elements recited, either individually or in combination with each other. Similarly, whenever a group is described as consisting of at least one of a group of elements or combinations thereof, it is understood that the group may consist of any number of those elements recited, either individually or in combination with each other. Unless otherwise specified, a range of values, when recited, includes both the upper and lower limits of the range as well as any ranges therebetween. As used herein, the indefinite articles "a," "an," and the corresponding definite article "the" mean "at least one" or "one or more," unless otherwise specified. It also is understood that the various features disclosed in the specification and the drawings can be used in any and all combinations.

[0014] As used herein, the terms "glass" and "glasses" includes both glasses and glass ceramics. The terms "glass article" and "glass articles" are used in their broadest sense to include any object made wholly or partly of glass and/or glass ceramic. As used herein, the terms "alkali metal oxide" and "alkali oxide" refer to the oxides of the alkali metals and are considered to be equivalent terms. Similarly, the terms "alkaline earth metal oxide" and "alkaline earth oxide" refer to the oxides of the alkaline earth metals and are considered to be equivalent terms.

[0015] It is noted that the terms "substantially" and "about" may be utilized herein to represent the inherent degree of uncertainty that may be attributed to any quantitative comparison, value, measurement, or other representation. These terms are also utilized herein to represent the degree by which a quantitative representation may vary from a stated reference without resulting in a change in the basic function of the subject matter at issue.

[0016] Described herein are ion exchangeable glasses that may be used to produce chemically strengthened glass sheets by ion exchange. The compositions of these glasses are chosen to promote simultaneously high compressive stress and deep depth of layer or reduced ion exchange time by including at least one transition metal oxide or rare earth oxide in the glass composition. Not all of the glass compositions described herein are fusion formable, and may be produced by other methods known in the art, such as the float glass process or the slot draw process.

[0017] Accordingly, alkali aluminosilicate glasses comprising at least one of a transition metal oxide and a rare earth oxide, at least 50 mole% (mol%) SiO_2, alumina (Al_2O_3) and at least one alkali metal oxide R_2O, wherein the alkali metal oxide includes Na_2O, and wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%. When ion exchanged, the alkali aluminosilicate glasses described herein may have a layer (also referred to herein as a compressive layer) under a compressive stress CS of at least about 1 gigaPascal (GPa) that extends from at least one surface of the alkali aluminosilicate glass into the central portion of the glass to a depth of layer (depth of layer, or DOL). In some embodiments, the depth of layer DOL is at least 20 microns (μm) and, in other embodiments, at least 30 μm.

[0018] The at least one transition metal oxide or rare earth oxide may, in some embodiments, include at least one of niobium oxide (Nb_2O_5), vanadium oxide (V_2O_5), zirconium (ZrO_2), iron oxide (Fe_2O_3), yttrium oxide (Y_2O_3), and manganese oxide (MnO_2). In some embodiments, the alkali aluminosilicate glass comprises: from about 62 mol% to about 72 mol% SiO_2; from about 5 mol% to about 12 mol% Al_2O_3; from 12 mol% to about 16 mol% Na_2O; and from more than 1 mol% to about 10 mol% of at one least metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides including, but not limited to, those described hereinabove.

[0019] Non-limiting examples of the glass compositions described herein and selected properties are listed in Tables 1a-d. In the examples listed, six different transition metal oxides were each added to a crucible-melt base glass ("base" in Tables 1a, 2, and 3). These oxides were added either to the top of the base glass melt or partially substituted for an oxide. Compositions were analyzed by x-ray fluorescence and/or inductively coupled plasma (ICP). Anneal and strain points were determined by beam bending viscometry, and softening points were determined by parallel plate viscometry. The coefficients of thermal expansion (CTE) values in Tables 1a-d represent the average value between room temperature and 300°C. Liquidus temperatures reported in Tables 1a-d are for 24 hours, elastic moduli were determined by resonant ultrasound spectroscopy, and refractive indices are reported for 589.3 nm. Stress optic coefficient (SOC) was determined by the diametral compression method.

[0020] Glass color was observed on 1 mm thick glass samples and is reported in Table 2. Transmission ultraviolet-visible-near infrared (UV-Vis-NIR) spectra measured before and after ion exchange are shown in FIGS. 1a-f. In some embodiments, the glasses described herein are colored. In other embodiments, the glasses are free of any coloration.

[0021] Properties of the glasses listed in Table 1a-d after ion exchange for fixed exchange times are provided in Table 2. Compressive stress (CS), expressed in gigapascals (GPa), and depth of layer (DOL), expressed in microns (μm), were obtained as a result of treatment of annealed samples in molten salt baths comprising technical grade KNO_3. The ion exchange treatments were carried out in the molten salt baths at 410°C for 4, 8, and 16 hours, and for 8 hours at 370°C and 450°C. The temperature dependence of the sodium-potassium interdiffusion coefficient for glasses selected from Tables 1a-d are plotted in FIGS. 2a-e.

[0022] Times required to ion exchange glasses selected from the compositions listed in Tables 1a-d to a fixed depth of layer of 50 μm are listed in Table 3. The compressive stress at a fixed depth of layer of 50 μm and ion exchange time required to a depth of layer of 50 μm were calculated from ion exchange data obtained at 410°C for annealed samples immersed for various times in the technical grade KNO_3 salt bath. Values in parentheses in Table 3 indicate that the ion exchange properties of the glasses are inferior to those of the base glass composition, whereas values which are not parenthesized indicate that the ion exchange properties are superior to those of the base glass composition. Depth of layer is plotted as a function of compressive stress in

FIGS. 3a-e for annealed samples ion exchanged at 410°C in technical grade KNO_3 for 4, 8, and 16 hours.

[0023] In the glass compositions described herein, SiO_2 serves as the primary glass-forming oxide, and comprises from about 62 mol% to about 72 mol% of the glass. The concentration of SiO_2 is high enough to provide the glass with high chemical durability that is suitable for applications such as, for example, touch screens or the like. However, the melting temperature (200 poise temperature, T_{200}) of pure SiO_2 or glasses containing higher levels of SiO_2 is too high, since defects such as fining bubbles tend to appear in the glass. In addition, SiO_2, in comparison to most oxides, decreases the compressive stress created by ion exchange. Accordingly, in some of the glasses described herein, transition metal oxides and/or rare earth oxides are substituted for SiO_2.

[0024] Alumina (Al_2O_3), which comprises from about 5 mol% to about 12 mol% of the glasses described herein, may also serve as a glass former. Like SiO_2, alumina generally increases the viscosity of the melt. An increase in Al_2O_3 relative to the alkalis or alkaline earths generally results in improved durability of the glass. The structural role of the aluminum ions depends on the glass composition. When the concentration of alkali metal oxides R_2O is greater than that of alumina, all aluminum is found in tetrahedral, four-fold coordination with the alkali metal ions acting as charge-balancers. This is the case for all of the glasses described herein. Divalent cation oxides (RO) can also charge balance tetrahedral aluminum to various extents. Elements such as calcium, strontium, and barium behave equivalently to two alkali ions, whereas the high field strength of magnesium ions cause them to not fully charge balance aluminum in tetrahedral coordination, resulting instead in formation of five- and six-fold coordinated aluminum. Al_2O_3 enables a strong network backbone (i.e., high strain point) while allowing relatively fast diffusivity of alkali ions, and thus plays an important role in ion-exchangeable glasses. High Al_2O_3 concentrations, however, generally lower the liquidus viscosity of the glass. One alternative is to partially substitute other oxides for Al_2O_3 while maintaining or improving ion exchange performance of the glass.

[0025] The glasses described herein comprise from about 12 mol% to about 16 mol% Na_2O and, optionally, at least one other alkali oxide such as, for example, K_2O. Alkali oxides (Li_2O, Na_2O, K_2O, Rb_2O, and Cs_2O) serve as aids in achieving low melting temperature and low

liquidus temperatures of glasses. The addition of alkali oxides, however, increases the coefficient of thermal expansion (CTE) and lowers the chemical durability of the glass. In order to achieve ion exchange, a small alkali oxide (such as, for example, Li_2O and Na_2O) must be present in the glass to exchange with larger alkali ions (e.g., K^+) from a molten salt bath. Three types of ion exchange may typically be carried out: Na^+-for-Li^+ exchange, which results in a deep depth of layer but low compressive stress; K^+-for-Li^+ exchange, which results in a small depth of layer but a relatively large compressive stress; and K^+-for-Na^+ exchange, which results in an intermediate depth of layer and compressive stress. A sufficiently high concentration of the small alkali oxide is necessary to produce a large compressive stress in the glass, since compressive stress is proportional to the number of alkali ions that are exchanged out of the glass. Accordingly, the glasses described herein comprise from 12 mol% to about 16 mol% Na_2O. The presence of a small amount of K_2O generally improves diffusivity and lowers the liquidus temperature of the glass, but increases the CTE (Table 1d). Partial substitutions of Rb_2O and/or Cs_2O for Na_2O decrease CS and DOL (Tables 3 and 4). While K^+-for-Na^+ exchange is described for the transition metal containing glasses described herein, ion exchange between alkali cation pairs (e.g., Na^+-for-Li^+ or Rb^+-for K^+) are within the scope of this disclosure.

[0026] Divalent cation oxides (such as alkaline earth oxides and ZnO) also improve the melting behavior of the glass. With respect to ion exchange performance, however, the presence of divalent cations tends to decrease alkali mobility. The effect of divalent ions on ion exchange performance is especially pronounced with larger divalent cations such as, for example, SrO, BaO, and the like. Furthermore, smaller divalent cation oxides generally enhance compressive stress more than larger divalent cations. MgO and ZnO, for example, offer several advantages with respect to improved stress relaxation while minimizing adverse effects on alkali diffusivity. Higher concentrations of MgO and ZnO, however, promote formation of forsterite (Mg_2SiO_4) and gahnite ($ZnAl_2O_4$), or willemite (Zn_2SiO_4), thus causing the liquidus temperature of the glass to rise very steeply with increasing MgO and/or ZnO content. MgO is the only divalent cation oxide in the glasses described herein. In some embodiments, transition metal oxides are substituted for at least a portion of the MgO in the glass while maintaining or improving the ion exchange performance of the glass.

[0027] Glasses typically also contain oxides that are added to eliminate and reduce defects, such as gaseous inclusions or "seeds," within the glass. In some embodiments, the glasses described herein comprise SnO_2 in the usual role as a fining agent. Alternatively, other oxides such as, but not limited to, As_2O_3 and/or Sb_2O_3 may serve as fining agents. The fining capacity is generally increased by increasing the concentration of SnO_2 (or As_2O_3 and/or Sb_2O_3) but, as these oxides are comparatively expensive raw materials, it is desirable to add no more than is required to drive the concentration of gaseous inclusions to an appropriately low level.

[0028] In addition to the oxides described above, the glasses described herein further comprise at least one transition metal oxide and/or rare earth oxide. In some embodiments, these transition metal oxides and rare earth oxides include, but are not necessarily limited to, Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2. The structural roles of these oxides and their impact on the ion exchange properties (CS and DOL) are described below.

[0029] The introduction of Nb_2O_5 in silicate glasses has been used in materials with, for example, non-linear optical coefficient and laser glasses of high-stimulated emission parameters. Nb_2O_5 acts as a network former even in low concentrations, as it forms Si-O-Nb network bonds. This substitution increases the anneal point, refractive index, and elastic moduli of the glass, but lowers the liquidus viscosity (Table 1a). With increasing degrees of substitution of Nb_2O_5 for MgO, the compressive stress created by ion exchange at 410°C to a fixed DOL of 50 μm increases but the ion exchange time required to reach 50 μm DOL also increases (FIG. 4). Substituting Nb_2O_5 for Al_2O_3 lowers both CS and DOL (FIGS. 5a and 5b). In summary, Nb_2O_5 adversely affects diffusivity, but may be used to increase the compressive stress when substituted for MgO (Tables 2 and 3).

[0030] Zirconia (ZrO_2) helps to improve the chemical durability of the glass. In the presence of charge-compensating cations, six-fold coordinated zirconium is inserted in the silicate network by forming Si-O-Zr bonds. Hence, the $[ZrO_6]^{2-}$ groups are charge-compensated by two positive charges; i.e., either two alkali ions or one alkaline earth ion. Because SiO_2 generally decreases the compressive stress due to ion exchange, ZrO_2 is partially substituted for SiO_2 in some of the glasses described herein. Zirconia substitution increases the anneal point, refractive index, and elastic moduli of the glass, but lowers the liquidus viscosity (Table 1a). With respect to ion exchange performance, the substitution of ZrO_2 for SiO_2 dramatically

increases the CS at a fixed DOL of 50 μm, whereas the time required to ion exchange the glass to a DOL of 50 μm increases (Table 3). Adding 1.5 mol% ZrO_2 on top of the base glass composition and scaling all other oxides proportionally also increases CS and decreases DOL (FIG. 6).

[0031] Iron is present in glasses as Fe^{2+}, Fe^{3+}, or metallic free iron (Fe^0). Unless reducing melting conditions are employed, however, only Fe^{2+} and Fe^{3+} will be present in significant concentrations. The structural roles of Fe^{2+} and Fe^{3+} differ markedly. Depending on the ratio $[Fe^{3+}]/[\Sigma Fe]$, where $[Fe^{3+}]$ is the Fe^{3+} concentration and $[\Sigma Fe]$ is the total concentration of Fe^{2+} and Fe^{3+}, Fe^{3+} can act as a network former (coordination number IV or V) and/or a network modifier (coordination number V or VI), whereas Fe^{2+} iron is generally considered to be a network modifier. As both ferric and ferrous iron can be present in liquids, changes in the oxidation state of iron can significantly affect the degree of iron polymerization. Therefore, any melt property that depends on the number of non-bridging oxygens (NBO) per tetrahedron (NBO/T) will also be affected by the ratio $[Fe^{3+}]/[\Sigma Fe]$. The structural role of Fe^{2+} is thus similar to that of Mg^{2+} or Ca^{2+}. The structural role of Fe^{3+} is similar to that of Al^{3+}, as tetrahedral Fe^{3+} also requires the presence of charge-compensating cations. In certain embodiments of the glasses described herein, iron oxide is substituted for both MgO and Al_2O_3 (Table 1b). Due to the intense dark coloring of these iron-containing glasses, it was not possible to determine their SOC. Consequently, the SOC value of the base glass was used as an approximate value when calculating compressive stresses resulting from ion exchange. Substitution of iron for aluminum significantly increases CS and decreases DOL (FIGS. 5a and 5b). This is also the case for the substitution of iron for magnesium, but in this case the increase in CS is even larger and the increase in diffusivity smaller (Tables 2 and 3). Adding iron on top of the base glass composition also increases CS and decreases DOL (FIG. 6). Iron is therefore a powerful oxide for increasing the compressive stress, even when the amount of Al_2O_3, which is normally a very good oxide for enhancing the compressive stress, is reduced.

[0032] Vanadium is another oxide that exists in different redox states in glasses and thus possesses different structural roles depending on the redox state. Usually, vanadium occurs in the states of V^{3+}, V^{4+}, and V^{5+} in glasses. The role of V^{5+} may be similar to that of P^{5+}; i.e., V^{5+} can remove modifiers such as, for example, Na^+, from the silicate network to form various alkali vanadate species. Hence, V_2O_5 can be present in various phosphate-like structural units such as

pyrovanadate and metavanadate units. P_2O_5 is known to dramatically increase DOL and decrease CS. In some embodiments of the glasses described herein, V_2O_5 has been introduced into the base glass in various ways (Table 1b). Substituting V for Al increases DOL, but dramatically lowers CS (FIG. 6). The decrease in CS is smaller when V_2O_5 is added on the top of the base glass or substituted for SiO_2 (Tables 2 and 3). The presence of vanadium, like phosphorus, in the glass generally increases the ion exchange interdiffusivity. Since Al_2O_3 is also good for increasing CS, V_2O_5 was added together with Al_2O_3 and taking out SiO_2 (to keep the viscosity at a reasonable value) in some embodiments of the glasses described herein. This substitution increases both CS and DOL (Tables 2 and 3).

[0033] Silicate glasses containing yttria (Y_2O_3) generally have high glass transition temperatures, low electrical conductivity, and high chemical durability. The trivalent cation Y^{3+} is chemically similar to Al^{3+}. In the glasses described herein, Y_2O_3 is partially substituted forAl_2O_3 at levels of 2, 5, and 10 mol% (Table 1c). When 2 mol% Y_2O_3 was substituted for Al_2O_3, a small increase in compressive stress was observed and the diffusivity decreased. Compressive stress and depth of layer could not be determined for samples in which 5 and 10 mol% Y_2O_3 were substituted for Al_2O_3. Hence, the role Y_2O_3 is very different from that of Al_2O_3 with respect to ion exchange properties.

[0034] Manganese ions mostly exist in glasses in the Mn^{2+} and Mn^{3+} oxidation states. Mn^{2+} occupies primarily network-forming positions within MnO_4 structural units, whereas Mn^{3+} occupies mostly network-modifying positions. The influence of manganese on ion exchange performance should thus strongly depend on the redox chemistry. When MnO_2 is substituted for Al_2O_3, both CS and DOL decrease dramatically (FIGS. 5a and 5b). Hence, its structural role is very different from that of Al_2O_3. On the other hand, when MnO_2 is added on the top or substituted for SiO_2, CS increases while the DOL increases (Tables 2 and 3). MnO_2 can be used to increase the compressive stress, but there is a corresponding decrease in diffusivity. Adding MnO_2 with Al_2O_3 and taking out SiO_2 produces the highest increase in CS and smallest decrease in DOL (Tables 2 and 3).

Table 1a. Compositions and properties of the base alkali aluminosilicate glass, glasses in which niobium oxide was substituted for magnesium oxide or alumina, and glasses in which zirconium oxide was substituted for silicon oxide or added directly to the base glass.

Composition (mol %)	Base Base Glass	Nb1 Nb for Mg	Nb2 Nb for Mg	Nb3 Nb for Mg	Nb4 Nb for Al	Zr1 Zr for Si	Zr2 Zr for Si	Zr3 Zr on top
SiO2	69.32	69.07	69.23	69.13	69.09	68.33	67.13	68.09
Al_2O_3	10.66	10.61	10.59	10.59	9.71	10.62	10.65	10.49
MgO	5.26	4.52	3.57	1.85	5.38	5.25	5.42	5.33
Na_2O	14.65	14.81	14.74	14.80	14.83	14.73	14.78	14.54
Nb_2O_5		0.89	1.79	3.54	0.89			
ZrO_2						0.98	1.93	1.46
Fe_2O_3								
V_2O_5								
Y_2O_3								
MnO_2								
SnO_2	0.10	0.10	0.09	0.09	0.10	0.09	0.09	0.09

Properties	Base	Nb1	Nb2	Nb3	Nb4	Zr1	Zr2	Zr3
Anneal Pt (°C):	663.5	673.2	677.1	680.2	660.5	683.6	699.6	694.6
Strain Pt (°C):	613.2	624.5	628.5	634.5	611.8	633.8	649	643.7
Softening Pt (°C):	905.3	903.6	907.4	893	892.6	920.8	936.6	934.1
Glass color	transparent	light yellow	light yellow	light yellow	light yellow	transparent	transparent	transparent
Density (g/cm^3):	2.429	2.473	2.513	2.586	2.477	2.460	2.492	2.473
CTE (x10^{-7}/°C):	79.6	78.5	77	74.6	77.9	81.1	78.8	78.9
Liquidus Temp (°C):	1075	1035	1070	1150	1040	1110	1250	1210
Primary Devit Phase:	Forsterite	Forsterite	Unknown	Unknown	Forsterite	Forsterite	Unknown	Zircon
Liquidus Visc. (Poise):	418339	787862	305069	41156	402012	264896	17111	43660
Poisson's Ratio:	0.207	0.21	0.214	0.209	0.206	0.211	0.218	0.214
Shear Modulus (Mpsi):	4.27	4.335	4.351	4.399	4.332	4.361	4.447	4.399
Young's Modulus (Mpsi):	10.307	10.488	10.561	10.64	10.453	10.559	10.834	10.685
Refractive Index:	1.50056	1.51177	1.52260	1.54472	1.51284	1.50668	1.51367	1.50949
SOC (nm/cm/MPa):	29.53	30.19	30.77	32.34	29.9	29.9	30.13	30.12

Table 1b. Compositions and properties of glasses in which iron oxide was substituted for magnesium oxide, aluminum oxide, or added to the base glass composition, and glasses in which vanadium oxide was substituted for alumina, silica, or added to the base composition.

Composition (mol %)	Fe1 Fe for Mg	Fe2 Fe for Al	Fe3 Fe on top	V1 V for Al	V2 V for Al	V3 V on top	V4 V for Si	V5 V-Al for Si
SiO2	68.94	69.04	68.14	68.12	68.91	67.22	66.33	66.02
Al_2O_3	10.97	8.89	10.46	8.44	5.62	10.26	10.38	11.45
MgO	3.51	5.50	5.42	5.74	5.67	5.41	5.54	5.49
Na_2O	14.55	14.55	14.44	15.56	14.76	15.45	15.63	15.86
Nb_2O_5								
ZrO_2								
Fe_2O_3	1.93	1.94	1.43					
V_2O_5				2.02	4.95	1.55	2.01	1.06
Y_2O_3								
MnO_2								
SnO_2	0.10	0.10	0.10	0.11	0.10	0.12	0.11	0.12
Properties	**Fe1**	**Fe2**	**Fe3**	**V1**	**V2**	**V3**	**V4**	**V5**
Anneal Pt. (°C):	634.7	616.8	642.4	596.1	522.1	633.6	617.9	654.8
Strain Pt. (°C):	586.1	569	594	550.8	477.1	585.3	572.3	605.6
Softening Pt. (°C):	892.8	846.1	888.6	825.7	719.7	873.3	850.5	895.5
Glass color	black/ brown	brown	brown	brown/ yellow	black	brown/ yellow	brown/ yellow	light brown/ yellow
Density (g/cm^3):	2.472	2.479	2.470	2.442	2.463	2.442	2.451	2.446
CTE ($x10^{-7}$/°C):	81.5	82.0	80.4	83.0	90.5	80.5	81.6	82.4
Liquidus Temp. (°C):	1250	1250	1170	975	920	1110	1110	1160
Primary Devit Phase:	Unknown	Unknown	Forsterite	Albite	Unknown	Forsterite	Forsterite	Forsterite
Liquidus Visc. (Poise):								
Poisson's Ratio:	0.214	0.221	0.212	0.22	0.221	0.237	0.216	0.219
Shear Modulus (Mpsi):	4.242	4.232	4.311	4.002	3.709	4.113	4.081	4.199
Young's Modulus (Mpsi):	10.304	10.333	10.445	9.768	9.059	10.173	9.923	10.235
Refractive Index:	1.51540	1.51670	1.51360	1.51560	1.54070	1.51366	1.51706	1.51006
SOC (nm/cm/MPa):				29.17	28.65	29.59	29.42	29.5

Table 1c. Compositions and properties of glasses in which yttrium oxide was substituted for aluminum oxide, and glasses in which manganese oxide was substituted for alumina, silica, or added to the base composition.

Composition (mol %)	Y1 Y for Al	Y2 Y for Al	Y3 Y for Al	Mn1 Mn for Al	Mn2 Mn for Al	Mn3 Mn on top	Mn4 Mn for Si	Mn5 Mn-Al for Si
SiO2	68.72	68.98	68.47	69.10	68.68	67.76	66.98	66.95
Al_2O_3	8.76	5.62	0.07	8.50	5.67	10.43	10.56	11.63
MgO	5.60	5.12	5.31	5.65	6.11	5.57	5.61	5.57
Na_2O	14.84	15.18	15.99	14.91	15.02	14.74	14.97	14.87
Nb_2O_5								
ZrO_2								
Fe_2O_3								
V_2O_5								
Y_2O_3	1.98	5.01	10.07					
MnO_2				1.75	4.42	1.33	1.77	0.90
SnO_2	0.10	0.08	0.09	0.09	0.09	0.17	0.10	0.09

Properties	Y1	Y2	Y3	Mn1	Mn2	Mn3	Mn4	Mn5
Anneal Pt. (°C):	671.3	677.7	697.5	617.7	569.7	651.3	644.6	668.6
Strain Pt. (°C):	624.1	632.1	655.3	570.9	525.5	603.2	595.3	619.6
Softening Pt. (°C):	883.9	880.1	871.1	844.7	773.9	884.7	876.2	909
Glass color	transparent	transparent	transparent	light red/ pink	red/pink	light red/ pink	light red/ pink	light red/pink
Density (g/cm^3):	2.539	2.703	3.016	2.457	2.504	2.46	2.467	2.453
CTE (x10^{-7}/°C):	79.9	80.3		86.5	87.7	83.1	85.4	85.6
Liquidus Temp. (°C):				965	870	1095	1100	1140
Primary Devit Phase:				Albite	Unknown	Forsterite	Forsterite	Forsterite
Liquidus Visc. (Poise):								
Poisson's Ratio:	0.22	0.221	0.249	0.225	0.219	0.228	0.224	0.216
Shear Modulus (Mpsi):	4.443	4.693	5.146	4.239	4.223	4.303	4.313	4.316
Young's Modulus (Mpsi):	10.844	11.459	12.852	10.384	10.299	10.566	10.562	10.493
Refractive Index:	1.51677	1.54113	1.58671	1.50600	1.51460	1.50560	1.50750	1.50510
SOC (nm/cm/MPa):	29.22	28.09	25.51	29.43	29.28	29.59	29.44	29.69

Table 1d. Compositions and properties of glasses in which potassium oxide, rubidium oxide, or cesium oxide were substituted for sodium oxide.

Composition (mol %)	K1 K for Na	K2 K for Na	Rb1 Rb for Na	Rb2 Rb for Na	Cs1 Cs for Na	Cs2 Cs for Na
SiO2	69.13	69.25	69.11	69.16	68.94	68.89
Al_2O_3	10.59	10.60	10.57	10.54	10.51	10.50
MgO	5.38	5.32	5.43	5.38	5.43	5.40
Na_2O	13.83	12.82	13.85	12.89	14.05	13.18
K_2O	0.97	1.92				
Rb_2O			0.94	1.94		
Cs_2O					0.97	1.92
SnO_2	0.10	0.10	0.09	0.10	0.10	0.10
Properties	**K1**	**K2**	**Rb1**	**Rb2**	**Cs1**	**Cs2**
Anneal Pt (C):	660.9	661	659.2	652	660.4	660
Strain Pt (C):	610.4	608.5	607.5	600.6	608.6	607.7
Softening Pt (C):	906.4	913.3	904.9	907	908.1	920.2
Glass color	transparent	transparent	transparent	transparent	transparent	transparent
Density (g/cm^3):	2.43	2.43	2.458	2.486	2.484	2.536
CTE (x10^-7/C):	86.0	89.0	84.0	87.6	84.4	82.4
Liquidus Temp (C):	1075	1085	1080	1060	1050	1175
Primary Devit Phase:	Forsterite	Forsterite	Forsterite	Forsterite	Forsterite	Unknown
Liquidus Visc (Poise):						
Poisson's Ratio:	0.209	0.211	0.212	0.21	0.214	0.218
Shear Modulus (Mpsi):	4.305	4.316	4.283	4.279	4.242	4.21
Young's Modulus (Mpsi):	10.412	10.457	10.385	10.351	10.303	10.255
Refractive Index:	1.50020	1.50025	1.50101	1.50146	1.50205	1.50400
SOC (nm/cm/MPa):	29.47	29.35	29.16	28.75	28.75	28.31

Table 2. Ion exchange properties of the glasses listed Tables 1a-d.

		Ion Exchange at 410°C						Ion Exchange for 8 hrs			
		CS (4 h)	CS (8 h)	CS (16 h)	DOL (4 h)	DOL (8 h)	DOL (16 h)	CS (370C)	CS (450C)	DOL (370C)	DOL (450C)
Base	**Base glass**	1061	1036	1007	29.6	42.3	56.0	1070	943	23.0	64.7
Nb1	**Nb for Mg**	1076	1053	1025	26.9	39.4	51.4	1081	981	21.7	57.8
Nb2	**Nb for Mg**	1076	1057	1044	25.3	37.2	48.4	1079	989	20.4	54.7
Nb3	**Nb for Mg**	1066	1066	1051		37.0	49.1	1064	1015	19.5	53.8
Nb4	**Nb for Al**	1066	1035	1004	24.9	36.6	48.6	1065	956	19.5	54.0
Zr1	**Zr for Si**	1129	1101	1086	26.7	35.4	51.8	1121	1056	20.8	55.0
Zr2	**Zr for Si**	1157	1140	1121	22.8	33.8	45.9	1130	1097	18.4	49.6
Zr3	**Zr on top**	1139	1119	1102	25.1	37.2	49.1	1117	1075	19.7	53.6
Fe1	**Fe for Mg**	1334	1254	1218	24.1	38.6	48.3	1300	1178	20.0	
Fe2	**Fe for Al**	1185	1148	1161	21.9	32.5	41.3	1225	1035	16.9	45.2
Fe3	**Fe on top**	1240	1209	1177	22.6	32.9	43.9	1233	1108	18.0	48.7
V1	**V for Al**	870	825	810	31.4	45.7	60.6	912	720	24.5	67.7
V2	**V for Al**	682			31.6			751		24.6	
V3	**V on top**	992	966	935	30.9	45.5	61.1	1014	879	25.3	66.9
V4	**V for Si**	981	958	927	31.1	45.9	60.2	1003	873	25.5	65.7
V5	**V-Al for Si**	1076	1050	1032	29.9	44.4	58.1	1085	980	23.7	64.1
Y1	**Y for Al**	1065	1059	1043	18.8	27.9	37.0	1059	1025	14.4	38.8
Y2	**Y for Al**			787			18.0				
Mn1	**Mn for Al**	996	958	898	23.0	33.1	46.1	1027	823	17.5	50.5
Mn2	**Mn for Al**	905	832	785	16.5	24.1	32.6	974	687	12.5	36.8
Mn3	**Mn on top**	1085	1067	1037	24.3	35.3	47.4	1101	978	18.7	51.9
Mn4	**Mn for Si**	1105	1079	1056	23.2	34.5	45.1	1120	994	18.2	50.1
Mn5	**Mn-Al for Si**	1122	1100	1086	25.3	38.0	50.4	1128	1035	20.0	54.9
K1	**K for Na**	1008	989	960	33.4	49.8	66.6	1012		26.5	
K2	**K for Na**	946	925	905	38.3	56.6	73.7	946	870	30.5	80.3
Rb1	**Rb for Na**	993	953	921	26.5	40.0	53.9	1025	876	20.8	59.9
Rb2	**Rb for Na**	922	881	850	25.2	37.8	51.4	946	809	18.9	55.8
Cs1	**Cs for Na**	995	972	943	23.0	33.2	45.1	994	903	17.1	49.2
Cs2	**Cs for Na**	916	903	890	18.7	27.4	35.3	906	857	14.1	41.0

Table 3. Ion exchange properties of selected glasses from Tables 1a-d. The compressive stress (CS) at a fixed depth of layer (DOL) of 50 μm and ion exchange time required to achieve a depth of layer of 50 μm were calculated from ion exchange data for annealed samples at 410°C for various times in technical grade KNO_3. Values in parentheses indicate that the ion exchange properties of the glasses are inferior to the base glass composition. Values not in parentheses indicate that the ion exchange properties are superior to those of the base glass composition.

		CS @ 50 μm (Mpa)	Time to 50 μm (h)
Base	**Base glass**	1019	12.1
Nb1	**Nb for Mg**	1029	(14.3)
Nb2	**Nb for Mg**	1041	(16.2)
Nb3	**Nb for Mg**	1050	(15.9)
Nb4	**Nb for Al**	(1000)	(16.3)
Zr1	**Zr for Si**	1086	(15.1)
Zr2	**Zr for Si**	1114	(18.6)
Zr3	**Zr on top**	1100	(15.9)
Fe1	**Fe for Mg**	1206	(16.0)
Fe2	**Fe for Al**	1141	(22.0)
Fe3	**Fe on top**	1159	(20.0)
V1	**V for Al**	(827)	10.4
V3	**V on top**	(957)	10.4
V4	**V for Si**	(947)	10.5
V5	**V-Al for Si**	1043	11.2
Y1	**Y for Al**	1028	(28.2)
Mn1	**Mn for Al**	(883)	(18.7)
Mn2	**Mn for Al**	(652)	(36.7)
Mn3	**Mn on top**	1033	(17.2)
Mn4	**Mn for Si**	1045	(18.8)
Mn5	**Mn-Al for Si**	1085	(15.2)
K1	**K for Na**	(986)	8.7
K2	**K for Na**	(932)	6.9
Rb1	**Rb for Na**	(930)	(13.5)
Rb2	**Rb for Na**	(852)	(14.9)
Cs1	**Cs for Na**	(932)	(19.2)
Cs2	**Cs for Na**	(867)	(30.3)

[0035] The glasses described herein, particularly when ion exchanged, may be used as cover plates or windows for portable or mobile electronic communication and entertainment devices, such as cellular phones, music players, and information terminal (IT) devices, such as laptop computers and the like.

[0036] While typical embodiments have been set forth for the purpose of illustration, the foregoing description should not be deemed to be a limitation on the scope of the disclosure or appended claims. Accordingly, various modifications, adaptations, and alternatives may occur to one skilled in the art without departing from the spirit and scope of the present disclosure or appended claims.

CLAIMS

1. An alkali aluminosilicate glass, the alkali aluminosilicate glass comprising at least 50 mol% SiO_2, up to 12 mol% Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the at least one alkali metal oxide includes Na_2O, wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%, and wherein the alkali aluminosilicate glass is ion exchangeable.

2. The alkali aluminosilicate glass of Claim 1, wherein the transition metal oxides and rare earth oxides are selected from the group consisting of Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2.

3. The alkali aluminosilicate glass of Claim 1, wherein the alkali aluminosilicate glass comprises: from about 62 mol% to about 72 mol% SiO_2; from about 5 mol% to about 12 mol% Al_2O_3; from 12 mol% to about 16 mol% Na_2O; and from more than 1 mol% to about 10 mol% of the at one least metal oxide.

4. The alkali aluminosilicate glass of Claim 3, wherein the at least one metal oxide is selected from the group consisting of Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2.

5. The alkali aluminosilicate oxide of any one of Claims 1-4, further comprising from 1 mol% to about 7 mol% MgO.

6. The alkali aluminosilicate glass of any one of Claims 1-4, wherein the alkali aluminosilicate glass is colorless.

7. The alkali aluminosilicate glass of any one of Claims 1-4, wherein the alkali aluminosilicate glass is ion exchanged and has a surface and a layer under compressive stress extending from the surface to a depth of layer, wherein the compressive stress is at least about 1 GPa and the depth of layer is at least about 25 μm.

8. An alkali aluminosilicate glass, the alkali aluminosilicate glass comprising at least 50 mol% SiO_2, up to 12 mol% Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the at least one alkali metal oxide includes Na_2O, wherein Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%, and wherein the alkali aluminosilicate glass is ion exchanged and has a surface and a

layer under compressive stress extending from the surface to a depth of layer, wherein the compressive stress is at least about 1 GPa and the depth of layer is at least about 25 μm.

9. The alkali aluminosilicate glass of Claim 8, wherein the transition metal oxides and rare earth oxides are selected from the group consisting of Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2.

10. The alkali aluminosilicate glass of Claim 8, wherein the alkali aluminosilicate glass comprises: from about 62 mol% to about 72 mol% SiO_2; from about 5 mol% to about 12 mol% Al_2O_3; from 12 mol% to about 16 mol% Na_2O; and from more than 1 mol% to about 10 mol% of the at one least metal oxide.

11. The alkali aluminosilicate glass of Claim 10, wherein the at least one metal oxide is selected from the group consisting of Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2.

12. The alkali aluminosilicate oxide of any one of Claims 8-10, further comprising from 1 mol% to about 7 mol% MgO.

13. The alkali aluminosilicate glass of any one of Claims 8-10, wherein the alkali aluminosilicate glass is colorless.

14. A method of making an ion exchanged alkali aluminosilicate glass, the method comprising:

a. providing an alkali aluminosilicate glass, the alkali aluminosilicate glass comprising at least 50 mol% SiO_2, up to 12 mol% Al_2O_3, at least one metal oxide selected from the group consisting of transition metal oxides and rare earth metal oxides, and at least one alkali metal oxide R_2O, wherein the alkali metal oxide includes Na_2O and Al_2O_3(mol%) – Na_2O(mol%) ≤ 2 mol%; and

b. ion exchanging the alkali aluminosilicate glass for a predetermined time to form a layer under a compressive stress extending from s surface of the alkali aluminosilicate glass to a depth of layer, wherein the compressive stress is at least about 1 GPa.

15. The method of Claim 14, wherein the alkali aluminosilicate glass comprises: from about 62 mol% to about 72 mol% SiO_2; from about 5 mol% to about 12 mol% Al_2O_3; from 12 mol% to about 16 mol% Na_2O; and from more than 1 mol% to about 10 mol% of the at one least metal oxide.

16. The method of Claim 14 or Claim 15, further comprising from 1 mol% to about 7 mol% MgO.

17. The method of Claim 14 or Claim 15, wherein the at least one metal oxide is selected from the group consisting of Nb_2O_5, ZrO_2, Fe_2O_3, V_2O_5, Y_2O_3, and MnO_2.

FIG. 1a

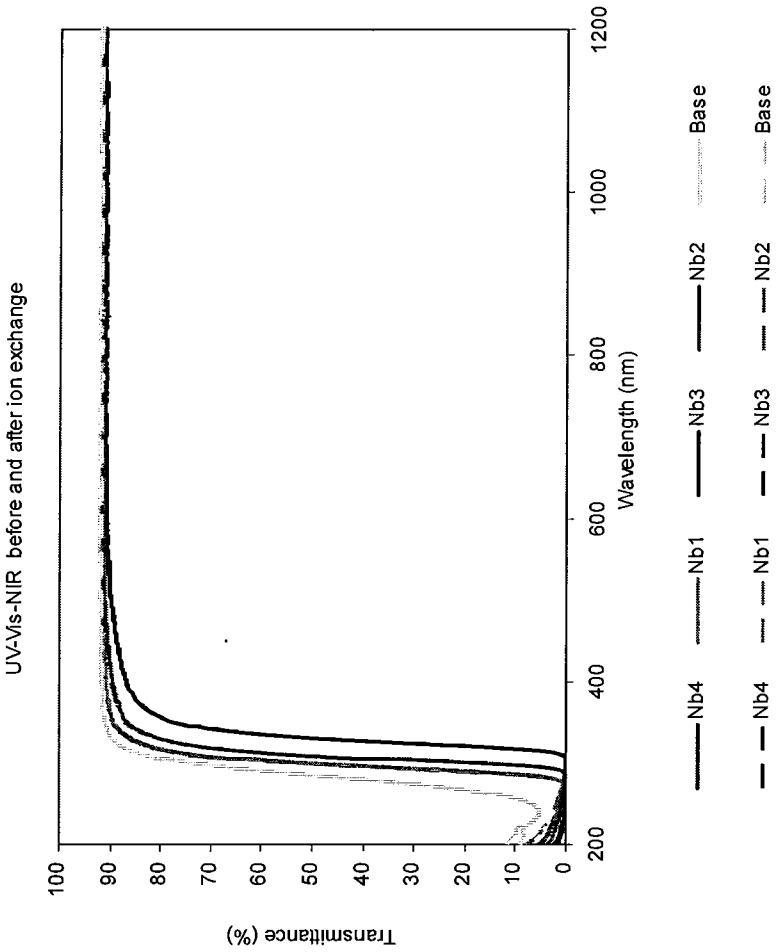

UV-Vis-NIR before and after ion exchange
Transmittance (%)
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
1000
1200
Wavelength (nm)
Nb4
Nb1
Nb3
Nb2
Base
Nb4
Nb1
Nb3
Nb2
Base

FIG. 1b

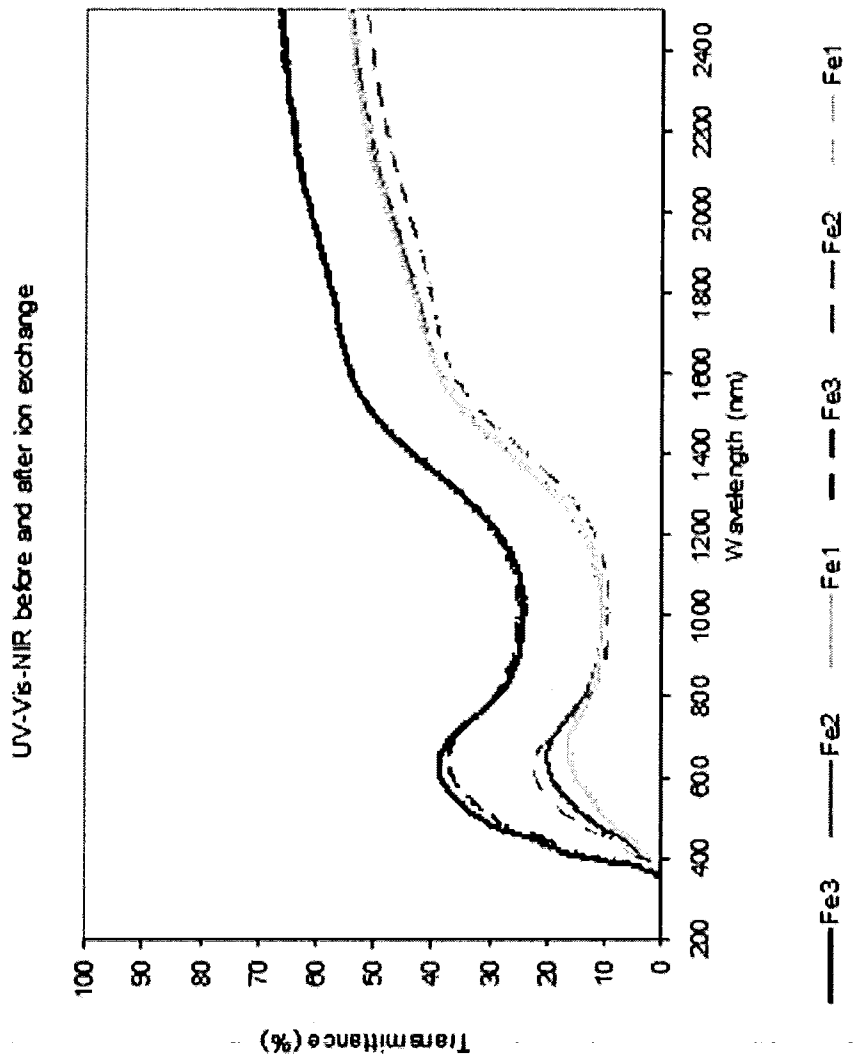

UV-Vis-NIR before and after ion exchange
Transmittance (%)
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
1000
1200
1400
1600
1800
2000
2200
2400
Wavelength (nm)
Fe3
Fe2
Fe1
Fe3
Fe2
Fe1

FIG. 1c

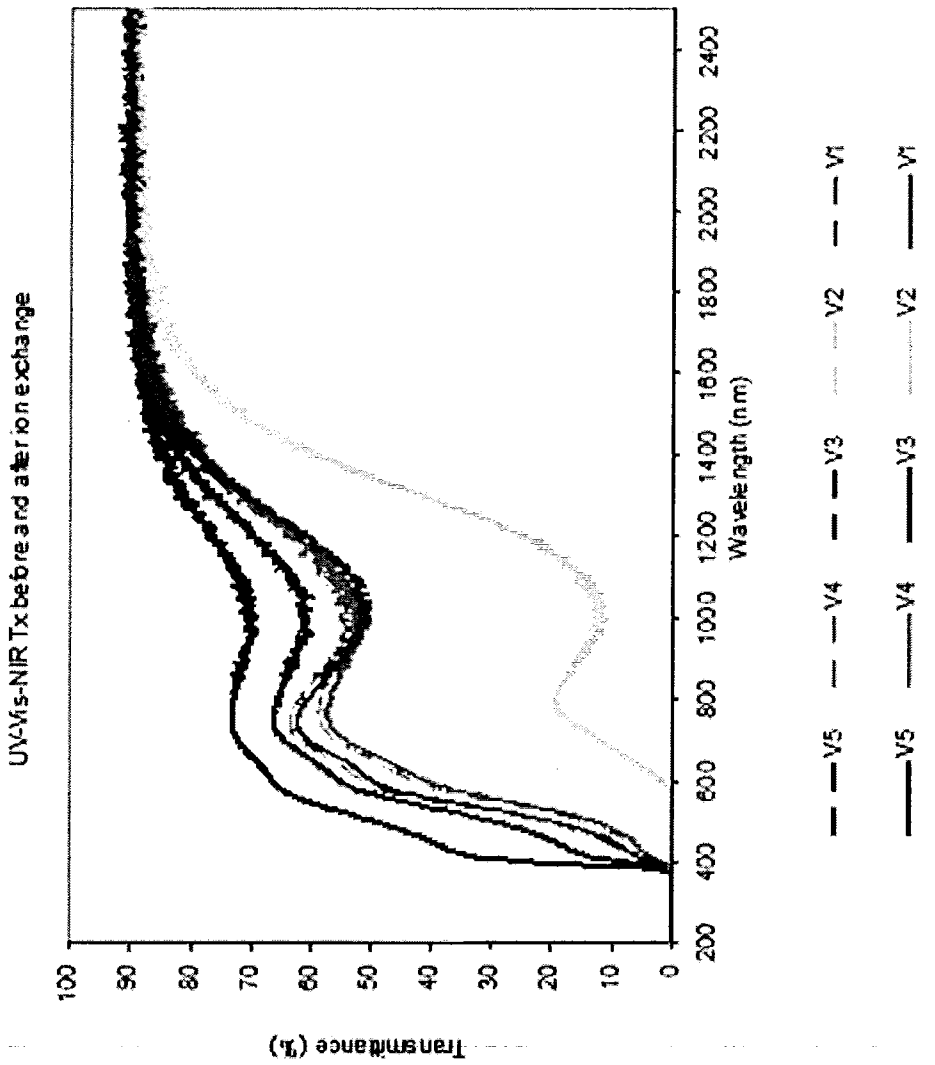

UV-Vis-NIR Tx before and after ion exchange
Transmittance (%)
Wavelength (nm)
V5
V4
V3
V2
V1

FIG. 1d

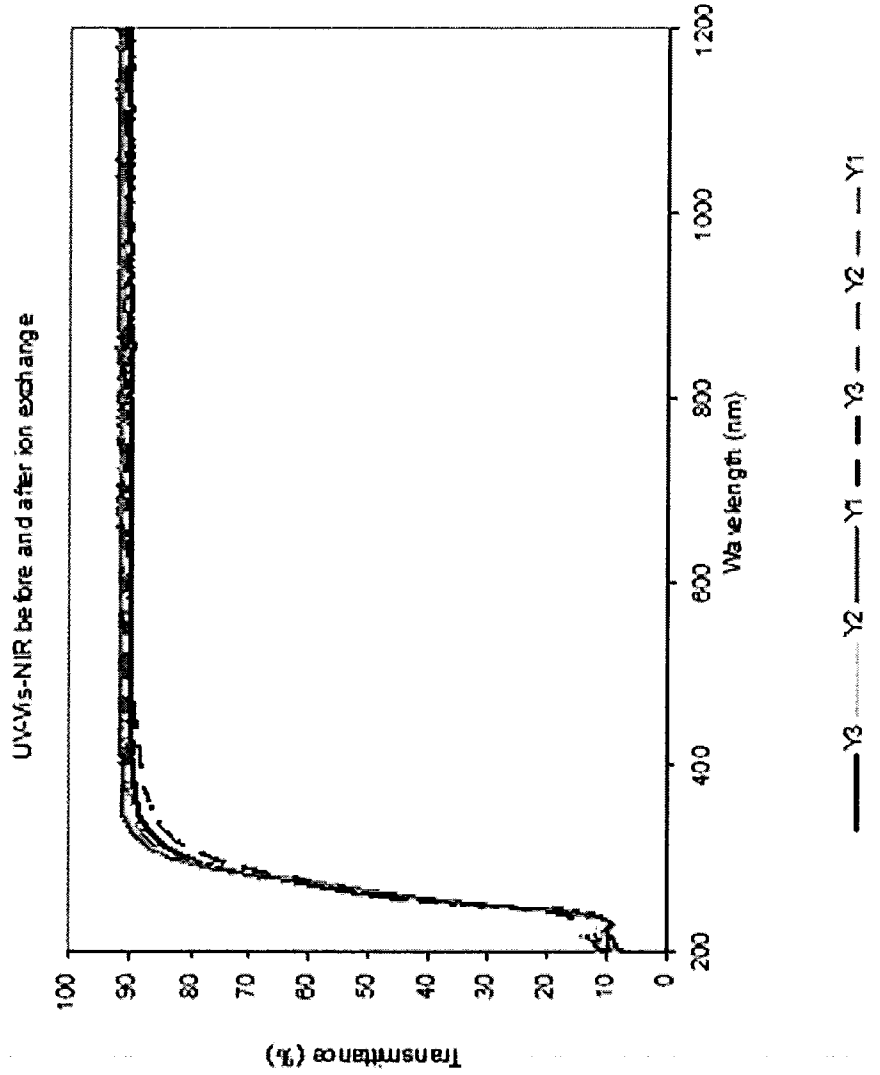

UV-Vis-NIR before and after ion exchange
Transmittance (%)
Wavelength (nm)
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
1000
1200
Y3
Y2
Y1
Y3
Y2
Y1

FIG. 1e

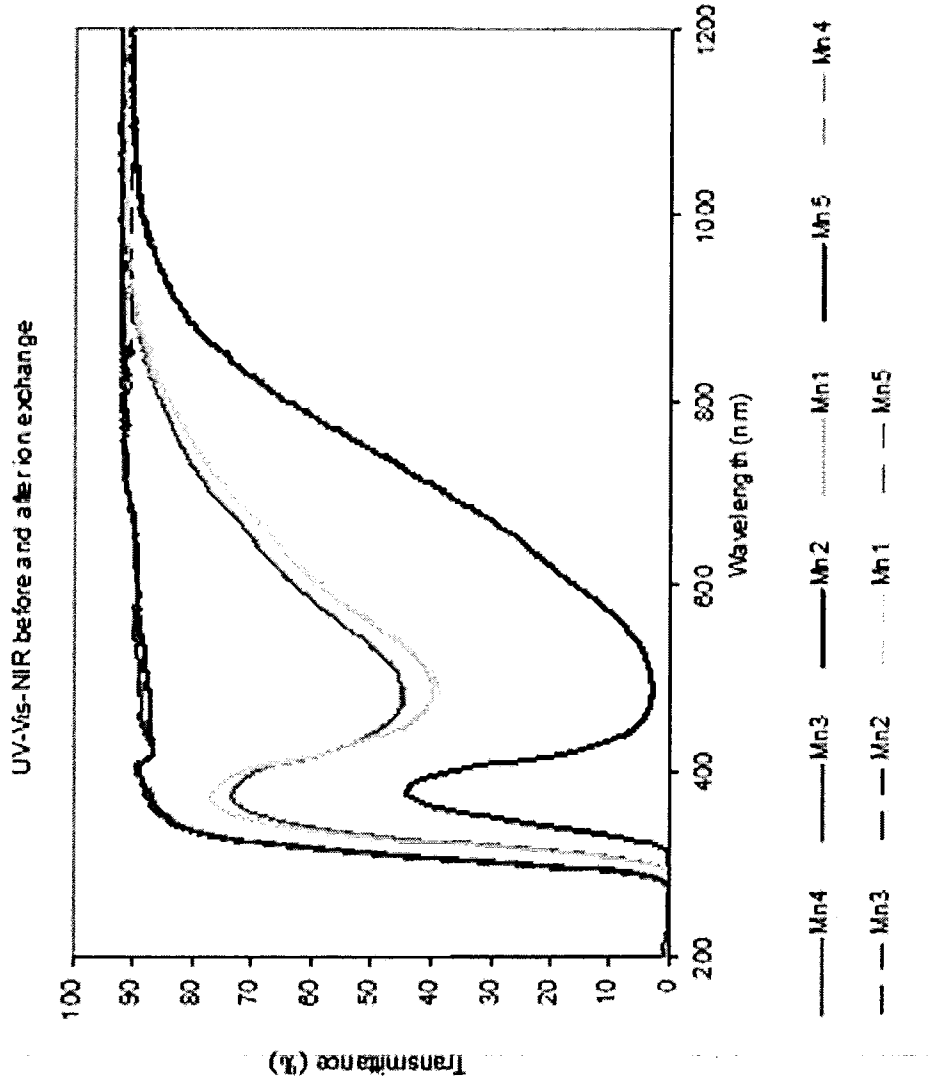

UV-Vis-NIR before and after ion exchange
Transmittance (%)
Wavelength (nm)
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
1000
1200
Mn4
Mn3
Mn2
Mn1
Mn5
Mn3
Mn2
Mn1
Mn5
Mn4

FIG. 1f

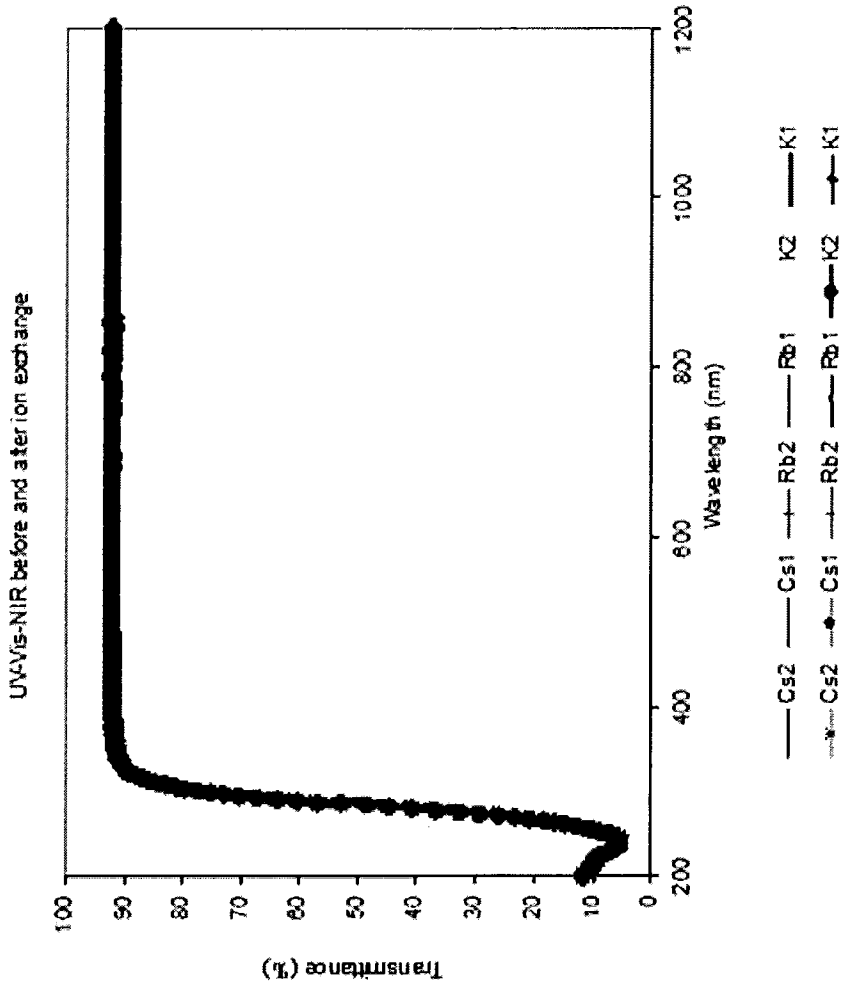
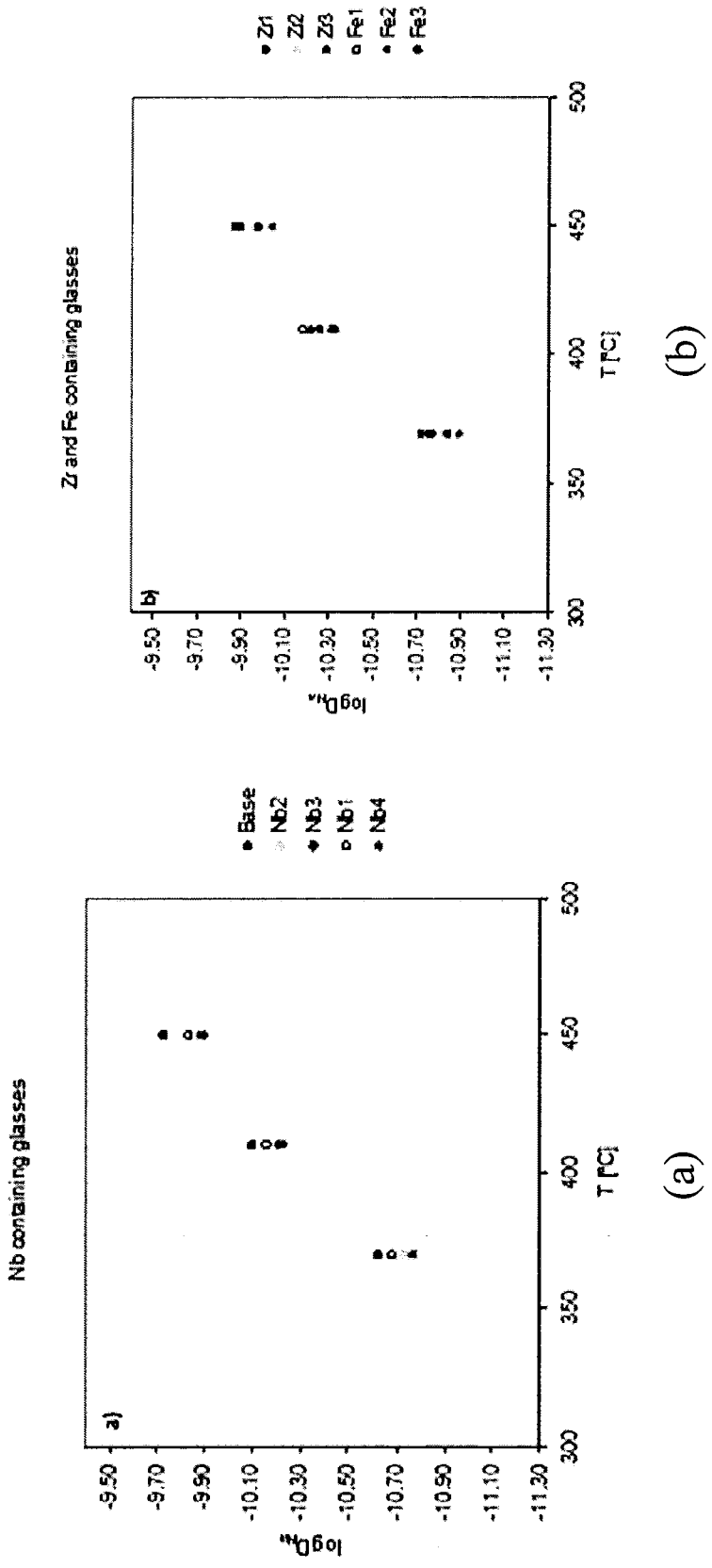

UV-Vis-NIR before and after ion exchange
Transmittance (%)
Wavelength (nm)
100
90
80
70
60
50
40
30
20
10
0
200
400
600
800
1000
1200
Cs2
Cs1
Rb2
Rb1
K2
K1
Cs2
Cs1
Rb2
Rb1
K2
K1

FIG. 2


Nb containing glasses
a)
Base
Nb2
Nb3
Nb1
Nb4
T [°C]
Zr and Fe containing glasses
b)
Zr1
Zr2
Zr3
Fe1
Fe2
Fe3
T [°C]

(a) (b)

FIG. 2

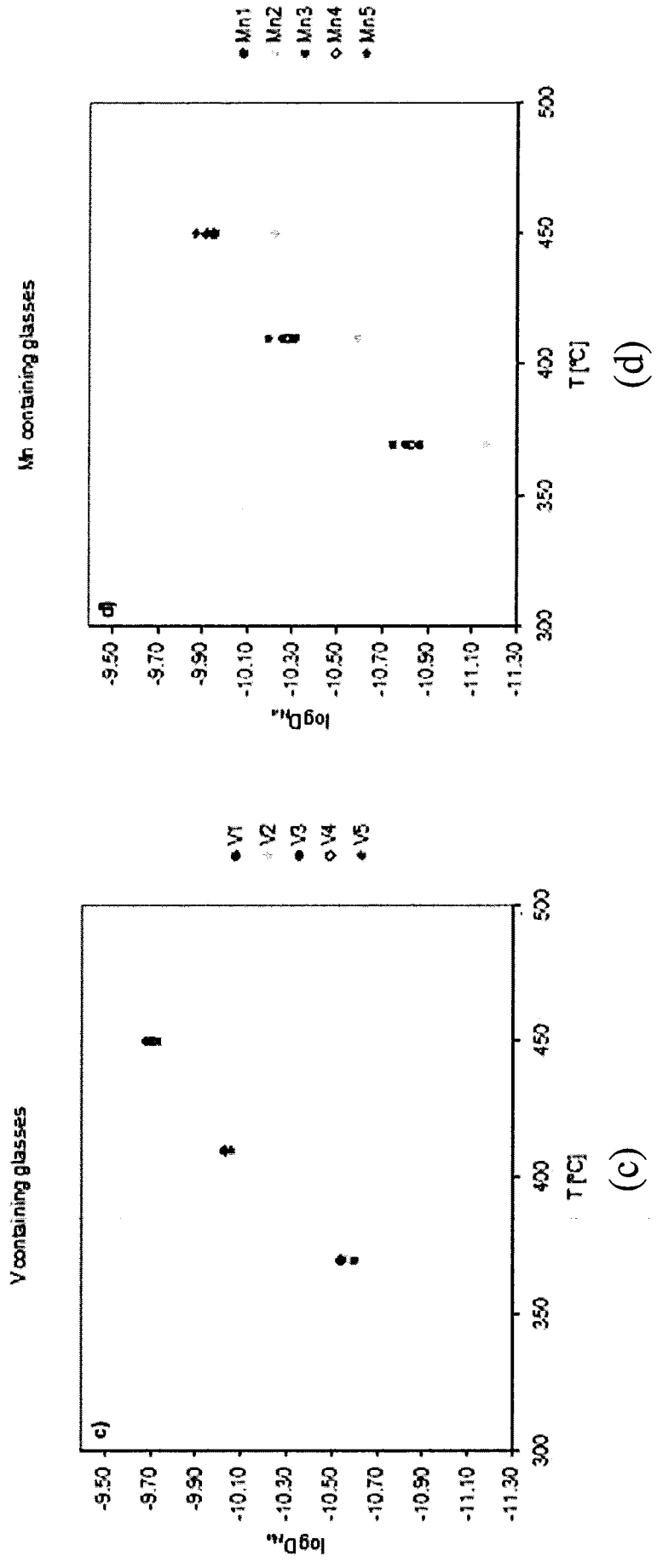
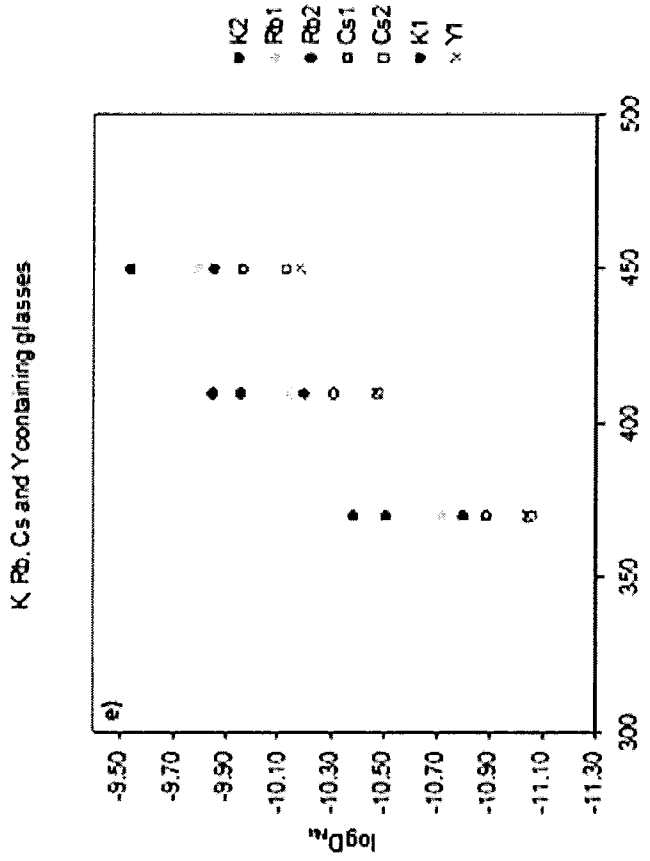

Mn containing glasses
Mn1
Mn2
Mn3
Mn4
Mn5
logD_{Li}
T [°C]
(d)
Y containing glasses
V1
V2
V3
V4
V5
logD_{Li}
T [°C]
(c)

FIG. 2


K Rb, Cs and Y containing glasses
e)
K2
Rb1
Rb2
Cs1
Cs2
K1
Y1
logD
-9.50
-9.70
-9.90
-10.10
-10.30
-10.50
-10.70
-10.90
-11.10
-11.30
300
350
400
450
500
T [°C]

(e)

FIG. 3

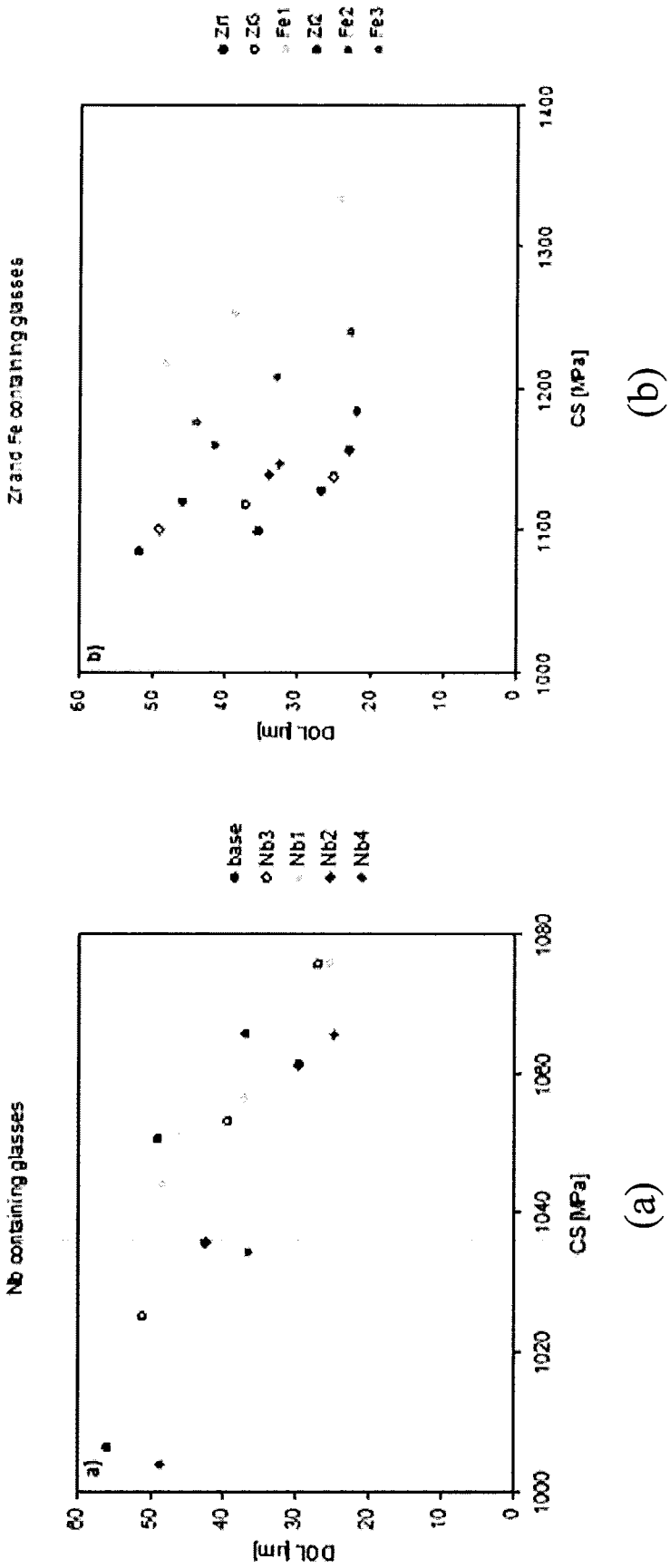

Zr and Fe containing glasses
Zn
Zr
Fe1
Zr
Fe2
Fe3
b)
DOL [µm]
CS [MPa]
(b)
Nb containing glasses
base
Nb3
Nb1
Nb2
Nb4
a)
DOL [µm]
CS [MPa]
(a)

FIG. 3

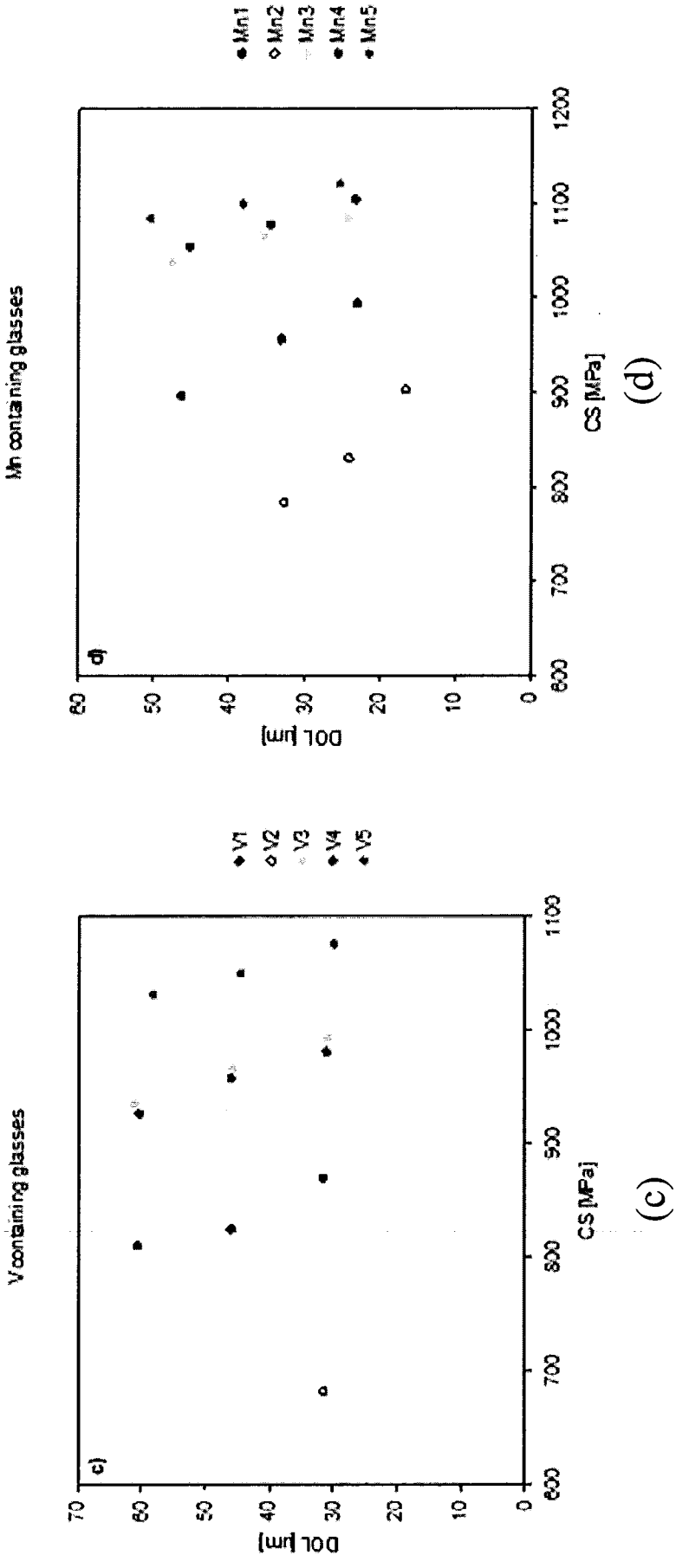
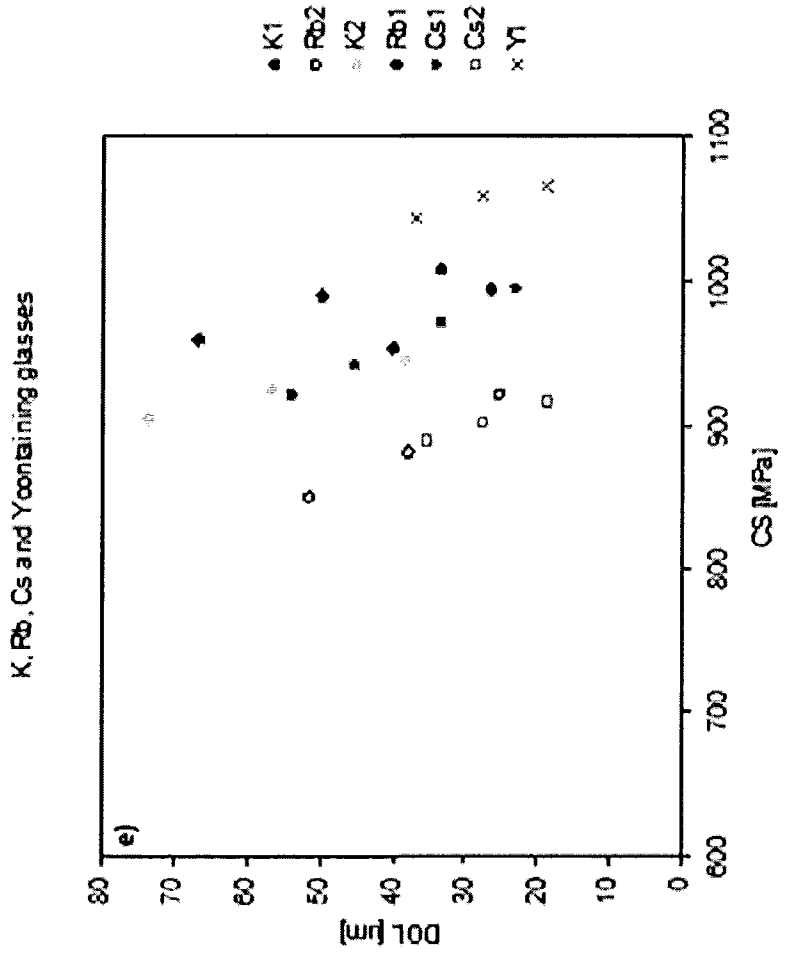

Mn containing glasses
Mn1
Mn2
Mn3
Mn4
Mn5
DOL [µm]
CS [MPa]
(d)
V containing glasses
V1
V2
V3
V4
V5
DOL [µm]
CS [MPa]
(c)

FIG. 3


K, Rb, Cs and Y containing glasses
K1
Rb2
K2
Rb1
Cs1
Cs2
Y1
e)
DOL [µm]
CS [MPa]
0
10
20
30
40
50
60
70
80
600
700
800
900
1000
1100

(e)

FIG. 4

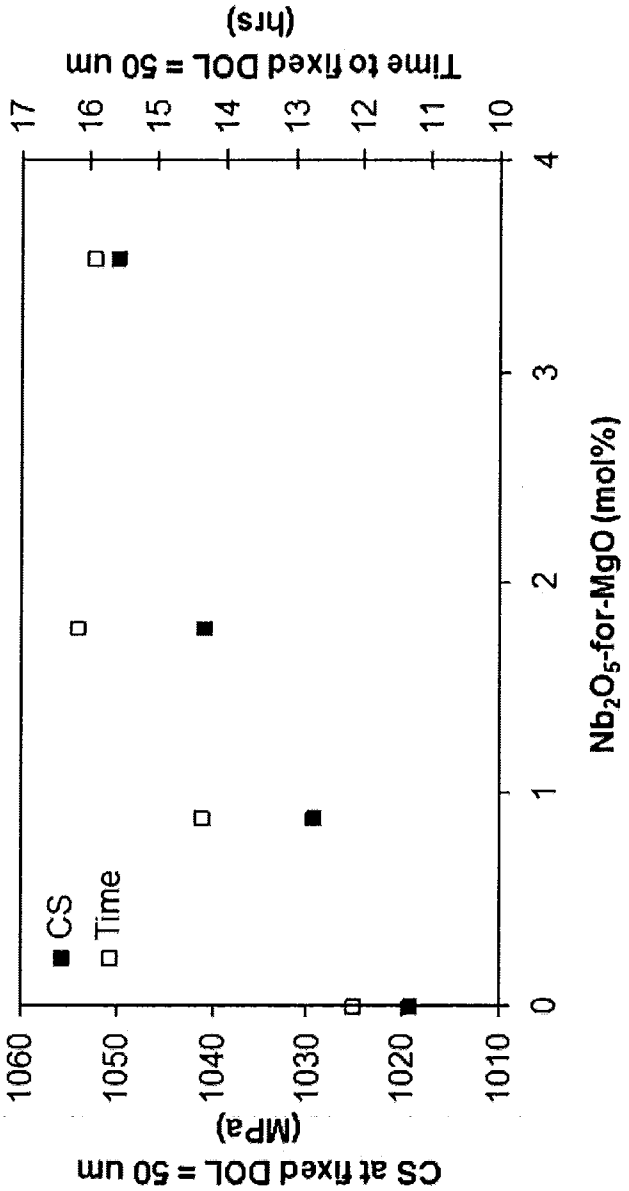
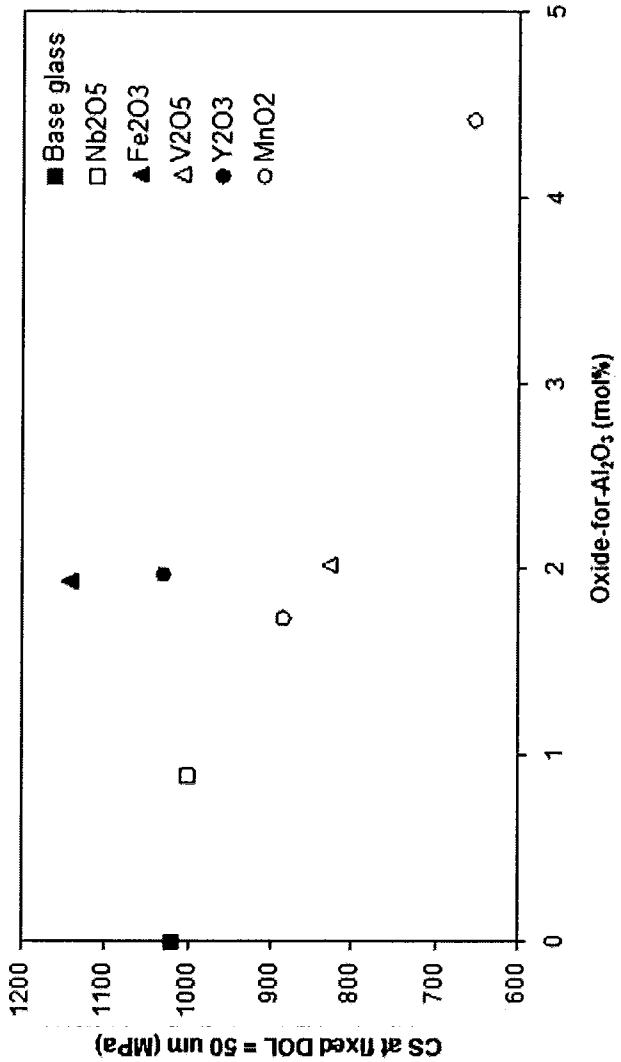
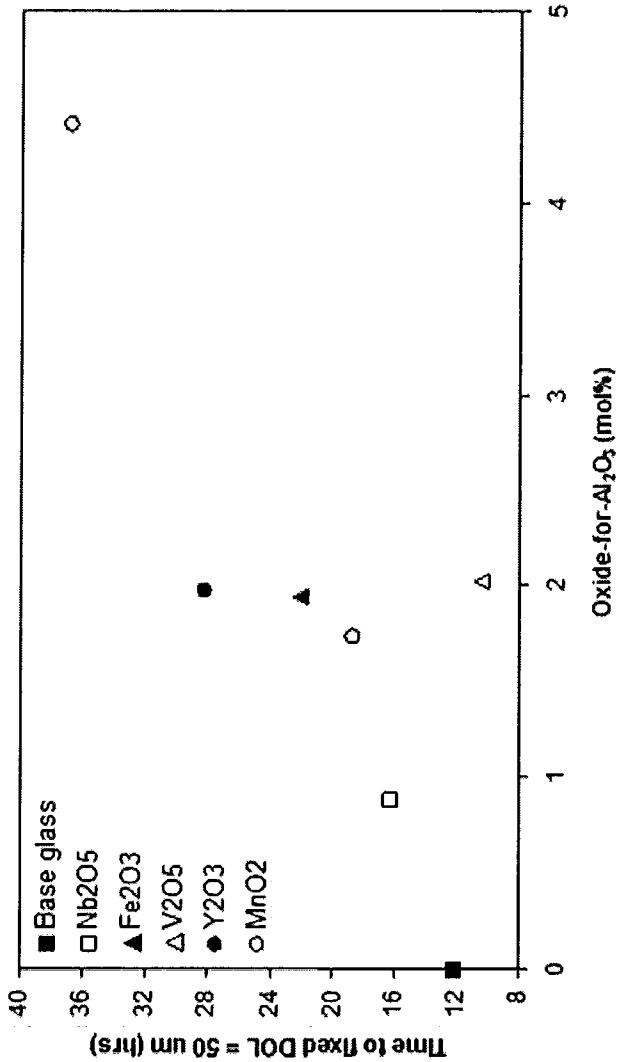

CS at fixed DOL = 50 um
(MPa)
1060
1050
1040
1030
1020
1010
Time to fixed DOL = 50 um
(hrs)
17
16
15
14
13
12
11
10
CS
Time
0
1
2
3
4
Nb2O5-for-MgO (mol%)

FIG. 5


Base glass
Nb2O5
Fe2O3
V2O5
Y2O3
MnO2
CS at fixed DOL = 50 um (MPa)
Oxide-for-Al2O3 (mol%)
1200
1100
1000
900
800
700
600
0
1
2
3
4
5

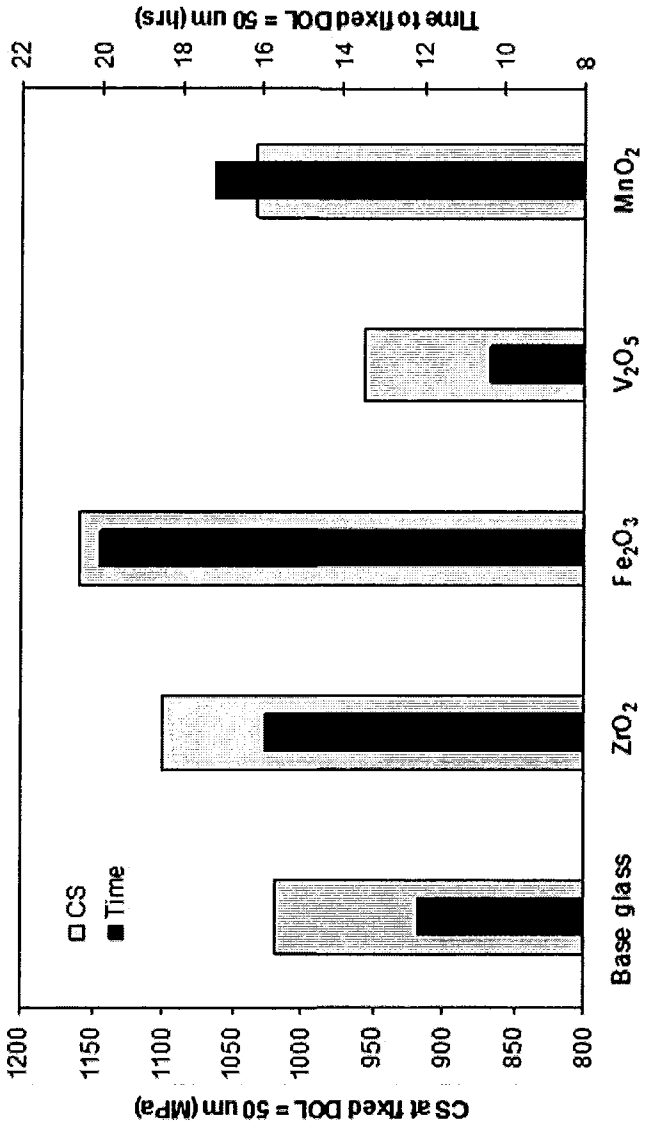
(a)

FIG. 5


Time to fixed DOL = 50 um (hrs)
Oxide-for-Al_2O_3 (mol%)
Base glass
Nb2O5
Fe2O3
V2O5
Y2O3
MnO2
40
36
32
28
24
20
16
12
8
0
1
2
3
4
5

(b)

FIG. 6


CS at fixed DOL = 50 um (MPa)
1200
1150
1100
1050
1000
950
900
850
800
Time to fixed DOL = 50 um (hrs)
22
20
18
16
14
12
10
8
CS
Time
Base glass
ZrO2
Fe2O3
V2O5
MnO2