



(51) International Patent Classification:

C03B 1/00 (2006.01) *C03C 3/095* (2006.01)
C03C 3/087 (2006.01) *C03C 3/118* (2006.01)
C03C 3/091 (2006.01) *C03B 5/173* (2006.01)

(21) International Application Number:

PCT/US2019/047112

(22) International Filing Date:

19 August 2019 (19.08.2019)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/721,233 22 August 2018 (22.08.2018) US

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(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN,

(54) Title: METHODS FOR MANUFACTURING GLASS ARTICLES

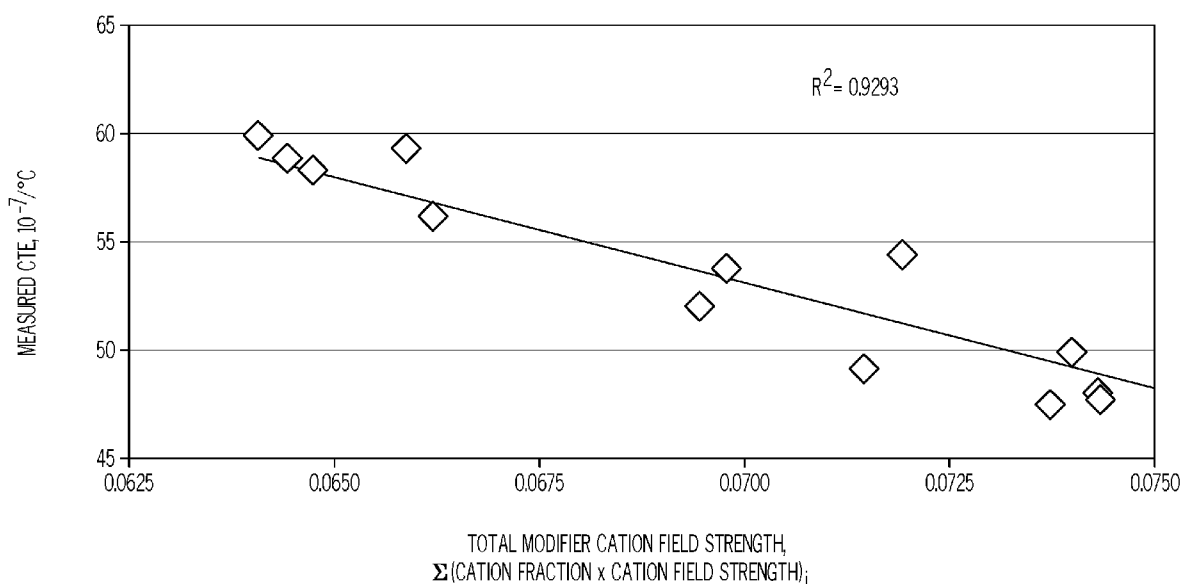


FIG. 2

(57) **Abstract:** Methods of producing a glass article include melting a first glass composition and feeding a second glass composition into the melter. Both glass compositions include the same combination of components but at least one component has a concentration that is different in each. At least three glass articles may be drawn from the melter, including: a first glass article formed from the first glass composition; at least one intermediate glass article composed of neither the first nor the second glass composition; and a final glass article not composed of the first glass composition. The concentration of the at least one component in the intermediate glass article may be between the concentration in the first and second glass compositions. The first glass article and final glass article may have differing values for certain properties, and the intermediate glass article may have an intermediate set of values for the same properties.



HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, 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, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, 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))*

METHODS FOR MANUFACTURING GLASS ARTICLES

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority to U.S. Provisional Application Serial No. 62/721,233 filed on August 22, 2018, the content of which is relied upon and incorporated herein by reference in its entirety.

BACKGROUND

FIELD

[0002] This disclosure relates to methods for manufacturing glass articles, and in particular, to methods for forming glass articles having target coefficients of thermal expansion.

TECHNICAL BACKGROUND

[0003] Glass articles are used in a variety of industries, including the semiconductor packaging industry. In the semiconductor packaging industry, chips are placed on carrier substrates (e.g., glass plates) for processing which may include thermo-mechanical and lithographic steps. However, processing techniques may vary among manufacturers, giving rise to different carrier requirements for different manufacturing techniques that, in turn, give rise to difficulties in manufacturing a single carrier substrate design that meets all the requirements for different manufacturers.

[0004] Accordingly, a need exists for alternative methods of manufacturing glass carriers for use in semiconductor manufacturing.

SUMMARY

[0005] According to various aspects disclosed herein, a method of producing a glass article includes melting a first glass composition in a melter, the first glass composition comprising a combination of glass constituent components. A second glass composition may then be fed into the melter. This second glass composition includes the same combination of glass constituent components but at least one glass constituent component has a concentration that is different from the concentration of the same component in the first glass composition. At least three glass articles

may be drawn from the melter while maintaining the contents of the melter in a molten state, including: (1) a first glass article that is formed from the first glass composition; (2) at least one intermediate glass article that is composed of neither the first glass composition nor the second glass composition; (3) and a final glass article that is composed of a composition that is different from the first glass composition. The concentration of the at least one component in the at least one intermediate glass article may be between the concentration of the at least one component in the first glass composition and the concentration of the at least one component in the second glass composition. The first glass article may have a first set of values for a set of properties. The final glass article may have a second set of values for the same set of properties, the second set of values being different from the first set of values. The at least one intermediate glass article may have an intermediate set of values for the set of properties that is between the first set of values and the second set of values.

[0006] Some aspects include the method of any of the foregoing aspects, wherein the final glass article comprises the second glass composition.

[0007] Some aspects include the method of any of the foregoing aspects, wherein the concentration of the at least one glass constituent component of the second glass composition is different from the concentration of the at least one glass constituent component of the first glass composition by no more than 2 weight %.

[0008] Some aspects include the method of any of the foregoing aspects, wherein the at least one component is selected from SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , MgO , CaO , AlF_3 , and Sb_2O_3 .

[0009] Some aspects include the method of any of the foregoing aspects, wherein the at least one component comprises AlF_3 .

[0010] Some aspects include the method of any of the foregoing aspects, wherein the set of properties comprises one or more of a coefficient of thermal expansion (“CTE”), a Young’s modulus, a density, a 200 Poise temperature, a surface quality, a refractive index, a resistivity, and an edge strength.

[0011] Some aspects include the method of any of the foregoing aspects, wherein the CTE of the first glass article is equal to or within $\pm 7.5 \times 10^{-7} / ^\circ\text{C}$ different from the CTE of the final glass article.

[0012] Some aspects include the method of any of the foregoing aspects, wherein the refractive index of the first glass article is less than or equal to ± 0.01 different from the refractive index of the final glass article.

[0013] Some aspects include the method of any of the foregoing aspects, wherein the difference between the CTE of the at least one intermediate glass article and the CTE of the first glass article, as a percentage of the CTE of the first glass article, is greater than the difference between the Young's modulus of the at least one intermediate glass article and the Young's modulus of the first glass article, as a percentage of the Young's modulus of the first glass article.

[0014] Some aspects include the method of any of the foregoing aspects, wherein a viscosity of the composition within the melter varies by no more than 25 Poise during the drawing the at least three glass articles.

[0015] Some aspects include the method of any of the foregoing aspects, wherein a 200 Poise temperature of the glass mixture within the melter is less than or equal to 1500 °C.

[0016] Some aspects include the method of any of the foregoing aspects, wherein the at least three glass articles are in the shape of a boule.

[0017] Some aspects include the method of any of the foregoing aspects, wherein the feeding the second glass composition is simultaneous with the drawing the at least three glass articles.

[0018] Some aspects include the method of any of the foregoing aspects, wherein the at least one intermediate glass article comprises at least 3 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.

[0019] Some aspects include the method of any of the foregoing aspects, wherein the at least one intermediate glass article comprises at least 8 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.

[0020] Some aspects include the method of any of the foregoing aspects, wherein the at least one intermediate glass article comprises at least 18 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.

[0021] Some aspects include the method of any of the foregoing aspects, wherein the at least one intermediate glass article comprises at least 28 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.

[0022] Some aspects include the method of any of the foregoing aspects, further comprising feeding into the melter a third glass composition comprising the same combination of glass constituent components. At least one glass constituent component has a concentration that is different from a concentration of the same component of the first glass composition and the second glass composition. The method further comprises drawing at least a first additional glass article and a final additional glass article from the melter while maintaining the contents of the melter in a molten state. The first additional glass article has a first additional set of values for the set of properties and the final additional glass article has a final additional set of values for the set of properties.

[0023] Some aspects include the method of any of the foregoing aspects, wherein the set of properties comprises one or more of a coefficient of thermal expansion (“CTE”), a Young’s modulus, a density, a 200 Poise temperature, a surface quality, a refractive index, a resistivity, and an edge strength.

[0024] Some aspects include the method of any of the foregoing aspects, wherein the CTE of the first glass article is equal to or within $\pm 15 \times 10^{-7}$ /°C different from the CTE of the final additional glass article.

[0025] Some aspects include the method of any of the foregoing aspects, wherein the difference between the CTE of the first additional glass article and the CTE of the first glass article, as a percentage of the CTE of the first glass article, is greater than the difference between the Young's modulus of the first additional glass article and the Young's modulus of the first glass article, as a percentage of the Young's modulus of the first glass article.

[0026] Some aspects include the method of any of the foregoing aspects, wherein a viscosity of the composition within the melter varies by no more than 25 Poise during the drawing the first glass article and the drawing the final additional glass article.

[0027] Some aspects include the method of any of the foregoing aspects, wherein a 200 Poise temperature of the glass mixture within the melter is less than or equal to 1500 °C.

[0028] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises an alkali boroaluminosilicate glass composition.

[0029] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises an alkaline earth boroaluminosilicate glass composition.

[0030] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises a zinc boroaluminosilicate glass composition.

[0031] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂; greater than or equal to 1.5 wt% and less than or equal to 5.0 wt% Al₂O₃; greater than or equal to 0 wt% and less than or equal to 2 wt% B₂O₃; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 10 wt% K₂O; greater than or equal to 2 wt% and less than or equal to 10 wt% MgO; greater than or equal to 0 wt% and less than or equal to 2 wt% CaO; greater than or equal to 0 wt% and less than or equal to 2 wt% TiO₂; and greater than or equal to 10 wt% and less than or equal to 15 wt% ZnO.

[0032] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂; greater than or equal to 10 wt% and less than or equal to 15 wt% Al₂O₃; greater than or equal to 2 wt% and less than or equal to 4 wt% B₂O₃; greater than or equal to 2 wt% and less than or equal to 5 wt% Li₂O; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than or equal to 1 wt% and less than or equal to 3 wt% MgO; and greater than or equal to 0 wt% and less than or equal to 3 wt% CaO.

[0033] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; and greater than or equal to 7 wt% and less than or equal to 9 wt% CaO.

[0034] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 56 wt% and less than or equal to 66 wt% SiO₂; greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al₂O₃; greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li₂O; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 14 wt% K₂O; greater than or equal to 0 wt% and less than or equal to 2 wt% MgO; and greater than or equal to 0 wt% and less than or equal to 8 wt% CaO.

[0035] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 22 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 8 wt% MgO; and greater than or equal to 7 wt% and less than or equal to 12 wt% CaO.

[0036] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 35 wt% and less than or equal to 48 wt% SiO₂; greater than or equal to 17 wt% and less than or equal to 20 wt% Al₂O₃; greater than or equal to 0

wt% and less than or equal to 5 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 7 wt% K₂O; greater than or equal to 0 wt% and less than or equal to 4 wt% MgO; greater than or equal to 0 wt% and less than or equal to 8.5 wt% CaO; and greater than or equal to 25 wt% and less than or equal to 32 wt% La₂O₃.

[0037] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and greater than 0 wt% and less than or equal to 1.5 wt% AlF₃.

[0038] Some aspects include the method of any of the foregoing aspects, wherein the first glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and greater than 0.5 wt% and less than or equal to 1.5 wt% AlF₃.

[0039] Some aspects include a glass article formed from a glass composition comprising: greater than or equal to 56 wt% and less than or equal to 66 wt% SiO₂; greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al₂O₃; greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li₂O; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 14 wt% K₂O; greater than or equal to 0 wt% and less than or equal to 2 wt% MgO; and greater than or equal to 0 wt% and less than or equal to 8 wt% CaO.

[0040] Some aspects include a glass article formed from a glass composition comprising: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than

or equal to 0 wt% and less than or equal to 6 wt% MgO; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and greater than 0 wt% and less than or equal to 1.5 wt% AlF₃.

[0041] Some aspects include a method for manufacturing a glass article having a target coefficient of thermal expansion (CTE_T). The method includes melting a molten base glass composition (or a “first glass composition”) having an initial overall cation field strength, determining the target CTE_T over a temperature range, and replacing an amount of a first alkaline earth component or a first alkali component having a first cation field strength in the molten base glass composition with an amount of a second alkaline earth component or a second alkali component having a second cation field strength that is different from the first cation field strength to produce a modified glass composition. A base glass article formed from the molten base glass composition comprises an average base glass coefficient of thermal expansion CTE_B over the temperature range. The modified glass composition comprising an average coefficient of thermal expansion CTE_M over the temperature range that is within $\pm 1.0 \times 10^{-7} / ^\circ\text{C}$ of the target CTE_T and a modified overall cation field strength that is different from the initial overall cation field strength.

[0042] Some aspects include the method of any of the foregoing aspects, wherein the second cation field strength is less than the first cation field strength; the modified overall cation field strength is less than the initial overall cation field strength; and CTE_M is greater than CTE_B .

[0043] Some aspects include the method of any of the foregoing aspects, wherein the replacing comprises replacing an amount of the first alkaline earth component with an amount of an alkali component.

[0044] Some aspects include the method of any of the foregoing aspects, wherein the first alkaline earth component comprises MgO and the alkali component comprises Na₂O.

[0045] Some aspects include the method of any of the foregoing aspects, wherein the replacing comprises replacing an amount of the first alkaline earth component with an amount of the second alkaline earth component.

[0046] Some aspects include the method of any of the foregoing aspects, wherein the replacing comprises replacing an amount of the first alkali component with an amount of the second alkali component.

[0047] Some aspects include the method of any of the foregoing aspects, wherein the second cation field strength is greater than the first cation field strength; the modified overall cation field strength is greater than the initial overall cation field strength; and CTE_M is less than CTE_B .

[0048] Some aspects include the method of any of the foregoing aspects, wherein the replacing comprises replacing an amount of the first alkali component with an amount of an alkaline earth component.

[0049] Some aspects include the method of any of the foregoing aspects, wherein the first alkali component comprises Na_2O and the alkaline earth component comprises MgO .

[0050] Some aspects include the method of any of the foregoing aspects, wherein the temperature range is from 0 °C to 300 °C.

[0051] Some aspects include the method of any of the foregoing aspects, wherein the temperature range is from 20 °C to 260 °C.

[0052] Some aspects include the method of any of the foregoing aspects, wherein CTE_B is greater than or equal to $85 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $95 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from 20 °C to 260 °C.

[0053] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $80 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $100 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from 20 °C to 260 °C.

[0054] Some aspects include the method of any of the foregoing aspects, wherein a glass article formed from the modified glass composition comprises a Young's modulus of greater than or equal to 68 GPa.

[0055] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $75 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $85 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[0056] Some aspects include the method of any of the foregoing aspects, wherein a glass article formed from the modified glass composition comprises a Young's modulus of greater than or equal to 73 GPa.

[0057] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $40 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $70 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[0058] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $40 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $60 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[0059] Some aspects include the method of any of the foregoing aspects, wherein a glass article formed from the modified glass composition comprises a Young's modulus of greater than or equal to 90 GPa.

[0060] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $40 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $54 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[0061] Some aspects include the method of any of the foregoing aspects, wherein the target CTE_T is greater than or equal to $90 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $150 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[0062] Some aspects include the method of any of the foregoing aspects, wherein a glass article formed from the modified glass composition comprises a Young's modulus of greater than or equal to 65 GPa.

[0063] Some aspects include the method of any of the foregoing aspects, wherein a glass article formed from the modified glass composition comprises a Young's modulus of greater than or equal to 72 GPa.

[0064] Some aspects include the method of any of the foregoing aspects, wherein the modified glass composition comprises a 200 P temperature of less than or equal to 1500 °C.

[0065] Some aspects include the method of any of the foregoing aspects, wherein the modified glass composition comprises a 200 P temperature of less than or equal to 1450 °C.

[0066] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises an alkali boroaluminosilicate glass composition.

[0067] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises an alkaline earth boroaluminosilicate glass composition.

[0068] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises a zinc boroaluminosilicate glass composition.

[0069] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises: greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂; greater than or equal to 1.5 wt% and less than or equal to 5.0 wt% Al₂O₃; greater than or equal to 0 wt% and less than or equal to 2 wt% B₂O₃; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 10 wt% K₂O; greater than or equal to 2 wt% and less than or equal to 10 wt% MgO; greater than or equal to 0 wt% and less than or equal to 2 wt% CaO; greater than or equal to 0 wt% and less than or equal to 2 wt% TiO₂; and greater than or equal to 10 wt% and less than or equal to 15 wt% ZnO.

[0070] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises: greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂; greater than or equal to 10 wt% and less than or equal to 15 wt% Al₂O₃; greater than or equal to 2 wt% and less than or equal to 4 wt% B₂O₃; greater than or equal to 2 wt% and less than or equal to 5 wt% Li₂O; greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O; greater than

or equal to 1 wt% and less than or equal to 3 wt% MgO; and greater than or equal to 0 wt% and less than or equal to 3 wt% CaO.

[0071] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; and greater than or equal to 7 wt% and less than or equal to 9 wt% CaO.

[0072] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises: greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 22 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 8 wt% MgO; and greater than or equal to 7 wt% and less than or equal to 12 wt% CaO.

[0073] Some aspects include the method of any of the foregoing aspects, wherein the base glass composition comprises: greater than or equal to 35 wt% and less than or equal to 48 wt% SiO₂; greater than or equal to 17 wt% and less than or equal to 20 wt% Al₂O₃; greater than or equal to 0 wt% and less than or equal to 5 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 7 wt% K₂O; greater than or equal to 0 wt% and less than or equal to 4 wt% MgO; greater than or equal to 0 wt% and less than or equal to 8.5 wt% CaO; and greater than or equal to 25 wt% and less than or equal to 32 wt% La₂O₃.

[0074] Some aspects include the method of any of the foregoing aspects, further comprising delivering the modified glass composition to a forming vessel.

[0075] Some aspects include the method of any of the foregoing aspects, further comprising forming the modified glass composition into a glass boule with the forming vessel.

[0076] Some aspects include the method of any of the foregoing aspects, wherein when the target CTE_T is greater than or equal to $80 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $100 \times 10^{-7} / ^\circ\text{C}$ over

the temperature range from 20 °C to 260 °C, determining the target CTE_T comprises determining the target CTE_T according to the following equation:

$$CTE_T = (-1.17[\text{wt}\% \text{SiO}_2]) - (1.31[\text{wt}\% \text{Al}_2\text{O}_3]) - (0.84[\text{wt}\% \text{B}_2\text{O}_3]) + (4.36[\text{wt}\% \text{Na}_2\text{O}]) + (0.98[\text{wt}\% \text{MgO}]) + (47.1[\text{wt}\% \text{TiO}_2]) - (0.64[\text{wt}\% \text{ZnO}]) + (4.45 [\text{wt}\% \text{K}_2\text{O}]) - (37.2[\text{wt}\% \text{CaO}]) - 1.17.$$

[0077] Some aspects include the method of any of the foregoing aspects, wherein when the target CTE_T is greater than or equal to $40 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $70 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from 20 °C to 260 °C, determining the target CTE_T comprises determining the target CTE_T according to the following equation:

$$CTE_T = (6.58[\text{wt}\% \text{SiO}_2]) + (0.67[\text{wt}\% \text{Al}_2\text{O}_3]) + (0.04[\text{wt}\% \text{B}_2\text{O}_3]) + (3.64[\text{wt}\% \text{Na}_2\text{O}]) + (0.59[\text{wt}\% \text{MgO}]) + (1.34[\text{wt}\% \text{CaO}]) + 6.58.$$

[0078] Some aspects include the method of any of the foregoing aspects, wherein when the target CTE_T is greater than or equal to $90 \times 10^{-7} / ^\circ\text{C}$ and less than or equal to $150 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from 20 °C to 260 °C, determining the target CTE_T comprises determining the target CTE_T according to the following equation:

$$CTE_T = (137.56[\text{wt}\% \text{SiO}_2]) - (5.47[\text{wt}\% \text{Al}_2\text{O}_3]) + (1.18[\text{wt}\% \text{Li}_2\text{O}]) + (2.22[\text{wt}\% \text{Na}_2\text{O}]) + (1.32[\text{wt}\% \text{K}_2\text{O}]) - (5.37[\text{wt}\% \text{MgO}]) - (0.09[\text{wt}\% \text{CaO}]) + 137.56.$$

[0079] Some aspects include a glass article formed from a glass composition including greater than or equal to 56 wt% and less than or equal to 66 wt% SiO_2 ; greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al_2O_3 ; greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li_2O ; greater than or equal to 6 wt% and less than or equal to 18 wt% Na_2O ; greater than or equal to 0 wt% and less than or equal to 14 wt% K_2O ; greater than or equal to 0 wt% and less than or equal to 2 wt% MgO ; and greater than or equal to 0 wt% and less than or equal to 8 wt% CaO .

[0080] Some aspects include the glass article of any of the foregoing aspects, comprising a coefficient of thermal expansion (CTE) of greater than or equal to 90×10^{-7} and less than or equal to $150 \times 10^{-7} / ^\circ\text{C}$ over the temperature range from 20 °C to 260 °C.

[0081] Some aspects include the glass article of any of the foregoing aspects, comprising a Young's modulus of greater than or equal to 70 GPa and less than or equal to 100 GPa.

[0082] Some aspects include the glass article of any of the foregoing aspects, wherein the Young's modulus is greater than or equal to 72 GPa and less than or equal to 85 GPa.

[0083] Some aspects include the glass article of any of the foregoing aspects, comprising a 200 Poise temperature of greater than or equal to 0 °C and less than or equal to 1500 °C.

[0084] Some aspects include the glass article of any of the foregoing aspects, wherein the 200 Poise temperature is greater than or equal to 1250 °C and less than or equal to 1500 °C.

[0085] Some aspects include the glass article of any of the foregoing aspects, wherein the glass composition comprises a density of greater than or equal to 2.25 g/cm³ and less than or equal to 2.75 g/cm³.

[0086] Some aspects include the glass article of any of the foregoing aspects, wherein:

$$13 \text{ wt\%} < [\text{wt\% Li}_2\text{O} + \text{wt\% Na}_2\text{O} + \text{wt\% K}_2\text{O}] < 31 \text{ wt\%}.$$

[0087] Various aspects disclosed herein may be combined in any permutation.

[0088] It is to be understood that both the foregoing general description and the following detailed description are merely exemplary, and are intended to provide an overview or framework to understanding the nature and character of the claimed subject matter. The accompanying drawings are included to provide a further understanding and are incorporated in and constitute a part of this specification. The drawings illustrate one or more embodiment(s), and together with the description, serve to explain principles and operation of the various embodiments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0089] FIG. 1 schematically depicts one example glass manufacturing apparatus for forming glass substrates in accordance with one or more embodiments shown and described herein;

[0090] FIG. 2 is a plot of measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of total modifier cation field strength (X-axis) in accordance with one or more embodiments shown and described herein; and

[0091] FIG. 3 is a plot of measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of total modifier cation field strength (X-axis) in accordance with one or more embodiments shown and described herein;

[0092] FIG. 4 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for example glass compositions in accordance with one or more embodiments shown and described herein;

[0093] FIG. 5 is a plot of the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa) for example glass compositions in accordance with one or more embodiments shown and described herein;

[0094] FIG. 6 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for different example glass compositions in accordance with one or more embodiments shown and described herein;

[0095] FIG. 7 is a plot of the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa) for different example glass compositions in accordance with one or more embodiments shown and described herein;

[0096] FIG. 8 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for example glass compositions in accordance with one or more embodiments shown and described herein;

[0097] FIG. 9 is a plot of the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa) for example glass compositions in accordance with one or more embodiments shown and described herein;

[0098] FIG. 10 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[0099] FIG. 11 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[00100] FIG. 12 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[00101] FIG. 13 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[00102] FIG. 14 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[00103] FIG. 15 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ for example glass compositions in accordance with one or more embodiments shown and described herein;

[00104] FIG. 16 is a plot of the measured CTE of several glasses containing fluorine (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the CTE of those same glasses made without fluorine (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) in accordance with one or more embodiments shown and described herein;

[00105] FIG. 17 is a plot of the measured elastic modulus of several glasses containing fluorine (Y-axis; values in GPa) versus the measured elastic modulus of those same glasses made without fluorine (X-axis; values in GPa) in accordance with one or more embodiments shown and described herein;

[00106] FIG. 18 is a plot of log viscosity (Y-axis; values in Poise) versus temperature (X-axis; values in °C) for two of the fluorine-free production glasses, HS5.1 and HS5.9, compared to the same glass compositions with 1.3 weight % fluorine and a standard production glass, QE, in accordance with one or more embodiments shown and described herein;

[00107] FIG. 19 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7}$ /°C) versus the measured CTE (X-axis; values $\times 10^{-7}$ /°C) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00108] FIG. 20 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7}$ /°C) versus the measured CTE (X-axis; values $\times 10^{-7}$ /°C) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00109] FIG. 21 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7}$ /°C) versus the measured CTE (X-axis; values $\times 10^{-7}$ /°C) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00110] FIG. 22 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7}$ /°C) versus the measured CTE (X-axis; values $\times 10^{-7}$ /°C) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00111] FIG. 23 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00112] FIG. 24 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00113] FIG. 25 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein;

[00114] FIG. 26 is a plot of the predicted Young's modulus (Y-axis; GPa), using alternative models, versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein; and

[00115] FIG. 27 is a plot of the predicted Young's modulus (Y-axis; GPa), using alternative models, versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions in accordance with one or more embodiments shown and described herein.

DETAILED DESCRIPTION

[00116] Reference will now be made in detail to various embodiments of methods for manufacturing glass articles having a target coefficient of thermal expansion CTE_T , embodiments of which are illustrated in the accompanying drawings. Whenever possible, the same reference numerals will be used throughout the drawings to refer to the same or like parts. The components in the drawings are not necessarily to scale, emphasis instead being placed upon illustrating the principles of the embodiments.

[00117] The terms “glass” and “glass composition” encompass both glass materials and glass-ceramic materials, as both classes of materials are commonly understood. Likewise, the term “glass structure” encompasses structures comprising glass.

[00118] The term “coefficient of thermal expansion” or CTE is an average CTE over a particular range of temperatures, as determined in accordance with ASTM E228. Unless specified otherwise, the temperature range is from about 20 °C to about 260 °C.

[00119] The elastic modulus (also referred to as Young's modulus) of the substrate is provided in units of gigapascals (GPa). The elastic modulus of the substrate is determined by resonant ultrasound spectroscopy on bulk samples of the substrate.

[00120] The density of the substrate is a measure of the degree of compactness of the substrate and is provided in g/cm^3 . The density is determined in accordance with ASTM C693.

[00121] The 200 Poise temperature is the temperature at which the glass melt demonstrates a viscosity of 200 Poise and is provided in °C. This temperature is determined in accordance with ASTM C965.

[00122] The surface quality of a substrate is a numerical description of the flatness or roughness of a surface and is determined using a frequency stepping interferometer, for example, a TROPEL® FLATMASTER® MSP (Multi-Surface Profiler).

[00123] The refractive index of a substrate is the ratio of the velocity of light in a vacuum to its velocity in the substrate. As a ratio, the refractive index is unitless. The refractive index may be determined a refractometer, for example, a Bausch and Lomb Low Range Precision Refractometer or a Metricon Prism Coupler.

[00124] The resistivity of a substrate is a measure of the resisting power of a specified material to the flow of an electric current and is provided in $\Omega \cdot m$. The resistivity may be determined in accordance with ASTM D-257 and/or ASTM D-657.

[00125] The edge strength of a substrate is a measure of the substrate's modulus of rupture and is provided in MPa. The edge strength may be determined by performing a four-point bend of the substrate.

[00126] The viscosity of the melt is a quantity expressing the magnitude of internal friction, as measured by the force per unit area resisting a flow in which parallel layers unit distance apart have unit speed relative to one another. Viscosity is provided in Poise herein and may be determined by ASTM C965.

[00127] Numerical values, including endpoints of ranges, can be expressed herein as approximations preceded by the term "about," "approximately," or the like. In such cases, other embodiments include the particular numerical values. Regardless of whether a numerical value is expressed as an approximation, two embodiments are included in this disclosure: one expressed as an approximation, and another not expressed as an approximation. It will be further understood that an endpoint of each range is significant both in relation to another endpoint, and independently of another endpoint.

[00128] Concentrations of the constituent components are specified in weight percent (wt% or weight %) on an oxide basis unless otherwise specified.

[00129] The term “formed from” can mean one or more of comprises, consists essentially of, or consists of. For example, a component that is formed from a particular material can comprise the particular material, consist essentially of the particular material, or consist of the particular material.

[00130] Directional terms as used herein – for example up, down, right, left, front, back, top, bottom, vertical, horizontal – are made only with reference to the figures as drawn and are not intended to imply absolute orientation unless otherwise expressly stated.

[00131] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order, nor that with any apparatus specific orientations be required. Accordingly, where a method claim does not actually recite an order to be followed by its steps, or that any apparatus claim does not actually recite an order or orientation to individual components, or it is not otherwise specifically stated in the claims or description that the steps are to be limited to a specific order, or that a specific order or orientation to components of an apparatus is not recited, it is in no way intended that an order or orientation be inferred, in any respect. This holds for any possible non-express basis for interpretation, including: matters of logic with respect to arrangement of steps, operational flow, order of components, or orientation of components; plain meaning derived from grammatical organization or punctuation, and; the number or type of embodiments described in the specification.

[00132] As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a” component includes aspects having two or more such components, unless the context clearly indicates otherwise. Also, the word “or” when used without a preceding “either” (or other similar language indicating that “or” is unequivocally meant to be exclusive – e.g., only one of x or y, etc.) shall be interpreted to be inclusive (e.g., “x or y” means one or both x or y).

[00133] The term “and/or” shall also be interpreted to be inclusive (e.g., “x and/or y” means one or both x or y). In situations where “and/or” or “or” are used as a conjunction for a group of three or more items, the group should be interpreted to include one item alone, all the items together, or any combination or number of the items. Moreover, terms used in the specification and claims

such as have, having, include, and including should be construed to be synonymous with the terms comprise and comprising.

[00134] Unless otherwise indicated, all numbers or expressions, such as those expressing dimensions, physical characteristics, and the like, used in the specification (other than the claims) are understood to be modified in all instances by the term “approximately.” At the very least, and not as an attempt to limit the application of the doctrine of equivalents to the claims, each numerical parameter recited in the specification or claims which is modified by the term “approximately” should be construed in light of the number of recited significant digits and by applying ordinary rounding techniques.

[00135] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, another embodiment includes from the one particular value and/or to the other particular value. Similarly, when values are expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another embodiment. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[00136] The drawings shall be interpreted as illustrating one or more embodiments that are drawn to scale and/or one or more embodiments that are not drawn to scale. This means the drawings can be interpreted, for example, as showing: (a) everything drawn to scale, (b) nothing drawn to scale, or (c) one or more features drawn to scale and one or more features not drawn to scale. Accordingly, the drawings can serve to provide support to recite the sizes, proportions, and/or other dimensions of any of the illustrated features either alone or relative to each other. Furthermore, all such sizes, proportions, and/or other dimensions are to be understood as being variable from 0-100% in either direction and thus provide support for claims that recite such values or any and all ranges or subranges that can be formed by such values.

[00137] The terms recited in the claims should be given their ordinary and customary meaning as determined by reference to relevant entries in widely used general dictionaries and/or relevant technical dictionaries, commonly understood meanings by those in the art, etc., with the understanding that the broadest meaning imparted by any one or combination of these sources should be given to the claim terms (e.g., two or more relevant dictionary entries should be

combined to provide the broadest meaning of the combination of entries, etc.) subject only to the following exceptions: (a) if a term is used in a manner that is more expansive than its ordinary and customary meaning, the term should be given its ordinary and customary meaning plus the additional expansive meaning, or (b) if a term has been explicitly defined to have a different meaning by reciting the term followed by the phrase “as used in this document shall mean” or similar language (e.g., “this term means,” “this term is defined as,” “for the purposes of this disclosure this term shall mean,” etc.). References to specific examples, use of “i.e.,” use of the word “invention,” etc., are not meant to invoke exception (b) or otherwise restrict the scope of the recited claim terms. Other than situations where exception (b) applies, nothing contained in this document should be considered a disclaimer or disavowal of claim scope.

[00138] In the semiconductor packaging industry, different manufacturers have overarching carrier substrate requirements (i.e., size, shape, etc.) that are somewhat uniform. However, the property specifications (i.e., coefficient of thermal expansion, elastic modulus, and the like) may differ from manufacturer to manufacturer or even from facility to facility. For example, the thermal profile of a semiconductor packaging process may be unique to a specific manufacturer, which in turn, gives rise to a need for carrier substrates having thermal characteristics tailored to the specific thermal profile, such as the coefficient of thermal expansion (CTE) or the like. In addition to particular CTE requirements, the glass carriers may also need to have certain other properties, such as elastic moduli, viscosity, surface quality, and edge strength requirements to be considered suitable for use in conjunction with particular semiconductor packaging operations. The wide array of property specifications for carrier substrates presents a unique challenge to manufacturers of glass substrates seeking to economically and efficiently mass produce carrier substrates compatible for use with different packaging operations.

[00139] For example, semiconductor fabrication labs may need to perform a wide array of post-fabrication processing of the semiconductor. This processing typically includes placing the semiconductor on the carrier substrate and then performing thermo-mechanical as well as lithographic steps. The steps may be used to add metal connects, epoxy molding compounds, soldering, and the like. Historically the semiconductor packaging industry used polymer material as the substrate carrier. The polymer material was sufficient for low-end chip packaging but has

proven unsatisfactory for manufacturing high-end products due to the inherent structural instability of polymers at the packaging processing temperatures.

[00140] A recent trend in this industry is to use glass wafers (200 mm / 300 mm diameter) or panels (500 mm x 500 mm) as substrates. Depending on the manufacturer and the particular steps involved in the post-fabrication processing, the carrier substrate may experience variable amounts of stress and warpage throughout the post-fabrication process, and therefore have custom CTE requirements, for example.

[00141] To simplify the process of obtaining glasses meeting these custom CTE requirements, a library of glass articles may be produced that have a composition within a certain range (i.e., the compositions are similar) but physical properties which differ among each article in the library. This range of properties for a similar composition allows an end user to select and test a particular glass article with a specific property to determine the viability of using the glass article for a particular application without the need to specifically create an entire batch of glass when only a few exemplary glasses may be needed to validate the process. Of course, a range of other properties and applications, beyond CTE in semiconductor fabrication, are contemplated and possible.

[00142] Methods described herein facilitate forming carrier substrates having compositions that are compatible with the processes employed by various manufacturers, while allowing the properties of the carrier substrates, including the CTE, to be tuned to meet the specifications of individual manufacturers. Specifically, some embodiments described herein relate to a method of producing a glass article. In some embodiments, the method includes melting a first glass composition in a melter, the first glass composition comprising a combination of glass constituent components. A second glass composition may then be fed into the melter. This second glass composition may include the same combination of glass constituent components but at least one glass constituent component has a concentration that is different from the concentration of the same component in the first glass composition (sometimes referred to as the “varied component”). In some embodiments, at least three glass articles may be drawn from the melter while maintaining the contents of the melter in a molten state. These at least three glass articles may include: (1) a first glass article that is formed from the first glass composition; (2) at least one intermediate glass

article that is composed of neither the first glass composition nor the second glass composition and which may be drawn either simultaneously with the feeding of the second glass composition or at some different time; (3) and a final glass article that is composed of a composition that is different from the first glass composition and may be the same as or different from the second glass composition. The concentration of the at least one component in the at least one intermediate glass article may be between the concentration of the at least one component in the first glass composition and the concentration of the at least one component in the second glass composition. The first glass article may have a first set of values for a set of properties. The final glass article may have a second set of values for the same set of properties, the second set of values being different from the first set of values. The at least one intermediate glass article may have an intermediate set of values for the set of properties that is between the first set of values and the second set of values.

[00143] Of course, more than a second glass composition could be added to the melter. For instance, the method may further include feeding a third glass composition into the melter. This third glass composition may include the same combination of glass constituent components, but just as with the second glass composition described above, at least one glass constituent component may have a concentration that differs from that of both the first glass composition and the second glass composition. Then, the method may further include drawing at least a first additional glass article and a final additional glass article from the melter while maintaining the contents of the melter in a molten state. The first additional glass article may have a first additional set of values for the same set of properties discussed above, and the final additional glass article may have a final additional set of values for the same set of properties.

[00144] In some embodiments, the concentration of the varied component in the first glass composition may be different from that in the second glass composition by no more than 2 weight %. For instance, the concentration of the varied component in the first glass composition may be different from that in the second glass composition by no more than 1.9 weight %, 1.8 weight %, 1.7 weight %, 1.6 weight %, 1.5 weight %, 1.4 weight %, 1.3 weight %, 1.2 weight %, 1.1 weight %, 1 weight %, 0.9 weight %, 0.8 weight %, 0.7 weight %, 0.6 weight %, 0.5 weight %, 0.4 weight %, 0.3 weight %, 0.2 weight %, 0.1 weight %, or any fractional part thereof. Further, all of the components of the first glass composition may have different concentrations in the second

glass composition or all the components except one may retain the concentration present in the first glass composition. Thus, the concentration of one component, two components, three components, and so on, up to and including the concentration of all the components of the first glass composition, may be different in the second glass composition.

[00145] The at least one component, the concentration of which may differ between the first and second glass compositions, i.e. the varied component, may be any of the constituent components. Exemplary varied components include, but are not limited to, SiO₂, Al₂O₃, B₂O₃, Na₂O, MgO, CaO, AlF₃, and Sb₂O₃. In one embodiment, the varied component is AlF₃. Although AlF₃ may not be present (i.e. 0 weight %) in some embodiments, in other embodiments, AlF₃ may be present from greater than 0 weight % to less than or equal to about 1.5 weight %. In further embodiments, AlF₃ may be present from greater than or equal to 0.5 weight % to less than or equal to about 1.5 weight %.

[00146] As noted above, the first glass article may have a first set of values for a set of properties, the final glass article may have a second set of values, and the at least one intermediate glass article may have an intermediate set of values. Such properties may include, but are not limited to, CTE, Young's modulus, density, 200 Poise temperature, surface quality, refractive index, resistivity, and edge strength. In some embodiments, the CTE of the first glass article may be equal to or within $\pm 7.5 \times 10^{-7}$ /°C different from the CTE of the final glass article. In some embodiments, where a third glass composition is added to the melter, the CTE of the first glass article may be equal to or within $\pm 15 \times 10^{-7}$ /°C different from the CTE of the final additional glass article. In the same or different embodiments, the refractive index of the first glass article may be less than or equal to ± 0.01 different from the refractive index of the final glass article.

[00147] Certain properties may remain substantially unchanged throughout the method, including the draws of all glass articles. For instance, in some embodiments, the viscosity of the composition within the melter may vary by no more than 25 Poise during the drawing the at least three glass articles. In the same or different embodiments, the 200 Poise temperature of the glass mixture within the melter may be less than or equal to 1500 °C. Similar effects may be observed when more than a second glass composition, e.g., a third glass composition, is added to the melter.

[00148] In some embodiments, the value of only one property of a set of properties differs between the first, final, and intermediate glass articles. In other embodiments, all such values differ. In further embodiments, the values of any number of properties of a set of properties, from a single property to all properties, may differ between the first, final, and intermediate glass articles.

[00149] In some embodiments, the values of two or more properties may not differ to the same extent between the first, final, and intermediate glass articles. For instance, the value of one property may differ to a much larger degree than the value of another property. In some embodiments, for example, the difference between the CTE of the at least one intermediate glass article and the CTE of the first glass article, as a percentage of the CTE of the first glass article, may be greater than the difference between the Young's modulus of the at least one intermediate glass article and the Young's modulus of the first glass article, as a percentage of the Young's modulus of the first glass article. Similar effects may be observed when more than a second glass composition, e.g., a third glass composition, is added to the melter.

[00150] The shape of the glass articles produced is not particularly limited. An exemplary shape includes, but is not limited to, a glass boule. Any number of glass articles with different and unique glass compositions may be drawn from the melter. For example, hundreds, or even thousands, of glass articles may be drawn. A smaller number may also be drawn. For example, at least 5 glass articles may be drawn, i.e., the first glass article, the final glass article, and 3 intermediate glass articles. In the same or different embodiments, at least 10 glass articles may be drawn, i.e., at least 8 intermediate glass articles. Similarly, in the same or different embodiments, at least 20 glass articles may be drawn, i.e., at least 18 intermediate glass articles. Similarly, in the same or different embodiments, at least 30 glass articles may be drawn, i.e., at least 28 intermediate glass articles. Similar numbers of glass articles may be drawn when more than a second glass composition, e.g., a third glass composition, is added to the melter, but of course, even more glass articles could be drawn under such conditions. Due to the change in the concentration of the at least one component between the first and second glass compositions, the glass composition drawn changes slowly over time from that of the first glass composition to that of the second glass composition. Each intermediate article may be drawn at a different time. So, each intermediate article has a different concentration of the at least one glass constituent component that is between the concentration of

the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition. If two intermediate articles are drawn at about the same time, the difference in composition may be slight. As more time passes, the difference in composition may become more pronounced.

[00151] Referring now to FIG. 1, an example glass manufacturing apparatus 100 for forming a library of glass articles from molten glass is schematically depicted according to one or more embodiments described herein. The glass manufacturing apparatus 100 includes a melting vessel 1, a fining vessel 3, a mixing vessel 4, a delivery vessel 8, and a forming vessel 10. Glass batch materials are introduced into the melting vessel 1 as indicated by arrow 2. The batch materials, including batch oxides, are melted to form molten glass 6. The melting vessel 1 may include heating elements (not shown) for melting the batch materials. The fining vessel 3 has a high temperature processing area that receives the molten glass 6 from the melting vessel 1 and in which bubbles are removed from the molten glass 6. The fining vessel 3 is fluidly coupled to the mixing vessel 4 by a connecting tube 5. That is, molten glass flowing from the fining vessel 3 to the mixing vessel 4 flows through the connecting tube 5. The mixing vessel 4 is, in turn, fluidly coupled to the delivery vessel 8 by a connecting tube 7 such that molten glass flowing from the mixing vessel 4 to the delivery vessel 8 flows through the connecting tube 7.

[00152] The delivery vessel 8 supplies the molten glass 6 through a downcomer 9 into the forming vessel 10. The delivery vessel 8 may include heating elements (not shown) for heating and/or maintaining the glass in a molten state. In some embodiments, the delivery vessel 8 may cool and condition the molten glass in order to increase the viscosity of the glass prior to providing the glass to the forming vessel 10. The forming vessel 10 may be, for example, a fusion draw device, a slot draw device or a mold. The form of the resulting glass article will vary depending on the particular forming vessel 10 employed. However, in some embodiments, the glass article resulting from the forming vessel 10 may be in the form of a glass boule, which may then be formed into a glass plate. As the composition in the melter is varied, the resulting glass articles will exhibit different properties due to slightly different composition of each.

[00153] One convenient application for the methods described herein is to manufacture a library of glass articles having a range of target CTE_T that can be achieved by making changes to a base

glass composition. In some embodiments, the method includes replacing an amount of a first alkaline earth component or a first alkali component having a first cation field strength in the molten base glass composition with an amount of a second alkaline earth component or a second alkali component having a second cation field strength that is different from the first cation field strength. Without being bound by theory, it is believed that the CTE of an oxide glass depends on the strength of the bonds between the cations and the oxygen network. Accordingly, adjusting the overall cation field strength of the glass can be an effective driver to change the CTE of a resultant glass article, as will be described in greater detail below.

[00154] In some embodiments described herein, the CTE of the glass article may be selectively modified, or “tuned,” by adjusting the amounts of various batch oxides added to the melting vessel 1, replacing one or more batch oxides with a different batch oxide. As used herein, the term “replaced” means that a batch oxide may be reduced in amount or even eliminated from the glass composition and a different batch oxide may be added to the glass composition or increased in amount. In embodiments in which the glass manufacturing process is a continuous method, replacement of one batch oxide with another batch oxide may include adding amounts of other batch oxides to the melting vessel 1 and not adding additional amounts of the batch oxide being replaced such that, over time, the batch oxide being replaced is reduced or eliminated from the molten glass composition in the melting vessel 1. Accordingly, the one or more batch oxides to be replaced may be replaced in the glass batch oxides introduced to the melting vessel 1 and ultimately may become the molten glass 6.

[00155] In some embodiments, an amount of one or more batch oxides (e.g., a first alkaline earth component or a first alkali component having a first cation field strength) in the molten base glass composition may be replaced with an amount of a different batch oxide (e.g., a second alkaline earth component or a second alkali component having a second cation field strength that is different from the first cation field strength) to achieve a target coefficient of thermal expansion CTE_T by modifying the overall cation field strength for the glass composition. That is, it has been determined that the coefficient of thermal expansion of the glass composition is related to the overall cation field strength of the glass composition. For example, if the target CTE_T is greater than the coefficient of thermal expansion of the base glass CTE_B , the overall cation field strength for the glass composition should be decreased to achieve the target CTE_T , whereas if the target

CTE_T is less than the base glass CTE_B , the overall cation field strength for the glass composition should be increased to achieve the target CTE_T . As used herein, the terms “base glass” and “base glass composition” refer to an initial base glass composition prior to modifications. The base glass composition may also be referred to as a “first glass composition.” The resulting, or modified base glass composition, is referred to herein as the “modified glass” or “modified glass composition.” The modified glass composition may also be referred to as a “second glass composition,” as well as a “third glass composition.”

[00156] The cation field strength of a cation may be represented as Z/r^2 , where Z is the charge (unitless) of the cation and r is the radius (in Angstrom) of the cation. The overall cation field strength of a glass composition is calculated as follows: the molar fraction of only certain oxides is calculated first. For purposes of the present application, only the following oxides are considered in the overall cation field strength calculation: SiO_2 , Na_2O , CaO , MgO , Al_2O_3 , K_2O , Li_2O , and ZnO . The number of cations/molecule is then multiplied by the mole fraction and the field strength for each cation to obtain the contribution to the overall cation field strength from each oxide. The overall cation field strength is the sum of each oxide contribution. Table 1 provides cation field strength values for various cations that may be included in the batch oxides.

[00157] Table 1:

Cation Field Strength in Silicate Glasses*	
Cation	Field strength
<u>Alkali</u>	
Li^{+1}	0.26
Na^{+1}	0.18
K^{+1}	0.12
Cs^{+1}	0.11
Rb^{+1}	0.10
<u>Alkaline Earth</u>	
Mg^{+2}	0.46
Ca^{+2}	0.36
Sr^{+2}	0.29
Ba^{+2}	0.26

*G.E. Brown, F. Farges, and G. Calas, Rev. Mineral., 32, 317-410, 1995.

[00158] One method of hardening these glasses is ion exchange hardening. FIGS. 2 and 3 are exemplary plots of measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of total modifier cation

field strength (X-axis). As may be seen from the R^2 value of FIGS. 2 and 3, the CTE is highly correlated with the total modifier cation field strength. In this example, when MgO is ion exchanged for Na₂O and CaO, the CTE ranges from about $45 \times 10^{-7} / ^\circ\text{C}$ to about $65 \times 10^{-7} / ^\circ\text{C}$, with increasing field strength associated with decreasing CTE. Similarly, when MgO and CaO are ion exchanged for K₂O, the CTE ranges from about $80 \times 10^{-7} / ^\circ\text{C}$ to about $100 \times 10^{-7} / ^\circ\text{C}$, with increasing field strength associated with decreasing CTE.

[00159] In order to achieve the desired overall cation field strength (and thus the target CTE_T) for the glass composition, an amount of a first alkaline earth component in the batch oxides can be replaced with an amount of a second alkaline earth component, an amount of a first alkali component in the batch oxides can be replaced with an amount of a second alkali component, an amount of an alkaline earth component in the batch oxides can be replaced with an amount of an alkali component, or an amount of an alkali component in the batch oxides can be replaced with an amount of an alkaline earth component. In some embodiments an amount of any component may be replaced by an amount of any other component.

[00160] For example, if the target CTE_T is greater than the base glass CTE_B , in some embodiments, an amount of a first alkaline earth component in the base glass composition may be replaced with an amount of an alkali component or with an amount of a second alkaline earth component having a cation field strength that is less than the cation field strength of the first alkaline earth component. In some embodiments, an amount of a first alkali component in the base glass composition may be replaced with an amount of a second alkali component having a cation field strength that is less than the cation field strength of the first alkali component. For example, in some embodiments, an amount of MgO is replaced with an amount of Na₂O.

[00161] As another example, if the target CTE_T is less than the base glass CTE_B , in some embodiments, an amount of a first alkali component in the base glass composition may be replaced with an amount of an alkaline earth component or with an amount of a second alkali component having a cation field strength that is greater than the cation field strength of the first alkali component. In some embodiments, an amount of a first alkaline earth component in the base glass composition may be replaced with an amount of a second alkaline earth component having a cation

field strength that is greater than the cation field strength of the first alkaline earth component. For example, in some embodiments, an amount of Na_2O is replaced with an amount of MgO .

[00162] In embodiments, an amount of one or more batch components to be replaced may be determined based on the target CTE_T using mathematical modeling including, without limitation, linear modeling. The particular model to be used depends on the embodiment, and may vary depending on factors including the base glass composition and the temperature range at which the CTE is measured. Accordingly, in embodiments, the method includes melting a base glass composition, forming a glass article from the base glass composition, modifying the base glass composition to form two or more modified base glass compositions, forming glass articles from each of the modified base glass compositions, measuring the CTE of each of the glass articles made from the base glass composition and the modified base glass compositions, and developing a linear regression based on the measured CTE of the glass articles and the glass composition of the glass articles. The number of glass compositions used in the linear regression analysis may vary depending on the particular embodiment. However, it should be understood that the number of glass compositions employed should be sufficient to result in a meaningful linear regression analysis.

[00163] The base glass composition may be any one of a number of suitable glass compositions. For example, the base glass composition may be an alkali boroaluminosilicate glass composition, an alkaline earth boroaluminosilicate glass composition, a zinc boroaluminosilicate glass composition, or the like. The glass composition may be selected based on its CTE at a particular temperature or over a range of temperatures (e.g., 0°C to 400°C , 0°C to 300°C , 0°C to 260°C , 20°C to 300°C , or 20°C to 260°C), its density, its Young's modulus, its 200 Poise temperature, or other properties that may be desired for processing or use of the glass article. The 200 Poise temperature is the minimum temperature at which the glass has a viscosity of 200 Poise, which is indicative of a minimum temperature of a well-melted glass.

[00164] The glass compositions may generally include a combination of SiO_2 , Al_2O_3 , at least one alkaline earth oxide and/or alkali oxides, such as Na_2O and K_2O . In some embodiments, the glass compositions may further include minor amounts of one or more additional oxides, such as, by

way of example and not limitation, SnO_2 , Sb_2O_3 , ZrO_2 , ZnO , or the like. These components may be added as fining agents and/or to further modify the CTE of the glass composition.

[00165] In embodiments, the glass composition generally includes SiO_2 in an amount greater than or equal to 35 wt% and less than or equal to 75 wt%. When the content of SiO_2 is too small, it becomes difficult to obtain a crystallized glass having suitable impact resistance. On the other hand, when the content of SiO_2 is too large, melting ability of the glass decreases and the viscosity increases, so forming of the glass becomes difficult. In some embodiments, SiO_2 is present in the glass composition in an amount greater than or equal to 60 wt% and less than or equal to 65 wt%, greater than or equal to 56 wt% and less than or equal to 66 wt%, greater than or equal to 45 wt% and less than or equal to 55 wt%, greater than or equal to 35 wt% and less than or equal to 48 wt%, greater than or equal to 35 wt%, or even greater than or equal to 45 wt%.

[00166] The glass compositions may also include Al_2O_3 . Al_2O_3 , in conjunction with alkali oxides present in the glass composition, such as Na_2O or the like, improves the susceptibility of the glass to ion exchange strengthening. Moreover, increased amounts of Al_2O_3 may also increase the softening point of the glass, thereby reducing the formability of the glass. The glass compositions described herein may include Al_2O_3 in an amount greater than or equal to 1.5 wt% and less than or equal to 27 wt%, greater than or equal to 1.5 wt% and less than or equal to 5 wt%, greater than or equal to 8 wt% and less than or equal to 15 wt%, greater than or equal to 10 wt% and less than or equal to 15 wt%, greater than or equal to 9.5 wt% and less than or equal to 12 wt%, greater than or equal to 17 wt% and less than or equal to 20 wt%, or greater than or equal to 22 wt% and less than or equal to 27 wt%.

[00167] In some embodiments described herein, the boron concentration in the glass compositions from which the glass articles are formed is a flux, which may be added to glass compositions to make the viscosity-temperature curve less steep as well as lowering the entire curve, thereby improving the formability of the glass and softening the glass. In embodiments, the glass compositions include greater than or equal to 0 wt% B_2O_3 and less than or equal to 2 wt% B_2O_3 , greater than or equal to 2 wt% and less than or equal to 4 wt% B_2O_3 , greater than or equal to 8 wt% and less than or equal to 10 wt% B_2O_3 , or greater than or equal to 10 wt% and less than

or equal to 15 wt% B_2O_3 . In some embodiments, the glass compositions may be free from boron and compounds containing boron.

[00168] Embodiments of the glass compositions may further include one or more alkali oxides (e.g., Na_2O , K_2O , Li_2O , or the like). The alkali oxides facilitate the melting of the glass composition, lower the 200 Poise temperature, and lower the softening point of the glass, thereby offsetting the increase in the softening point due to higher concentrations of SiO_2 and/or Al_2O_3 in the glass composition. The alkali oxides also assist in improving the chemical durability of the glass composition and tuning the CTE to a desired value. The alkali oxides are generally present in the glass composition in an amount greater than or equal to 6 wt% and less than or equal to 40 wt%. In some embodiments, the amount of alkali oxides may be greater than or equal to 6 wt% and less than or equal to 28 wt%, greater than or equal to 8 wt% and less than or equal to 23 wt%, greater than or equal to 9 wt% and less than or equal to 17 wt%, or greater than or equal to 1 wt% and less than or equal to 8 wt%. In all of the glass compositions described herein, the alkali oxides include at least Na_2O and K_2O . Some embodiments the alkali oxides further include Li_2O .

[00169] In order to achieve the desired CTE, embodiments of the glass compositions include Na_2O in an amount greater than or equal to 1 wt% and less than or equal to 18 wt%, greater than or equal to 6 wt% and less than or equal to 18 wt%, greater than or equal to 0 wt% and less than or equal to 8 wt%, greater than or equal to 0 wt% and less than or equal to 5 wt%, or greater than or equal to 1 wt% and less than or equal to 8 wt%.

[00170] The concentration of K_2O in the glass also influences the CTE of the glass composition. Accordingly, in some embodiments, the amount of K_2O is greater than or equal to 0 wt% and less than or equal to 14 wt%, greater than or equal to 0 wt% and less than or equal to 10 wt%, or greater than or equal to 0 wt% and less than or equal to 7 wt%, greater than 0 wt% and less than or equal to 14 wt%, greater than 0 wt% and less than or equal to 10 wt%, or greater than 0 wt% and less than or equal to 7 wt%.

[00171] In embodiments of the glass composition that include Li_2O , the Li_2O may be present in an amount greater than or equal to 2 wt% and less than or equal to 7.5 wt%, greater than or equal to 2 wt% and less than or equal to 5 wt%, or greater than or equal to 3 wt% and less than or equal

to 7.5 wt%. However, in some embodiments, the glass composition may be substantially free of lithium and compounds containing lithium.

[00172] As provided hereinabove, embodiments of the glass compositions may further include one or more alkaline earth oxides. The alkaline earth oxide may include, for example, MgO, CaO, SrO, or combinations thereof. Alkaline earth oxides improve the meltability of the glass batch oxides and increase the chemical durability of the glass composition, in addition to influencing the CTE. In the glass compositions described herein, the glass compositions generally include at least one alkaline earth oxide in an amount greater than or equal to 1 wt% and less than or equal to 22 wt%, greater than or equal to 2 wt% and less than or equal to 12 wt%, greater than or equal to 1 wt% and less than or equal to 6 wt%, greater than or equal to 9 wt% and less than or equal to 22 wt%, greater than or equal to 12.5 wt% and less than or equal to 21 wt%, greater than or equal to 7 wt% and less than or equal to 20 wt%, greater than 0 wt% and less than or equal to 12.5 wt%, or greater than 0 wt% and less than or equal to 10 wt%.

[00173] MgO may be present in an amount from greater than or equal to 0 wt% to less than or equal to 12 wt%, greater than or equal to 1 wt% and less than or equal to 10 wt%, greater than or equal to 2 wt% and less than or equal to 10 wt%, greater than or equal to 1 wt% and less than or equal to 3 wt%, greater than or equal to 9 wt% and less than or equal to 12 wt%, greater than 0 wt% and less than or equal to 8 wt%, or even greater than 0 wt% and less than or equal to 4 wt%. However, it is contemplated that in some embodiments, MgO may not be included in the glass composition.

[00174] As another example, CaO may be present in the glass composition in an amount from greater than or equal to 0 wt% to less than or equal to 12 wt%. In embodiments, CaO may be present in an amount of from greater than 0 wt% to less than or equal to 8.5 wt%, greater than 0 wt% to less than or equal to 8 wt%, greater than 0 wt% to less than or equal to 3 wt%, greater than 0 wt% to less than or equal to 2 wt%, greater than or equal to 3 wt% to less than or equal to 6 wt%, greater than or equal to 7 wt% to less than or equal to 12 wt%, or greater than or equal to 8 wt% to less than or equal to 12 wt%. In some embodiments, CaO may be not be present in the glass composition.

[00175] In some embodiments, SrO may be included in the glass composition in an amount greater than 0.5 wt% and less than or equal to 3 wt%. In some embodiments, SrO may not be present in the glass composition.

[00176] In addition to the SiO₂, Al₂O₃, alkali oxides and alkaline earth oxides, a first embodiment of exemplary base glass compositions may optionally include one or more fining agents, such as, by way of example and not limitation, SnO₂, Sb₂O₃, As₂O₃, F⁻, and/or Cl⁻ (from NaCl or the like). When a fining agent is present in the glass composition, the fining agent may be present in amount less than or equal to 1 wt% or even less than or equal to 0.5 wt%. When the content of the fining agent is too large, the fining agent may enter the glass structure and affect various glass properties. However, when the content of the fining agent is too low, the glass may be difficult to form. For example, in some embodiments, SnO₂ is included as a fining agent in an amount greater than or equal to 0.25 wt% to less than or equal to 0.50 wt%.

[00177] Other metal oxides may additionally be included in the glass compositions of some embodiments. For example, the glass composition may further include ZnO or ZrO₂, each of which improves the resistance of the glass composition to chemical attack. In such embodiments, the additional metal oxide may be present in an amount greater than or equal to 10 wt% and less than or equal to 15 wt%. For example, the glass composition may include ZrO₂ in an amount less than or equal to 15 wt%. If the content of ZrO₂ is too high, it may not dissolve in the glass composition, may result in defects in the glass composition, and may drive the Young's modulus up. In embodiments, ZnO may be included in an amount of less than or equal to 15 wt%, or less than or equal to 12 wt%. In some embodiments, ZnO may be included as a substitute for one or more of the alkaline earth oxides, such as a partial substitute for MgO or in addition to or in place of at least one of CaO or SrO. Accordingly, the content of ZnO in the glass composition can have the same effects as described above with respect to alkaline earth oxides if it is too high or too low.

[00178] In some embodiments, the base glass composition comprises greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂, greater than or equal to 1.5 wt% and less than or equal to 5.0 wt% Al₂O₃, greater than or equal to 0 wt% and less than or equal to 2 wt% B₂O₃, greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O, greater than or equal to 0 wt% and less than or equal to 10 wt% K₂O, greater than or equal to 2 wt% and less than or equal to 10 wt%

MgO, greater than or equal to 0 wt% and less than or equal to 2 wt% CaO, greater than or equal to 0 wt% and less than or equal to 2 wt% TiO₂, and greater than or equal to 10 wt% and less than or equal to 15 wt% ZnO.

[00179] In some embodiments, the base glass composition comprises greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂, greater than or equal to 10 wt% and less than or equal to 15 wt% Al₂O₃, greater than or equal to 2 wt% and less than or equal to 4 wt% B₂O₃, greater than or equal to 2 wt% and less than or equal to 5 wt% Li₂O, greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O, greater than or equal to 1 wt% and less than or equal to 3 wt% MgO, and greater than or equal to 0 wt% and less than or equal to 3 wt% CaO.

[00180] In some embodiments, the base glass composition comprises greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂; greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃; greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃; greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; and greater than or equal to 7 wt% and less than or equal to 9 wt% CaO.

[00181] In some embodiments, the base glass composition comprises greater than or equal to 56 wt% and less than or equal to 66 wt% SiO₂, greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al₂O₃, greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li₂O, greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O, greater than or equal to 0 wt% and less than or equal to 14 wt% K₂O, greater than or equal to 0 wt% and less than or equal to 2 wt% MgO, and greater than or equal to 0 wt% and less than or equal to 8 wt% CaO.

[00182] In some embodiments, the base glass composition comprises greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂, greater than or equal to 22 wt% and less than or equal to 27 wt% Al₂O₃, greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃, greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O, greater than or equal to 0 wt% and less than or equal to 8 wt% MgO, and greater than or equal to 7 wt% and less than or equal to 12 wt% CaO.

[00183] In some embodiments, the base glass composition comprises greater than or equal to 35 wt% and less than or equal to 48 wt% SiO_2 , greater than or equal to 17 wt% and less than or equal to 20 wt% Al_2O_3 , greater than or equal to 0 wt% and less than or equal to 5 wt% Na_2O , greater than or equal to 0 wt% and less than or equal to 7 wt% K_2O , greater than or equal to 0 wt% and less than or equal to 4 wt% MgO , greater than or equal to 0 wt% and less than or equal to 8.5 wt% CaO , and greater than or equal to 25 wt% and less than or equal to 32 wt% La_2O_3 .

[00184] In some embodiments, the base glass composition comprises greater than or equal to 45 wt% and less than or equal to 55 wt% SiO_2 ; greater than or equal to 20 wt% and less than or equal to 27 wt% Al_2O_3 ; greater than or equal to 8 wt% and less than or equal to 10 wt% B_2O_3 ; greater than or equal to 0 wt% and less than or equal to 8 wt% Na_2O ; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO ; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO ; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb_2O_3 ; and greater than 0 wt% and less than or equal to 1.5 wt% AlF_3 .

[00185] In some embodiments, the base glass composition comprises greater than or equal to 45 wt% and less than or equal to 55 wt% SiO_2 ; greater than or equal to 20 wt% and less than or equal to 27 wt% Al_2O_3 ; greater than or equal to 8 wt% and less than or equal to 10 wt% B_2O_3 ; greater than or equal to 0 wt% and less than or equal to 8 wt% Na_2O ; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO ; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO ; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb_2O_3 ; and greater than 0.5 wt% and less than or equal to 1.5 wt% AlF_3 .

[00186] In some embodiments, the base glass composition comprises greater than or equal to 45 wt% and less than or equal to 55 wt% SiO_2 ; greater than or equal to 20 wt% and less than or equal to 27 wt% Al_2O_3 ; greater than or equal to 8 wt% and less than or equal to 10 wt% B_2O_3 ; greater than or equal to 0 wt% and less than or equal to 8 wt% Na_2O ; greater than or equal to 0 wt% and less than or equal to 6 wt% MgO ; greater than or equal to 7 wt% and less than or equal to 9 wt% CaO ; greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb_2O_3 ; and greater than 0 wt% and less than or equal to 1.5 wt% AlF_3 .

[00187] As described above, following selection of a base glass composition, a linear regression analysis may be performed to develop a linear regression equation relating the coefficient of

thermal expansion to the concentrations of the constituent components of the glass composition. In embodiments, the linear regression fit to the plurality of glass compositions may be used to determine a particular amount of one or more constituents needed to achieve the target CTE_T . For example, the linear regression fit can provide a coefficient for each of the constituents in the glass batch mixture. In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$CTE_T = (-1.17[\text{wt}\% \text{SiO}_2]) - (1.31[\text{wt}\% \text{Al}_2\text{O}_3]) - (0.84[\text{wt}\% \text{B}_2\text{O}_3]) + (4.36[\text{wt}\% \text{Na}_2\text{O}]) + (0.98[\text{wt}\% \text{MgO}]) + (47.1[\text{wt}\% \text{TiO}_2]) - (0.64[\text{wt}\% \text{ZnO}]) + (4.45 [\text{wt}\% \text{K}_2\text{O}]) - (37.2[\text{wt}\% \text{CaO}]) - 1.17.$$

[00188] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$CTE_T = (6.58[\text{wt}\% \text{SiO}_2]) + (0.67[\text{wt}\% \text{Al}_2\text{O}_3]) + (0.04[\text{wt}\% \text{B}_2\text{O}_3]) + (3.64[\text{wt}\% \text{Na}_2\text{O}]) + (0.59[\text{wt}\% \text{MgO}]) + (1.34[\text{wt}\% \text{CaO}]) + 6.58.$$

[00189] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$CTE_T = (137.56[\text{wt}\% \text{SiO}_2]) - (5.47[\text{wt}\% \text{Al}_2\text{O}_3]) + (1.18[\text{wt}\% \text{Li}_2\text{O}]) + (2.22[\text{wt}\% \text{Na}_2\text{O}]) + (1.32[\text{wt}\% \text{K}_2\text{O}]) - (5.37[\text{wt}\% \text{MgO}]) - (0.09[\text{wt}\% \text{CaO}]) + 137.56.$$

[00190] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$CTE_T = (156.52[\text{wt}\% \text{SiO}_2]) - (3.41[\text{wt}\% \text{Al}_2\text{O}_3]) - (6.38[\text{wt}\% \text{B}_2\text{O}_3]) + (4.70[\text{wt}\% \text{Na}_2\text{O}]) + (3.56[\text{wt}\% \text{MgO}]) - (0.62[\text{wt}\% \text{CaO}]) - (7.68[\text{wt}\% \text{F}]) + 156.52.$$

[00191] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$\begin{aligned}
CTE_T = & (142.70[\text{wt}\% \text{SiO}_2]) - (2.62[\text{wt}\% \text{Al}_2\text{O}_3]) - (8.08[\text{wt}\% \text{B}_2\text{O}_3]) \\
& + (0.45[\text{wt}\% \text{CaO}]) - (8.99[\text{wt}\% \text{F}]) + (4.35[\text{wt}\% \text{MgO}]) \\
& + (4.31[\text{wt}\% \text{Na}_2\text{O}]) + 142.70.
\end{aligned}$$

[00192] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$\begin{aligned}
CTE_T = & (115.77[\text{wt}\% \text{SiO}_2]) + (0.07[\text{wt}\% \text{Al}_2\text{O}_3]) - (4.24[\text{wt}\% \text{B}_2\text{O}_3]) \\
& + (3.72[\text{wt}\% \text{Na}_2\text{O}]) - (3.00[\text{wt}\% \text{MgO}]) - (1.38[\text{wt}\% \text{CaO}]) \\
& - (9.49[\text{wt}\% \text{F}]) + 115.77.
\end{aligned}$$

[00193] In some embodiments, the target CTE_T over the temperature range from 20 °C to 260 °C may be determined according to the following equation:

$$\begin{aligned}
CTE_T = & (119.24[\text{wt}\% \text{SiO}_2]) + (0.20[\text{wt}\% \text{Al}_2\text{O}_3]) - (3.20[\text{wt}\% \text{B}_2\text{O}_3]) \\
& - (1.95[\text{wt}\% \text{CaO}]) - (0.86[\text{wt}\% \text{F}]) - (5.48[\text{wt}\% \text{MgO}]) \\
& + (3.20[\text{wt}\% \text{Na}_2\text{O}]) + 119.24.
\end{aligned}$$

[00194] Other equations based on linear regression modeling are contemplated. The specific linear regression and coefficients can vary based on the base glass composition, the target CTE_T , and the range of temperatures over which the CTE is measured. Accordingly, the target CTE_T may be inserted into the equation and the equation may be solved to determine the concentration of the batch oxides to form a modified glass composition with a modified coefficient of thermal expansion CTE_M closely approximating the target CTE_T .

[00195] A linear regression analysis may also be performed to develop a linear regression equation relating the Young's modulus to the concentrations of the constituent components of the glass composition. In embodiments, the linear regression fit to the plurality of glass compositions may be used to determine a particular amount of one or more constituents needed to achieve the target Young's modulus (E_T). For example, the linear regression fit can provide a coefficient for each of the constituents in the glass batch mixture. In some embodiments, the target E_T may be determined according to the following equation:

$$E_T = (4.77[\text{wt}\% \text{SiO}_2]) - (4.31[\text{wt}\% \text{Al}_2\text{O}_3]) - (3.33[\text{wt}\% \text{B}_2\text{O}_3]) + (1.67[\text{wt}\% \text{Na}_2\text{O}]) \\ + (25.88[\text{wt}\% \text{MgO}]) + (5.32[\text{wt}\% \text{CaO}]) - (3.01[\text{wt}\% \text{F}]) + 4.77.$$

[00196] In some embodiments, the target E_T may be determined according to the following equation:

$$E_T = (113.95[\text{wt}\% \text{SiO}_2]) + (0.22[\text{wt}\% \text{Al}_2\text{O}_3]) - (2.75[\text{wt}\% \text{B}_2\text{O}_3]) - (0.39[\text{wt}\% \text{CaO}]) \\ - (0.94[\text{wt}\% \text{F}]) - (0.49[\text{wt}\% \text{MgO}]) - (0.47[\text{wt}\% \text{Na}_2\text{O}]) + 113.95.$$

[00197] In some embodiments, the target E_T may be determined according to the following equation:

$$E_T = (91.49[\text{wt}\% \text{SiO}_2]) + (0.21[\text{wt}\% \text{Al}_2\text{O}_3]) - (2.67[\text{wt}\% \text{B}_2\text{O}_3]) + (0.15[\text{wt}\% \text{CaO}]) \\ + (1.86[\text{wt}\% \text{F}]) - (0.16[\text{wt}\% \text{MgO}]) - (6.53[\text{wt}\% \text{Na}_2\text{O}]) + 91.49.$$

[00198] In some embodiments, the target E_T may be determined according to the following equation:

$$E_T = (-10.97[\text{wt}\% \text{SiO}_2]) + (3.95[\text{wt}\% \text{Al}_2\text{O}_3]) - (1.97[\text{wt}\% \text{B}_2\text{O}_3]) + (3.03[\text{wt}\% \text{CaO}]) \\ + (0.39[\text{wt}\% \text{F}]) + (0.09[\text{wt}\% \text{MgO}]) - (1.60[\text{wt}\% \text{Na}_2\text{O}]) - 10.97.$$

[00199] In embodiments, the CTE_M of the modified glass composition is within $\pm 1.0 \times 10^{-7} / ^\circ\text{C}$ of the target CTE_T over a corresponding temperature range. It should be understood that the accuracy of the CTE_M may vary depending on the specific linear regression used, the temperature range over which the CTE is measured and approximated, and the glass composition.

[00200] It is further contemplated that other properties may be predicted based on linear regression modeling. For example, in embodiments, the Young's modulus (sometimes referred to as the "elastic modulus" or "E-mod") for a glass composition may be predicted based on linear regression modeling. Accordingly, one or more properties of a modified glass composition can be predicted prior to manufacturing a glass article from the glass composition. This may enable confirmation that the modified glass composition will meet processing requirements and that the glass article formed from the modified glass composition will have the desired properties before mixing the batch oxides and manufacturing the glass article.

[00201] Although the desired properties may vary depending on the particular embodiment, end use, and the processing requirements for the glass composition, in embodiments, the glass articles have a Young's modulus of greater than or equal to 65 GPa, which may minimize flexing of the glass during processing and prevent damage to devices attached to the glass, such as when the glass is used as a carrier substrate for electronic devices. For example, the glass articles may have a Young's modulus of greater than or equal to 68 GPa, greater than or equal to 70 GPa, greater than or equal to 72 GPa, greater than or equal to 73 GPa, greater than or equal to 74 GPa, greater than or equal to 75 GPa, greater than or equal to 76 GPa, greater than or equal to 78 GPa, greater than or equal to 80 GPa, greater than or equal to 82 GPa, greater than or equal to 84 GPa, greater than or equal to 86 GPa, greater than or equal to 88 GPa, or greater than or equal to 90 GPa. The glass article may have a Young's modulus of greater than or equal to 65 GPa and less than or equal to 100 GPa, greater than or equal to 70 GPa and less than or equal to 100 GPa, or greater than or equal to 72 GPa and less than or equal to 85 GPa.

[00202] In embodiments, the glass composition has a 200 Poise (200 P) temperature of less than 1500 °C, which may enable the glass to be melted in a variety of processing facilities. For example, the glass composition may have a 200 P temperature of less than or equal to 1500 °C or less than or equal to 1450 °C. In some embodiments, the glass composition has a 200 P temperature of greater than or equal to 1000 °C to 1500 °C, greater than or equal to 1050 °C and less than or equal to 1500 °C, greater than or equal to 1100 °C and less than or equal to 1500 °C, greater than or equal to 1150 °C and less than or equal to 1500 °C, greater than or equal to 1200 °C and less than or equal to 1500 °C, greater than or equal to 1250 °C and less than or equal to 1500 °C, greater than or equal to 1300 °C and less than or equal to 1500 °C, greater than or equal to 1000 °C and less than or equal to 1450 °C, greater than or equal to 1050 °C and less than or equal to 1450 °C, greater than or equal to 1100 °C and less than or equal to 1450 °C, greater than or equal to 1150 °C and less than or equal to 1450 °C, greater than or equal to 1200 °C and less than or equal to 1450 °C, greater than or equal to 1250 °C and less than or equal to 1450 °C, or greater than or equal to 1300 °C and less than or equal to 1450 °C.

Examples

[00203] The following examples illustrate one or more features of the embodiments described herein.

Example 1

[00204] A base glass composition of alkali/alkaline earth zincboroaluminosilicate glass and a base glass composition of alkali/alkaline earth boroaluminosilicate glass were selected based on their CTE (from 85 to 95 x 10⁻⁷ /°C over the range from 20 °C to 260 °C), Young's modulus (greater than 65 GPa), and ease of melting (a 200 Poise temperature of less than 1500 °C). Each of the base glass compositions were varied slightly to produce modified glass compositions. The glass compositions were melted in covered Pt crucibles at a temperature between 1450 °C and 1475 °C, poured into patties, and annealed to form glass articles. The alkali/alkaline earth zincboroaluminosilicate glass articles were coarse ground, then melted a second time to ensure good glass homogeneity. All glass articles were then characterized. In particular, X-ray fluorescence (XRF) was used to characterize the chemical composition, the coefficient of thermal expansion (CTE) was measured using dilatometry, and Young's modulus was measured using resonant ultrasound spectroscopy (RUS). For instance, one or more measurements may be conducted in accordance with ASTM E228 and/or ASTM C623 and/or ASTM C1198-09(2013).

[00205] Tables 2 and 3 show the compositions, measured CTE, and measured Young's modulus for the alkali/alkaline earth zincboroaluminosilicate glass compositions, while Table 3 shows the compositions and measured CTE for the alkali/alkaline earth boroaluminosilicate glass compositions. For the compositions provided in Tables 2 and 3, Composition 1 ("Comp. 1") served as the base glass composition. Note that the CTE range from 78 to 100 x 10⁻⁷ /°C could be obtained by replacing Na₂O with MgO, or by replacing MgO with Na₂O. Accordingly, the data provided in Tables 2 and 3 demonstrates that the CTE can be controlled by adjusting the cation field strength.

[00206] Table 2:

Table 2: Glasses in the Alkali/Alkaline Earth Zincboroaluminosilicate glass family with CTE Values from 78-100 x 10⁻⁷ /°C and Young's Modulus > 68 GPa										
	Comp. 1	Comp. 2	Comp. 3	Comp. 4	Comp. 5	Comp. 6	Comp. 7	Comp. 8	Comp. 9	Comp. 10
Oxide (wt%) measured by XRF										
SiO ₂	62.8	61.5	62.9	62.9	62.9	63.0	62.8	61.0	63.4	59.7
Al ₂ O ₃	2.87	2.78	2.91	2.96	2.92	2.91	2.91	2.81	2.92	2.72
B ₂ O ₃	0.80	0.92	0.95	0.82	0.95	0.79	0.95	0.87	0.94	0.90
Na ₂ O	8.33	8.29	16.4	15.3	14.4	13.6	13.6	13.4	13.2	12.9
K ₂ O	9.16	9.15	0.01	0.01	0.01	0.00	0.01	0.01	0.00	0.01
MgO	3.03	3.31	4.13	4.98	6.13	6.79	7.14	8.26	7.15	9.76
CaO	0.04	0.04	0.05	0.06	0.07	0.07	0.08	0.08	0.08	0.09
TiO ₂	0.70	0.69	0.70	0.70	0.70	0.70	0.69	0.68	0.70	0.67
ZnO	11.2	11.9	11.5	11.7	11.4	11.4	11.4	12.6	11.4	12.8
Sb ₂ O ₃	0.43	0.44	0.44	0.40	0.44	0.44	0.44	0.41	0.44	0.42
Measured CTE (x10 ⁻⁷ /°C)	99.0	97.6	93.8	88.8	84.2	83.7	82.3	81.8	81.4	80.4
Predicted CTE (x10 ⁻⁷ /°C)	98.8	97.8	93.1	89.2	85.9	83.5	83.0	81.8	81.3	80.2
Measured Young's Modulus (GPa)	69.3	69.6	70.7	73.4	72.5	74.4	73.4	74.6	76.1	75.6
Predicted Young's Modulus (GPa)	70.1	68.8	69.7	73.3	73.6	74.1	74.6	74.6	75.5	75.4
Predicted 200 Poise Temp. (°C)	1367	1356	1273	1326	1326	1332	1281	1331	1348	1301

[00207] Table 3:

Table 3: Glasses in the Alkali/Alkaline Earth Zincboroaluminosilicate glass family with CTE Values from 78-84 x 10⁻⁷/°C and Young's Modulus > 73 GPa									
	Comp. 11	Comp. 12	Comp. 13	Comp. 14	Comp. 15	Comp. 16	Comp. 17	Comp. 18	Comp. 19
Oxide (wt%) measured by XRF									
SiO ₂	63.38	64.19	63.53	63.07	62.66	63.46	63.23	63.05	62.69
Al ₂ O ₃	2.93	3.10	2.93	2.91	2.89	2.99	2.99	2.90	2.89
B ₂ O ₃	0.74	0.94	0.91	0.95	0.92	0.81	0.84	0.94	0.94
Na ₂ O	12.66	12.70	12.24	13.09	13.54	13.34	13.89	13.34	13.79
K ₂ O	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
MgO	7.48	6.96	7.87	7.48	7.44	6.57	6.50	7.18	7.15
CaO	0.08	0.08	0.09	0.08	0.08	0.07	0.07	0.08	0.08
TiO ₂	0.70	0.70	0.70	0.69	0.69	0.69	0.68	0.69	0.69
ZnO	11.27	10.82	11.25	11.45	11.36	11.56	11.44	11.40	11.41
Sb ₂ O ₃	0.44	0.38	0.44	0.44	0.44	0.42	0.42	0.44	0.44
Measured CTE (x10 ⁻⁷ /°C)	79.7	79.4	78.1	81.6	82.0	81.0	83.2	81.9	83.9
Predicted CTE (x10 ⁻⁷ /°C)	79.7	79.4	77.7	80.9	82.8	81.2	83.2	81.8	83.8
Measured Young's Modulus (GPa)	75.3	80.0	76.3	74.5	74.6	73.5	73.5	74.1	74.1
Predicted Young's Modulus (GPa)	75.0	78.9	76.4	74.7	74.2	74.5	73.2	73.6	73.9
Predicted 200 Poise Temp. (°C)	1402	1406	1384	1285	1281	1280	1267	1279	1279

[00208] For each of the glass compositions provided in Tables 2 and 3, the measured Young's modulus values exceeded 69 GPa, while the predicted 200 Poise temperature for each of the glass compositions was below 1450 °C.

[00209] Table 4:

Table 4: Glasses in the Alkali/Alkaline Earth Boroaluminosilicate glass family with CTE Values from 85-96 x 10⁻⁷ /°C				
	Comp. 20	Comp. 21	Comp. 22	Comp. 23
Oxide (wt%) measured by XRF				
SiO ₂	64.28	64.28	63.72	63.98
Al ₂ O ₃	14.33	14.39	14.31	14.33
B ₂ O ₃	2.74	2.73	2.79	2.45
Li ₂ O	4.3	4.3	4.28	4.31
Na ₂ O	9	10.87	10.88	12.83
MgO	2.61	2.58	1.3	1.25
CaO	2.39	0.5	2.37	0.5
SnO ₂	0.36	0.36	0.37	0.35
Measured CTE (x10 ⁻⁷ /°C)	85	90	91	96
Predicted CTE (x10 ⁻⁷ /°C)	85	89	81	96

[00210] For the alkali/alkaline earth boroaluminosilicate glass compositions shown in Table 4, the CTE values are shown for the range of 85 to 96 x 10⁻⁷ /°C range, although compositions could have been selected to encompass the entire range from 78 to 100 x 10⁻⁷ /°C. Because of the lower amount of MgO present in the starting glass composition (Comp. 20) as compared to the amount of MgO in Comp. 1, both MgO and CaO replacement by Na₂O was needed to achieve the CTEs throughout the range.

[00211] The composition and property data provided in Tables 2-4 were combined and standard linear regression analysis was used to construct a predictive model for both CTE and Young's modulus. The regression coefficients that were obtained are provided in Table 5.

[00212] Table 5:

Table 5: Linear Regression Coefficients for CTE and Young's Modulus				
Oxide	CTE (20 °C – 260 °C)	Coefficient	Young's Modulus	Coefficient
SiO ₂	Intercept	-1.171629046	Intercept	-228.971
Al ₂ O ₃	X Variable 1	-1.314280351	X Variable 1	34.66347
B ₂ O ₃	X Variable 2	-0.844484203	X Variable 2	4.593175
Na ₂ O	X Variable 3	4.364221579	X Variable 3	1.645936
MgO	X Variable 4	0.97884678	X Variable 4	3.349705
TiO ₂	X Variable 5	47.09788707	X Variable 5	174.5979
ZnO	X Variable 6	-0.645462742	X Variable 6	2.703049
K ₂ O	X Variable 7	4.45477385	X Variable 7	2.123741
CaO	X Variable 8	-37.20821358	X Variable 8	5.121629

[00213] The predicted results from these linear regression models are provided in Tables 2-4 above. In all cases, the predicted values for CTE are within $1.0 \times 10^{-7} / ^\circ\text{C}$ and the predicted values for Young's modulus are within 1.0 GPa. The agreement between the measured and predicted values is shown in FIGS. 4 and 5. Specifically, FIG. 4 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for the glasses from Tables 2 and 3. FIG. 5 is a plot of the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa). As may be seen from the R^2 value for both of FIGS. 4 and 5, the model has a high predictive capability for both CTE and Young's modulus over the CTE range from $78\text{-}100 \times 10^{-7} / ^\circ\text{C}$ measured from 20 °C to 260 °C.

[00214] In order to confirm the utility of the model for manufacturing a glass with a target CTE_T , a week-long trial was conducted in which the amounts of Na₂O and MgO were varied. Minor variations in other oxide components are related to issues such as the need to overcompensate for particular components due to raw material losses during batching or to selective volatilization losses during melting. The compositions and predicted CTEs are reported in Table 6. For each of the glass compositions, the predicted CTE was in the range from 84 to $93 \times 10^{-7} / ^\circ\text{C}$ from 20 °C to 260 °C and the predicted Young's modulus was greater than 65 GPa based on the regression coefficients provided in Table 4.

[00215] Table 6:

Table 6: Glasses made in production tank with predicted CTE values											
	Oxide (wt%) measured by XRF										Predicted CTE ($\times 10^{-7} / ^\circ\text{C}$)
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	MgO	TiO ₂	ZnO	K ₂ O	CaO	Sb ₂ O ₃	
Comp. 24	62.66	2.97	0.94	14.17	6.66	0.69	11.30	0.16	0.04	0.41	87
Comp. 25	62.61	2.98	0.94	14.19	6.68	0.69	11.30	0.15	0.04	0.42	87
Comp. 26	62.59	2.98	0.96	14.23	6.68	0.69	11.28	0.14	0.04	0.41	87
Comp. 27	62.67	2.99	0.94	14.17	6.67	0.69	11.29	0.14	0.04	0.41	87
Comp. 28	62.63	2.87	0.92	14.66	6.37	0.70	11.39	0.02	0.02	0.42	89
Comp. 29	62.60	2.87	0.95	14.66	6.35	0.70	11.41	0.02	0.02	0.42	89
Comp. 30	62.69	2.87	0.93	14.63	6.33	0.70	11.39	0.02	0.02	0.42	89
Comp. 31	62.74	2.87	0.93	14.60	6.34	0.69	11.37	0.02	0.02	0.42	89
Comp. 32	62.7	2.88	0.93	14.66	6.32	0.69	11.36	0.02	0.02	0.42	89
Comp. 33	62.76	2.87	0.92	14.62	6.32	0.70	11.35	0.02	0.02	0.42	89
Comp. 34	62.80	2.87	0.92	14.62	6.28	0.69	11.36	0.02	0.02	0.42	89
Comp. 35	62.82	2.86	0.92	14.74	6.19	0.69	11.33	0.02	0.02	0.41	89
Comp. 36	62.86	2.86	0.93	14.65	6.24	0.69	11.32	0.02	0.02	0.41	89
Comp. 37	62.81	2.85	0.94	14.71	6.21	0.69	11.33	0.02	0.02	0.42	89
Comp. 38	62.91	2.87	0.93	14.65	6.19	0.69	11.31	0.02	0.02	0.41	89
Comp. 39	62.72	2.86	0.95	14.76	6.21	0.69	11.35	0.02	0.02	0.42	89
Comp. 40	62.76	2.86	0.94	14.79	6.18	0.69	11.33	0.02	0.02	0.41	90
Comp. 41	62.74	2.96	0.94	14.20	6.75	0.69	11.27	0.02	0.02	0.41	87
Comp. 42	62.82	2.90	0.93	14.59	6.33	0.69	11.29	0.02	0.02	0.41	89
Comp. 43	62.63	2.90	0.98	14.11	6.96	0.69	11.28	0.02	0.02	0.41	87
Comp. 44	62.74	2.88	0.93	14.08	6.95	0.69	11.28	0.02	0.02	0.41	87
Comp. 45	62.71	2.87	0.93	14.15	6.89	0.69	11.30	0.02	0.02	0.42	87
Comp. 46	62.62	2.88	0.94	14.20	6.88	0.69	11.32	0.02	0.03	0.42	87
Comp. 47	62.59	2.88	1.02	14.20	6.85	0.69	11.30	0.02	0.03	0.42	87
Comp. 48	62.67	2.90	0.95	14.17	6.86	0.69	11.30	0.03	0.03	0.41	87
Comp. 49	63.08	2.91	0.93	13.54	7.16	0.69	11.23	0.02	0.03	0.41	85
Comp. 50	62.78	2.91	0.93	13.35	7.56	0.69	11.32	0.02	0.03	0.41	84
Comp. 51	62.79	2.88	0.92	13.34	7.59	0.69	11.33	0.02	0.03	0.42	84
Comp. 52	62.77	2.88	0.93	13.37	7.58	0.69	11.33	0.02	0.02	0.41	84
Comp. 53	62.77	2.87	0.94	13.40	7.56	0.69	11.32	0.02	0.02	0.41	85
Comp. 54	62.81	2.88	0.92	13.39	7.55	0.69	11.31	0.02	0.02	0.41	85
Comp. 55	62.78	2.88	0.92	13.43	7.53	0.69	11.31	0.02	0.02	0.42	85
Comp. 56	62.83	2.90	0.91	13.42	7.51	0.69	11.29	0.02	0.02	0.41	85
Comp. 57	62.86	2.88	0.90	13.45	7.48	0.69	11.29	0.02	0.02	0.41	85
Comp. 58	62.82	2.94	0.93	13.45	7.43	0.69	11.29	0.02	0.02	0.4	85
Comp. 59	62.96	2.97	0.91	13.51	7.28	0.68	11.27	0.02	0.02	0.41	84
Comp. 60	62.86	2.96	0.94	13.54	7.31	0.69	11.25	0.02	0.02	0.41	85
Comp. 61	63.21	2.86	0.92	15.71	4.93	0.69	11.24	0.02	0.02	0.41	92
Comp. 62	63.36	2.84	0.91	15.90	4.62	0.68	11.25	0.02	0.02	0.41	93

[00216] Example 2

[00217] Another base glass composition was selected based on their CTE (from 40 to 70 x 10⁻⁷ /°C over the range from 20 °C to 260 °C), Young's modulus (greater than 72 GPa), and ease of melting (a 200 Poise temperature of less than 1500 °C). The glass compositions were prepared as described above. Tables 7 and 8 show the compositions, measured CTE, and measured Young's modulus for the glass compositions.

[00218] Table 7:

Table 7: Adjustable Glass Compositions with CTE in the range of 40-70 x 10⁻⁷ /°C (Reported in Oxide wt%)								
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	MgO	CaO	Sb ₂ O ₃	SnO ₂
Comp. 63	49.70	24.94	9.76	3.22	3.46	8.13	0.57	0.00
Comp. 64	48.93	24.90	10.33	3.58	3.15	8.47	0.00	0.21
Comp. 65	48.91	24.95	10.28	3.56	3.17	8.44	0.00	0.21
Comp. 66	49.81	24.94	9.68	3.85	2.80	8.14	0.57	0.00
Comp. 67	49.07	24.93	10.05	3.69	3.06	8.43	0.00	0.21
Comp. 68	49.19	25.16	9.57	5.10	1.57	8.58	0.00	0.20
Comp. 69	49.56	25.33	9.01	4.99	1.64	8.65	0.00	0.19
Comp. 70	49.39	25.05	9.52	5.75	0.81	8.53	0.00	0.20
Comp. 71	49.39	25.04	9.77	6.30	0.36	8.50	0.00	0.20
Comp. 72	49.09	24.99	9.86	6.77	0.13	8.37	0.00	0.20
Comp. 73	48.88	25.03	9.71	6.83	0.26	8.41	0.00	0.20
Comp. 74	49.13	25.01	9.84	6.73	0.09	8.38	0.00	0.20
Comp. 75	47.37	25.12	9.82	7.43	1.10	8.45	0.00	0.20
Comp. 76	47.62	25.44	9.11	7.54	1.21	8.39	0.00	0.20
Comp. 77	47.46	25.35	9.29	7.50	1.20	8.39	0.00	0.20
Comp. 78	43.86	24.93	9.80	5.33	5.26	10.17	0.52	0.00
Comp. 79	43.87	25.45	14.78	5.30	2.38	7.46	0.51	0.00

[00219] Table 8:

Table 8: Measured and Predicted Properties of Adjustable Glass Compositions with CTE in the range of $40\text{--}70 \times 10^{-7} / ^\circ\text{C}$				
	Modeled CTE <T _g ($\times 10^{-7} / ^\circ\text{C}$)	Measured CTE ($\times 10^{-7} / ^\circ\text{C}$)	Modeled Young's Modulus (GPa)	Measured Young's Modulus (GPa)
Comp. 63	47.0	47.5	80	80
Comp. 64	48.7	47.7	78	78
Comp. 65	48.5	48.0	78	78
Comp. 66	49.1	49.1	79	79
Comp. 67	49.0	49.9	78	78
Comp. 68	53.6	52	75	76
Comp. 69	53.2	53.8	76	76
Comp. 70	55.7	56.1	74	74
Comp. 71	57.6	58.3	72	72
Comp. 72	59.3	58.8	72	72
Comp. 73	59.7	59.3	72	72
Comp. 74	59.1	59.9	72	72
Comp. 75	63.0	62.6	74	74
Comp. 76	63.3	63.1	75	75
Comp. 77	63.2	63.4	75	75
Comp. 78	59.7	59.9	83	83
Comp. 79	54.3	54.4	74	74

[00220] Standard linear regression analysis was used to construct a predictive model for both CTE and Young's modulus based on the composition and property data provided in Tables 7-8. The regression coefficients that were obtained are provided in Table 8.

[00221] Table 9:

Table 9: Linear Regression Coefficients for CTE and Young's Modulus				
Oxide	CTE (20 °C – 260 °C)	Coefficient	Young's Modulus	Coefficient
SiO ₂	Intercept	31.98615022	Intercept	119.6278898
Al ₂ O ₃	X Variable 1	-0.430953446	X Variable 1	-0.724461839
B ₂ O ₃	X Variable 2	0.061922264	X Variable 2	-1.752943291
Na ₂ O	X Variable 3	4.247079525	X Variable 3	-0.094245376
MgO	X Variable 4	0.904545076	X Variable 4	2.199434789
CaO	X Variable 5	1.026704946	X Variable 5	-1.43091694

[00222] The predicted results from these linear regression models are provided in Table 8 above. In all cases, the predicted values for CTE are within $1.6 \times 10^{-7} / ^\circ\text{C}$, with all but one predicted value being within $1.0 \times 10^{-7} / ^\circ\text{C}$, and the predicted values for Young's modulus are within 1.0 GPa. The agreement between the measured and predicted values is shown in FIGS. 6 and 7. Specifically, FIG. 6 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE

(X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for the glasses from Table 7. FIG. 7 is a plot of the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa). As may be seen from the R^2 value for both of FIGS. 6 and 7, the model has a high predictive capability for both CTE and Young's modulus over the CTE range from $40\text{-}70 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00223] Using the models described in Table 9, CTEs and Young's modulus values for additional various glass compositions were predicted. In particular, Comp. 80 below was used as a base glass composition to generate various additional glass compositions. The compositions are provided in Table 10, and predicted values of various properties are provided in Table 11.

[00224] Table 10:

Table 10: Adjustable Glass Compositions with CTE in the range of $40\text{-}70 \times 10^{-7} / ^\circ\text{C}$ (Reported in Oxide wt%)								
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	MgO	CaO	F	Sb ₂ O ₃
Comp. 80	49.95	25.00	9.83	0.00	6.72	8.34	0.00	0.50
Comp. 81	49.95	25.00	9.83	0.00	4.72	10.34	0.00	0.50
Comp. 82	49.95	25.00	9.83	1.51	5.20	8.34	0.00	0.50
Comp. 83	49.95	25.00	9.83	1.88	4.84	8.34	0.00	0.50
Comp. 84	49.95	25.00	9.83	2.25	4.46	8.34	0.00	0.50
Comp. 85	49.95	25.00	9.83	3.10	3.61	8.34	0.00	0.50
Comp. 86	49.95	25.00	9.83	3.35	3.36	8.34	0.00	0.50
Comp. 87	49.95	25.00	9.83	3.35	3.36	8.34	1.15	0.50
Comp. 88	49.95	25.00	9.83	4.00	2.71	8.34	0.00	0.50
Comp. 89	49.95	25.00	9.83	4.00	2.71	8.34	1.15	0.50
Comp. 90	49.95	25.00	9.83	5.25	1.47	8.34	0.00	0.50
Comp. 91	49.95	25.00	9.83	5.35	1.37	8.34	0.00	0.50
Comp. 92	49.95	25.00	9.83	5.51	1.20	8.34	0.00	0.50
Comp. 93	49.95	25.00	9.83	6.26	0.45	8.34	0.00	0.50
Comp. 94	49.95	25.00	9.83	6.46	0.25	8.34	0.00	0.50
Comp. 95	49.95	25.00	9.83	6.71	0.00	8.34	0.00	0.50
Comp. 96	47.95	25.00	9.83	7.52	1.20	8.34	0.00	0.50
Comp. 97	47.95	25.00	9.83	7.52	1.20	8.34	1.00	0.50
Comp. 98	47.95	25.00	9.83	7.52	1.20	8.34	1.50	0.50

[00225] Table 11:

Table 11: Predicted Properties of Adjustable Glass Compositions with CTE in the range of $40\text{-}70 \times 10^{-7} / ^\circ\text{C}$					
	Modeled CTE <T _g ($\times 10^{-7} / ^\circ\text{C}$)	Modeled Young's Modulus (GPa)	Predicted Density (g/cm^3)	Predicted 200 Poise Temperature ($^\circ\text{C}$)	Predicted Liquidus Temperature ($^\circ\text{C}$)
Comp. 80	37	82	3	1446	1269
Comp. 81	39	81	3	1446	1200
Comp. 82	41	81	3	1483	1215
Comp. 83	43	80	3	1460	1147
Comp. 84	45	80	3	1437	1185
Comp. 85	46	79	2	1482	1148
Comp. 86	48	78	2	1487	1122
Comp. 87	48	--	--	--	--
Comp. 88	51	77	2	1492	1231
Comp. 89	51	--	--	--	--
Comp. 90	53	77	2	1467	1230
Comp. 91	56	76	2	1487	1228
Comp. 92	57	76	2	1482	1228
Comp. 93	59	75	2	1444	1223
Comp. 94	66	75	2	1454	1222
Comp. 95	60	74	2	1467	1163
Comp. 96	71	74	2	1467	1063
Comp. 97	71	--	--	--	--
Comp. 98	71	--	--	--	--

[00226] As shown in Table 11, each of the glass compositions is expected to have a CTE between $40 \times 10^{-7} / ^\circ\text{C}$ and $60 \times 10^{-7} / ^\circ\text{C}$, a Young's modulus greater than 72 GPa, and a 200 Poise temperature of less than $1500 ^\circ\text{C}$.

[00227] To further confirm that the concept could be used for a variety of glasses and to achieve a variety of CTEs, different starting glass compositions were studied. Two modeled glass compositions were selected to cover CTE_Ts in the range below $60 \times 10^{-7} / ^\circ\text{C}$, and the CTE was modeled using the linear regression model provided in Table 8. The results are provided in Table 12 below.

[00228] Table 12:

Table 12: Adjustable Glass Compositions with Modeled CTE in the range of 41-60 x 10 ⁻⁷ /°C											
	Starting Glass	Replacing Na ₂ O for MgO								Replacing MgO for Na ₂ O	
Oxide (wt%)	Comp. 99	Comp. 100	Comp. 101	Comp. 102	Comp. 103	Comp. 104	Comp. 105	Comp. 106	Comp. 107	Comp. 108	Comp. 109
SiO ₂	49.95	49.95	54.1	50	50	50	50	50	50	50	50
Al ₂ O ₃	25	25	22.9	25	25	25	25	25	25	25	25
B ₂ O ₃	9.83	9.83	9	9.8	9.8	9.8	9.8	9.8	9.8	9.8	9.8
Na ₂ O	5.51	1.51	1.7	3.1	3.3	3.4	4	5.3	5.4	6.3	6.7
MgO	1.2	5.2	4.4	3.6	3.4	3.3	2.7	1.5	1.4	0.4	0
CaO	8.34	8.34	7.6	8.3	8.3	8.3	8.4	8.3	8.3	8.3	8.4
SnO ₂	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16	0.16
Modeled CTE <T _g (x10 ⁻⁷ /°C)	57	41	43	46	48	49	51	53	56	59	60
Modeled Young's Modulus (GPa)	76.4	80.9	80.3	78.9	78.4	78	77.5	76.5	75	75.1	74.4
Modeled Density (g/cm ³)	2.45	2.51	2.51	2.49	2.49	2.49	2.48	2.45	2.44	2.45	2.45
Modeled 200 Poise Temp (°C)	1482	1483	1460	1482	1487	1485	1492	1467	1487	1444	1467
Modeled Liquidus Temp (°C)	1228	1215	1147	1148	1121	1303	1230	1230	1227	1223	1162

[00229] Based on the modeled data, the CTE can be tuned within the range from 40 to 60 x 10⁻⁷ /°C by starting with different base glass compositions and adjusting the composition. Each of the compositions had a CTE within the target range, a Young's modulus of greater than 72 GPa and a 200 Poise temperature of less than 1500 °C, indicating that these glasses would remain suitable for processing under the same or similar conditions as the base glass composition.

[00230] Using the models described in Table 9, CTEs and Young's modulus values for glass compositions modified from a different base glass composition were predicted. In particular, Comp. 110 below was modified to generate various additional glass compositions. The compositions are provided in Table 13, and predicted values of various properties are provided in Table 14.

[00231] Table 13:

Table 13: Adjustable Glass Compositions with CTE in the range of 40-60 x 10⁻⁷ /°C (Reported in Oxide wt%)								
	SiO ₂	Al ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	La ₂ O ₃	Sb ₂ O ₃
Comp. 110	46.12	18.49	0.00	0.00	3.77	1.44	30.02	0.00
Comp. 111	46.12	18.49	0.00	0.00	3.77	6.44	25.02	0.00
Comp. 112	39.50	18.49	0.00	4.54	0.00	7.42	30.02	0.00
Comp. 113	39.50	18.49	0.00	5.04	0.00	6.92	30.02	0.00
Comp. 114	39.50	18.49	0.00	5.54	0.00	6.42	30.02	0.00
Comp. 115	39.50	18.49	0.00	5.78	0.00	6.18	30.02	0.00
Comp. 116	39.50	18.49	0.00	6.78	0.00	5.18	30.02	0.00
Comp. 117	39.50	18.49	3.53	0.00	0.00	8.42	30.02	0.00
Comp. 118	39.50	18.49	3.53	0.50	0.00	7.2	30.02	0.00
Comp. 119	39.50	18.49	1.77	5.77	0.00	4.42	30.02	0.00
Comp. 120	39.50	18.49	2.77	4.77	0.00	4.42	30.02	0.00
Comp. 121	39.50	18.49	4.03	0.00	0.00	7.92	30.02	0.00
Comp. 122	39.50	18.49	3.77	3.77	0.00	4.42	30.02	0.00

[00232] Table 14:

Table 14: Predicted Properties of Adjustable Glass Compositions with CTE in the range of 40-60 x 10⁻⁷ /°C					
	Modeled CTE <T _g (x10 ⁻⁷ /°C)	Modeled Young's Modulus (GPa)	Predicted Density (g/cm ³)	Predicted 200 Poise Temperature (°C)	Predicted Liquidus Temperature (°C)
Comp. 110	42	96	3.16	1452	1188.7
Comp. 111	43	94	3.07	1469	1259.7
Comp. 112	45	93	3.18	1462	1194.9
Comp. 113	46	93	3.17	1463	1200.2
Comp. 114	48	93	3.17	1462	1186.0
Comp. 115	49	93	3.19	1462	1183.0
Comp. 116	50	93	3.19	1458	1182.5
Comp. 117	51	94	3.20	1440	1194.8
Comp. 118	52	93	3.19	1457	1166.6
Comp. 119	53	93	3.18	1463	1164.0
Comp. 120	55	92	3.18	1460	1157.3
Comp. 121	56	93	3.19	1445	1125.9
Comp. 122	58	90	3.16	1416	1138.0

[00233] As shown in Table 14, each of the glass compositions is expected to have a CTE between 40 x 10⁻⁷ /°C and 60 x 10⁻⁷ /°C, a Young's modulus greater than 90 GPa, and a 200 Poise temperature of less than 1500 °C.

Example 3

[00234] In order to achieve higher CTEs, a glass composition including Li_2O was studied. In particular, Comp. 123 below was modified to generate additional glass compositions having CTEs between $90 \times 10^{-7} / ^\circ\text{C}$ and $130 \times 10^{-7} / ^\circ\text{C}$. The compositions are provided in Table 15, and predicted values of various properties are provided in Table 16.

[00235] Table 15:

Table 15: Adjustable Glass Compositions with CTE in the range of $90\text{-}130 \times 10^{-7} / ^\circ\text{C}$ (Reported in Oxide wt%)								
	SiO_2	Al_2O_3	Li_2O	Na_2O	K_2O	MgO	CaO	Sb_2O_3
Comp. 123	65.96	11.55	6.20	7.54	0.36	1.27	6.83	0.25
Comp. 124	65.96	11.55	6.2	9.54	0.36	1.27	4.83	0.25
Comp. 125	65.96	11.55	6.2	11.54	0.36	1.27	2.83	0.25
Comp. 126	65.96	11.55	5.2	10.54	5.36	0.27	0.82	0.25
Comp. 127	65.96	11.55	7.2	10.54	3.36	0.27	0.83	0.25
Comp. 128	65.96	11.55	3.2	17.54	0.36	0.27	0.83	0.25
Comp. 129	62.6	9.55	9.2	10.00	8.36	0	0	0.25
Comp. 130	62.6	9.55	3.2	11.00	13.36	0	0	0.25
Comp. 131	62.6	9.55	6.2	12.00	9.36	0	0	0.25
Comp. 132	62.6	9.55	3.2	14.73	9.36	0.27	0	0.25
Comp. 133	60.6	9.55	3.2	13.00	13.36	0	0	0.25
Comp. 134	59.6	9.55	3.2	14.00	13.36	0	0	0.25
Comp. 135	58.6	9.55	3.2	15.00	13.36	0	0	0.25
Comp. 136	57.1	9.55	3.2	16.50	13.36	0	0	0.25

[00236] Table 16:

Table 16: Predicted Properties of Adjustable Glass Compositions with CTE in the range of 90-130 x 10⁻⁷ /°C					
	Modeled CTE <T _g (x10 ⁻⁷ /°C)	Modeled Young's Modulus (GPa)	Predicted Density (g/cm ³)	Predicted 200 Poise Temperature (°C)	Predicted Liquidus Temperature (°C)
Comp. 123	92	83	2.49	1340	901.93
Comp. 124	95	83	2.48	1341	855.03
Comp. 125	98	82	2.47	1278	794.94
Comp. 126	102	82	2.45	1388	759.21
Comp. 127	103	82	2.45	1266	809.78
Comp. 128	106	74	2.46	1484	781.26
Comp. 129	109	83	2.48	1268	877.35
Comp. 130	115	75	2.46	1364	974.46
Comp. 131	117	81	2.47	1303	741.1
Comp. 132	119	75	2.47	1403	935.18
Comp. 133	121	72	2.47	1440	726.7
Comp. 134	123	72	2.49	1404	763.69
Comp. 135	128	77	2.48	1406	779.49
Comp. 136	131	77	2.5	1394	752.21

[00237] Standard linear regression analysis was used to construct a predictive model for both CTE and Young's modulus based on the compositions provided in Table 15 and corresponding measured properties. The regression coefficients that were obtained are provided in Table 17.

[00238] Table 17:

Table 17: Linear Regression Coefficients for CTE and Young's Modulus				
Oxide	CTE (20 °C – 260 °C)	Coefficient	Young's Modulus	Coefficient
SiO ₂	Intercept	137.5612129	Intercept	72.03447013
Al ₂ O ₃	X Variable 1	-5.471592999	X Variable 1	0.096444782
Li ₂ O	X Variable 2	1.181240915	X Variable 2	0.92453515
Na ₂ O	X Variable 3	2.221133922	X Variable 3	0.092136596
K ₂ O	X Variable 4	1.319063347	X Variable 4	-0.464253215
MgO	X Variable 5	-5.372521274	X Variable 5	-1.197632544
CaO	X Variable 6	-0.097587446	X Variable 6	1.117490089

[00239] The predicted results from these linear regression models are provided in Table 16 above. As shown in Table 16, each of the glass compositions is expected to have a CTE between 90 x 10⁻⁷ /°C and 130 x 10⁻⁷ /°C, a Young's modulus greater than 72 GPa, and a 200 Poise temperature of less than 1500 °C. The agreement between the measured and predicted values is shown in FIGS. 8 and 9. Specifically, FIG. 8 is a plot of the measured CTE (Y-axis; values x 10⁻⁷ /°C) as a function of the predicted CTE (X-axis; values x 10⁻⁷ /°C) for the glasses from Table 16. FIG. 9 is a plot of

the measured Young's modulus (Y-axis; in GPa) as a function of the predicted Young's modulus (X-axis; in GPa). As may be seen from the R^2 value for both of FIGS. 8 and 9, the model has a high predictive capability for both CTE and Young's modulus over the CTE range from $90\text{--}130 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00240] Additional compositions were studied to explore the ability to adjust the CTE over a wider range of temperatures. In particular, previous experiments observed the CTE over the range from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$. Additional glass compositions having CTEs between $90 \times 10^{-7} / ^\circ\text{C}$ and $150 \times 10^{-7} / ^\circ\text{C}$ measured over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ are provided in Table 18, and predicted values of CTE over various ranges are provided in Table 19.

[00241] Table 18:

Table 18: Adjustable Glass Compositions with CTE in the range of $90\text{--}150 \times 10^{-7} / ^\circ\text{C}$ over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ (Reported in Oxide wt%)								
	SiO ₂	Al ₂ O ₃	Li ₂ O	Na ₂ O	K ₂ O	MgO	CaO	Sb ₂ O ₃
Comp. 137	65.73	11.55	6.02	7.3	0.34	1.34	6.62	0.51
Comp. 138	65.82	11.57	6.03	11.18	0.35	1.3	2.74	0.51
Comp. 139	65.89	11.61	6.98	10.2	3.02	0.29	0.82	0.5
Comp. 140	63.28	9.65	8.74	9.54	7.47	0.012	0.026	0.49
Comp. 141	63.44	9.62	3.16	10.62	12	0.007	0.025	0.47
Comp. 142	6.303	9.7	6.12	11.65	8.44	0.009	0.026	0.48
Comp. 143	61.5	9.63	3.13	12.47	11.99	0.01	0.026	0.46
Comp. 144	59.64	9.66	3.12	14.37	11.98	0.01	0.026	0.46
Comp. 145	58.29	9.67	3.11	15.69	12	0.008	0.029	0.45

[00242] Table 19:

Table 19: Properties of Adjustable Glass Compositions with CTE in the range of $90\text{--}150 \times 10^{-7} / ^\circ\text{C}$ over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$				
	Measured CTE ($20\text{ }^\circ\text{C}$ – $300\text{ }^\circ\text{C}$)	Predicted CTE ($20\text{ }^\circ\text{C}$ – $300\text{ }^\circ\text{C}$)	Measured CTE ($20\text{ }^\circ\text{C}$ – $390\text{ }^\circ\text{C}$)	Predicted CTE ($20\text{ }^\circ\text{C}$ – $390\text{ }^\circ\text{C}$)
Comp. 137	92	92.29	96.8	96.79
Comp. 138	102	101.62	107.2	107.22
Comp. 139	110	109.58	115	114.98
Comp. 140	129	128.46	134.8	134.75
Comp. 141	128	130.06	132.4	134.74
Comp. 142	131	130.88	137.1	137.19
Comp. 143	136	134.22	141.8	139.66
Comp. 144	142	138.43	148.4	144.65
Comp. 145	139	141.46	144.7	148.22

[00243] Standard linear regression analysis was used to construct a predictive model for CTE over 20 °C to 300 °C and over 20 °C to 390 °C based on the compositions provided in Table 18 and corresponding measured properties. The regression coefficients that were obtained are provided in Table 20.

[00244] Table 20:

Table 20: Linear Regression Coefficients for CTE over 20 °C to 300 °C and 20 °C to 390 °C				
Oxide	CTE (20 °C – 300 °C)	Coefficient	CTE (20 °C – 390 °C)	Coefficient
SiO ₂	Intercept	131.9093419	Intercept	138.5093769
Al ₂ O ₃	X Variable 1	-5.053570424	X Variable 1	-5.655734141
Li ₂ O	X Variable 2	1.397804857	X Variable 2	1.673991001
Na ₂ O	X Variable 3	2.312944293	X Variable 3	2.731779214
K ₂ O	X Variable 4	1.485189419	X Variable 4	1.36455255
MgO	X Variable 5	-4.972563994	X Variable 5	-5.519456652
CaO	X Variable 6	-0.05878923	X Variable 6	0.078265306

[00245] The predicted results from these linear regression models are provided in Table 19 above. As shown in Table 19, each of the glass compositions is expected to have a CTE between $90 \times 10^{-7} / ^\circ\text{C}$ and $150 \times 10^{-7} / ^\circ\text{C}$. The agreement between the measured and predicted values is shown in FIGS. 10 and 11. Specifically, FIG. 10 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 300 °C for the glasses from Table 18. FIG. 11 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 390 °C for the glasses from Table 18. As may be seen from the R^2 value for both of FIGS. 10 and 11, the model has a high predictive capability for CTE from $90\text{-}150 \times 10^{-7} / ^\circ\text{C}$ measured from 20 °C to 300 °C and from 20 °C to 390 °C.

Example 4

[00246] Additional compositions were studied to explore the ability to adjust the CTE over a wider range of temperatures. In particular, previous experiments observed the CTE over the range from 20 °C to 260 °C. Additional glass compositions having CTEs between $40 \times 10^{-7} / ^\circ\text{C}$ and $70 \times 10^{-7} / ^\circ\text{C}$ measured over 20 °C to 300 °C and 20 °C to 390 °C are provided in Table 21, and predicted CTE values are provided in Table 22.

[00247] Table 21:

Table 21: Adjustable Glass Compositions with CTE in the range of 40-70 x 10⁻⁷ /°C over 20 °C to 300 °C and 20 °C to 390 °C (Reported in Oxide wt%)								
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	MgO	CaO	Sb ₂ O ₃	SnO ₂
Comp. 146	49.7	24.94	9.76	3.22	3.46	8.13	0.57	0
Comp. 147	49.7	29.94	9.76	3.22	3.46	8.13	0.57	0
Comp. 148	48.93	24.9	10.33	3.581	3.152	8.47	0.00	0.21
Comp. 149	48.91	24.95	10.28	3.56	3.17	8.44	0.00	0.21
Comp. 150	49.81	24.94	9.68	3.85	2.8	8.14	0.57	0
Comp. 151	49.81	24.94	9.68	3.85	2.8	8.14	0.57	0
Comp. 152	49.07	24.93	10.05	3.69	3.06	8.43	0.00	0.21
Comp. 153	49.19	25.16	9.57	5.102	1.573	8.58	0.00	0.2
Comp. 154	49.56	25.33	9.01	4.99	1.64	8.65	0.00	0.19
Comp. 155	49.39	25.05	9.52	5.75	0.81	8.53	0.00	0.2
Comp. 156	49.39	25.04	9.77	6.296	0.358	8.5	0.00	0.2
Comp. 157	49.09	24.99	9.86	6.77	0.13	8.37	0.00	0.203
Comp. 158	48.88	25.03	9.71	6.83	0.26	8.41	0.00	0.203
Comp. 159	49.13	25.01	9.84	6.73	0.093	8.38	0.00	0.204
Comp. 160	47.37	25.12	9.82	7.43	1.1	8.45	0.00	0.2
Comp. 161	47.62	25.44	9.11	7.54	1.21	8.39	0.00	0.2
Comp. 162	47.46	25.34	9.29	7.498	1.196	8.39	0.00	0.199
Comp. 163	43.86	24.93	9.8	5.33	5.26	10.17	0.52	0
Comp. 164	43.87	25.45	14.78	5.3	2.38	7.46	0.51	0
Comp. 165	49.73	24.87	9.79	0.02	6.74	8.17	0.52	0
Comp. 166	49.75	24.88	9.8	1.41	5.255	8.16	0.515	0
Comp. 167	49.82	24.88	9.8	1.78	4.88	8.15	0.52	0
Comp. 168	49.63	25.01	9.8	2.14	4.54	8.22	0.52	0
Comp. 169	49.7	24.96	9.8	2.97	3.7	8.19	0.51	0
Comp. 170	49.25	24.92	9.57	6.47	0.19	8.46	0	0.2
Comp. 171	49.44	25.2	9.15	4.38	2.25	8.6	0	0.2

[00248] Table 22:

Table 22: Properties of Adjustable Glass Compositions with CTE in the range of $40\text{-}70 \times 10^{-7} / ^\circ\text{C}$ over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$				
	Measured CTE ($20\text{ }^\circ\text{C}$ - $300\text{ }^\circ\text{C}$)	Predicted CTE ($20\text{ }^\circ\text{C}$ - $300\text{ }^\circ\text{C}$)	Measured CTE ($20\text{ }^\circ\text{C}$ - $390\text{ }^\circ\text{C}$)	Predicted CTE ($20\text{ }^\circ\text{C}$ - $390\text{ }^\circ\text{C}$)
Comp. 146	48	48.8	49	50.99
Comp. 147	49	48.5	50	49.54
Comp. 148	49	49.9	50	51.56
Comp. 149	49	49.9	49	51.53
Comp. 150	50	50.6	51	52.62
Comp. 151	50	50.6	51	52.62
Comp. 152	51	50.3	52	52.02
Comp. 153	52	54.4	54	55.66
Comp. 154	54	54.1	55	55.43
Comp. 155	57	56.1	58	57.25
Comp. 156	59	57.7	61	58.77
Comp. 157	60	59.4	61	60.51
Comp. 158	60	59.8	62	61.03
Comp. 159	61	59.2	62	60.27
Comp. 160	63	63.5	65	65.03
Comp. 161	64	64.2	65	65.97
Comp. 162	64	64.0	66	65.71
Comp. 163	61	60.7	62	62.00
Comp. 164	55	54.9	57	56.30
Comp. 165	42	39.7	43	42.67
Comp. 166	44	43.6	45	46.17
Comp. 167	45	44.7	56	47.14
Comp. 168	46	45.7	47	48.04
Comp. 169	47	48.1	49	50.25
Comp. 170	59	58.3	60	59.39
Comp. 171	53	52.3	54	53.83

[00249] Standard linear regression analysis was used to construct a predictive model for CTE over $20\text{ }^\circ\text{C}$ to $300\text{ }^\circ\text{C}$ and over $20\text{ }^\circ\text{C}$ to $390\text{ }^\circ\text{C}$ based on the compositions provided in Table 21 and corresponding measured properties. The regression coefficients that were obtained are provided in Table 23.

[00250] Table 23:

Table 23: Linear Regression Coefficients for CTE over 20 °C to 300 °C and 20 °C to 390 °C				
Oxide	CTE (20 °C – 300 °C)	Coefficient	CTE (20 °C – 390 °C)	Coefficient
SiO ₂	Intercept	31.86272	Intercept	47.81324443
Al ₂ O ₃	X Variable 1	-0.06728	X Variable 1	-0.28850455
B ₂ O ₃	X Variable 2	-0.2062	X Variable 2	-0.442997258
Na ₂ O	X Variable 3	4.215118	X Variable 3	4.387516515
MgO	X Variable 4	1.336897	X Variable 4	1.751246324
CaO	X Variable 5	0.301558	X Variable 5	-0.675842501

[00251] The predicted results from these linear regression models are provided in Table 22 above. As shown in Table 22, each of the glass compositions is expected to have a CTE between $40 \times 10^{-7} / ^\circ\text{C}$ and $70 \times 10^{-7} / ^\circ\text{C}$. The agreement between the measured and predicted values is shown in FIGS. 12 and 13. Specifically, FIG. 12 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 300 °C for the glasses from Table 21. FIG. 13 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 390 °C for the glasses from Table 21. As may be seen from the R^2 value for both of FIGS. 12 and 13, the model has a high predictive capability for CTE from $40\text{-}70 \times 10^{-7} / ^\circ\text{C}$ measured from 20 °C to 300 °C and from 20 °C to 390 °C.

[00252] Additional glass compositions having CTEs between $80 \times 10^{-7} / ^\circ\text{C}$ and $100 \times 10^{-7} / ^\circ\text{C}$ measured over 20 °C to 300 °C and 20 °C to 390 °C are provided in Table 24, and predicted CTE values are provided in Table 25.

[00253] Table 24:

Table 24: Adjustable Glass Compositions with CTE in the range of 80-100 x 10⁻⁷ /°C over 20 °C to 300 °C and 20 °C to 390 °C (Reported in Oxide wt%)										
	SiO ₂	Al ₂ O ₃	B ₂ O ₃	Na ₂ O	K ₂ O	MgO	CaO	TiO ₂	ZnO	Sb ₂ O ₃
Comp. 172	62.77	2.87	0.8	8.33	9.16	3.03	0.04	0.7	11.15	0.43
Comp. 173	61.45	2.78	0.92	8.29	9.15	3.31	0.041	0.69	11.98	0.44
Comp. 174	62.96	2.913	0.95	16.35	0.01	4.125	0.051	0.695	11.45	0.44
Comp. 175	62.9	2.96	0.82	15.31	0.01	4.98	0.06	0.7	11.64	0.4
Comp. 176	62.93	2.923	0.95	14.41	0.009	6.127	0.068	0.695	11.44	0.44
Comp. 177	63.01	2.91	0.79	13.64	0	6.79	0.07	0.7	11.38	0.44
Comp. 178	62.84	2.905	0.95	13.59	0.01	7.144	0.075	0.693	11.42	0.438
Comp. 179	61.03	2.81	0.87	13.42	0.009	8.255	0.081	0.676	12.57	0.407
Comp. 180	63.42	2.92	0.94	13.16	0	7.15	0.08	0.7	11.35	0.44
Comp. 181	59.69	2.72	0.9	12.86	0.009	9.76	0.09	0.671	12.77	0.417
Comp. 182	63.38	2.93	0.74	12.66	0.01	7.48	0.08	0.7	11.27	0.44
Comp. 183	64.19	3.1	0.94	12.7	0.01	6.96	0.075	0.7	10.82	0.38
Comp. 184	63.53	2.93	0.91	12.24	0.01	7.87	0.09	0.7	11.25	0.44
Comp. 185	63.07	2.91	0.95	13.09	0.009	7.48	0.078	0.69	11.45	0.44
Comp. 186	62.66	2.89	0.94	13.54	0.009	7.44	0.08	0.69	11.36	0.44
Comp. 187	63.46	2.99	0.87	13.34	0.009	6.57	0.071	0.69	11.56	0.42
Comp. 188	63.23	2.99	0.86	13.89	0.009	6.5	0.07	0.68	11.44	0.42
Comp. 189	63.05	2.9	0.95	13.34	0.01	7.18	0.076	0.69	11.4	0.44
Comp. 190	62.69	2.89	0.94	13.79	0.009	7.15	0.076	0.69	11.41	0.44

[00254] Table 25:

Table 25: Properties of Adjustable Glass Compositions with CTE in the range of 80-100 x 10⁻⁷ /°C over 20 °C to 300 °C and 20 °C to 390 °C				
	Measured CTE (20 °C-300 °C)	Predicted CTE (20 °C-300 °C)	Measured CTE (20 °C-390 °C)	Predicted CTE (20 °C-390 °C)
Comp. 172	99.8	99.51	101.7	101.3
Comp. 173	98.6	98.89	100.8	101.2
Comp. 174	95	94.00	97.7	97.3
Comp. 175	90	89.99	92.8	93.0
Comp. 176	85.1	86.79	89.9	89.7
Comp. 177	84.5	84.48	86.9	86.8
Comp. 178	83.3	83.87	85.9	86.5
Comp. 179	82.7	82.72	85.3	85.4
Comp. 180	82.4	82.14	84.7	84.6
Comp. 181	81.5	81.12	84	83.6
Comp. 182	80.3	80.53	82.1	82.3
Comp. 183	80.4	80.03	82.8	82.8
Comp. 184	78.9	78.48	80.9	80.4
Comp. 185	82.6	81.79	85	84.3
Comp. 186	82.8	83.55	84.9	85.9
Comp. 187	81.9	82.13	84.4	84.7
Comp. 188	83.8	83.89	86.6	86.4
Comp. 189	82.8	82.74	85.1	85.2
Comp. 190	84.8	84.54	87	87.1

[00255] Standard linear regression analysis was used to construct a predictive model for CTE over 20 °C to 300 °C and over 20 °C to 390 °C based on the compositions provided in Table 24 and corresponding measured properties. The regression coefficients that were obtained are provided in Table 26.

[00256] Table 26:

Table 26: Linear Regression Coefficients for CTE over 20 °C to 300 °C and 20 °C to 390 °C				
Oxide	CTE (20 °C – 300 °C)	Coefficient	CTE (20 °C – 390 °C)	Coefficient
SiO ₂	Intercept	12.4017	Intercept	-24.4848
Al ₂ O ₃	X Variable 1	-4.18178	X Variable 1	-0.37352
B ₂ O ₃	X Variable 2	-0.3376	X Variable 2	2.690242
Na ₂ O	X Variable 3	3.983931	X Variable 3	4.298453
K ₂ O	X Variable 4	4.043165	X Variable 4	4.238349
MgO	X Variable 5	0.820754	X Variable 5	1.194832
CaO	X Variable 6	-64.9976	X Variable 6	-100.006
TiO ₂	X Variable 7	49.88685	X Variable 7	69.03159
ZnO	X Variable 8	-0.50671	X Variable 8	0.193678

[00257] The predicted results from these linear regression models are provided in Table 25 above. As shown in Table 25, each of the glass compositions is expected to have a CTE between $80 \times 10^{-7} / ^\circ\text{C}$ and $100 \times 10^{-7} / ^\circ\text{C}$. The agreement between the measured and predicted values is shown in FIGS. 14 and 15. Specifically, FIG. 14 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 300 °C for the glasses from Table 23. FIG. 15 is a plot of the measured CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) as a function of the predicted CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) over 20 °C to 390 °C for the glasses from Table 23. As may be seen from the R^2 value for both of FIGS. 14 and 15, the model has a high predictive capability for CTE from $80\text{-}100 \times 10^{-7} / ^\circ\text{C}$ measured from 20 °C to 300 °C and from 20 °C to 390 °C.

Example 5

[00258] During a production run of the method described above, it was discovered that the viscosity of the glass was not conducive to the forming process being used. Referring to FIG. 1, this forming process involved flowing glass from a downcomer **9** into a forming vessel **10** to form a boule. The steep viscosity curve of the glass resulted in the boule forms not filling completely the forming vessel **10**. The glass accumulated in the center directly beneath the downcomer **9** and

would not flow to the edges of the forming vessel **10**. After the forming vessel **10** was allowed to fill for a pre-determined amount of time, the forming vessel **10** was moved away from the downcomer **9**, and a press was used to force the glass outward toward the edges of the mold. When the glass viscosity was too high, the press was not able to move the glass enough to fill properly the forming vessel **10**, causing boules that did not have the desired dimensions for the boule. An unacceptable boule has a rounded edge and a non-uniform thickness throughout, whereas a properly made boule has straight edges and maintains a uniform thickness throughout. To correct this issue, the steepness of the viscosity curve may be reduced so the glass will flow more during filling of the forming vessel **10** and will remain fluid enough during the subsequent pressing that it will move outward to fill the entire forming vessel **10**.

[00259] Adding fluorine to the glass lowers the viscosity of the glass at both melting and forming temperatures; however, the fluorine has a larger impact at lower temperatures. Thus, fluorine softens the glass more at the forming temperatures than at melting temperatures, resulting in a shallower viscosity curve. Several glasses at various CTE values were melted with fluorine (in the form of AlF_3) and properties were measured. Table 27 shows the compositions melted with fluorine along with data including viscosity, coefficient of thermal expansion (CTE) and elastic modulus. Included in these tables is also the measured CTE and elastic modulus for the same composition without fluorine. In addition, a liquidus temperature of 1200 °C was measured for Composition 193, the liquid phase of which was a Ca/Na solid solution feldspar.

[00260] Table 27:

Table 27: Compositions with fluorine added and property data							
Oxide (wt%)	Comp. 191	Comp. 192	Comp. 193	Comp. 194	Comp. 195	Comp. 196	Comp. 197
SiO_2	49.56	49.96	47.68	47.65	45.43	45.68	46.39
Al_2O_3	24.79	24.56	24.91	24.86	24.41	24.2	24.61
B_2O_3	9.75	9.66	9.31	9.24	8.61	8.64	8.98
Na_2O	3.2	3.8	7.23	7.2	5	4.46	2.69
MgO	3.43	2.83	1.3	1.29	6.53	6.3	6.43
CaO	8.09	7.99	8.19	8.15	9.38	9.32	9.42
AlF_3	0.83	0.83	0.75	1.03	1.29	1.28	1.34
Sb_2O_3	0.6	0.58	0.51	0.51	0.50	0.5	0.55
Measured CTE w/o F^1 ($\times 10^{-7} / ^\circ\text{C}$)	47.5	49.1	61.6	61.6	58.70	55.9	50.2
Measured CTE ($\times 10^{-7} / ^\circ\text{C}$)	47.8	48.7	62.6	62	60.3	57	51.6

Modeled CTE ($\times 10^{-7} / ^\circ\text{C}$)	47.7	49	61.1	60.8	58.5	56	50.1
Measured Young's Modulus w/o F ¹ (GPa)	80.48	79.10	76	76	85.3	85.7	86.8
Measured Young's Modulus (GPa)	79.9	78.3	75.4	75	84.7	84.3	85.2
Modeled Young's Modulus (GPa)	78.8	77	73.8	73.7	84.6	84	85.6
Measured 200 P temperature ($^\circ\text{C}$)	1417	N/D ²	N/D ²	N/D ²	N/D ²	N/D ²	1303
Measured 400 P temperature ($^\circ\text{C}$)	1350	N/D ²	N/D ²	N/D ²	N/D ²	N/D ²	1251
Measured 2000 P temperature ($^\circ\text{C}$)	1224	N/D ²	N/D ²	N/D ²	N/D ²	N/D ²	1150
Measured 4000 P temperature ($^\circ\text{C}$)	1179	N/D ²	N/D ²	N/D ²	N/D ²	N/D ²	1113
Measured 35000 P temperature ($^\circ\text{C}$)	1064	N/D ²	N/D ²	N/D ²	N/D ²	N/D ²	1019
Oxide (wt%)	Comp. 198	Comp. 199	Comp. 200	Comp. 201	Comp. 202	Comp. 203	
SiO ₂	46.95	44.26	43.98	43.11	42.23	41.77	
Al ₂ O ₃	24.73	24.71	24.41	24.34	24.27	24.25	
B ₂ O ₃	8.882	8.82	8.24	7.29	7.18	8.02	
Na ₂ O	2.1	4.66	8.69	9.43	10.22	10.23	
MgO	6.45	6.46	5.93	5.76	6.07	6	
CaO	9.43	9.39	7.01	8.45	8.33	8.12	
AlF ₃	1.28	1.28	1.03	0.97	1.01	1.11	
Sb ₂ O ₃	0.52	0.51	0.52	0.52	0.52	0.54	
Measured CTE w/o F ¹ ($\times 10^{-7} / ^\circ\text{C}$)	49.4	57.6	68.6	75	78.4	76.7	
Measured CTE ($\times 10^{-7} / ^\circ\text{C}$)	49	59	71	74.8	78.6	N/D ²	
Modeled CTE ($\times 10^{-7} / ^\circ\text{C}$)	48.1	57.5	68.1	72.8	75.8	75.4	
Measured Young's Modulus w/o F ¹ (GPa)	87.2	85.6	80.8	80.5	80.8	80.6	
Measured Young's Modulus (GPa)	86.4	84.9	80.1	81.7	81.7	N/D ²	
Modeled Young's Modulus (GPa)	86.2	85	80	81	81.1	80.3	
Measured 200 P temperature ($^\circ\text{C}$)	1319	1275	1287	1271	1258	N/D ²	
Measured 400 P temperature ($^\circ\text{C}$)	1265	1223	1227	1212	1200	N/D ²	
Measured 2000 P temperature ($^\circ\text{C}$)	1162	1121	1113	1100	1088	N/D ²	
Measured 4000 P temperature ($^\circ\text{C}$)	1126	1084	1073	1061	1049	N/D ²	
Measured 35000 P temperature ($^\circ\text{C}$)	1031	990	969	961	948	N/D ²	

¹ w/o F refers to the same glass composition without AlF₃.

² N/D = not determined

[00261] FIG. 16 is a plot of the measured CTE of several glasses containing fluorine (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the CTE of those same glasses made without fluorine (X-axis; values $\times 10^{-7} / ^\circ\text{C}$). As shown in FIG. 16, and in particular the trend line slope of about 1.0, the addition of up to about 1.3 weight % of fluorine does not produce a significant impact on measured CTE of the glasses. From the size of the error bars, it is possible to conclude that the difference between the CTE of the glasses with and without fluorine is within the accuracy of the measurement system.

[00262] FIG. 17 is a plot of the measured elastic modulus of several glasses containing fluorine (Y-axis; values in GPa) versus the measured elastic modulus of those same glasses made without fluorine (X-axis; values in GPa). As shown in FIG. 17, and in particular the trend line slope of about 1.0, the addition of up to about 1.3 weight % of fluorine does not produce a significant impact on measured elastic modulus of the glasses. From the size of the error bars, it is possible to conclude that the difference between the elastic modulus of the glasses with and without fluorine is within the accuracy of the measurement system.

[00263] FIG. 18 is a plot of log viscosity (Y-axis; values in Poise) versus temperature (X-axis; values in $^\circ\text{C}$) for two of the fluorine-free production glasses, HS5.1 and HS5.9, compared to the same glass compositions with 1.3 weight % fluorine and a standard production glass, QE. As can be seen in FIG. 18, the addition of fluorine to the HS5.1 and HS5.9 glasses results in a lowering of the glass high temperature viscosity and also causes a shallowing of the viscosity curve as compared to the viscosity curve of the glass without fluorine. The standard production glass, QE, exhibits the shallowest viscosity curve slope, and thus is the most processable of the tested systems. However, the observed differences in behavior of the glasses with fluorine are sufficient to allow boule production. This change in viscosity was shown to aid forming boules in a production melt.

[00264] FIG. 19 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the measured CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 19, the model has a high predictive capability for CTE from $50\text{--}59 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{--}260\text{ }^\circ\text{C}$.

[00265] FIG. 20 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the measured CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for exemplary fluorine-containing glass compositions. As may

be seen from the R^2 value of FIG. 20, the model has a high predictive capability for CTE from $49\text{--}62 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00266] FIG. 21 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the measured CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 21, the model has a high predictive capability for CTE from $70\text{--}80 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00267] FIG. 22 is a plot of the predicted CTE (Y-axis; values $\times 10^{-7} / ^\circ\text{C}$) versus the measured CTE (X-axis; values $\times 10^{-7} / ^\circ\text{C}$) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 22, the model has a high predictive capability for CTE from $68\text{--}80 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00268] FIG. 23 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 23, the model has predictive capability for Young's modulus for materials having a CTE ranging from $50\text{--}59 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00269] FIG. 24 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 24, the model has predictive capability for Young's modulus for materials having a CTE ranging from $49\text{--}62 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00270] FIG. 25 is a plot of the predicted Young's modulus (Y-axis; GPa) versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIG. 25, the model has predictive capability for Young's modulus for materials having a CTE ranging from $70\text{--}80 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$.

[00271] FIGS. 26 and 27 are plots of the predicted Young's modulus (Y-axis; GPa), using alternative models, versus the measured Young's modulus (X-axis; GPa) for exemplary fluorine-containing glass compositions. As may be seen from the R^2 value of FIGS. 26 and 27, these models do not have significant predictive capability for Young's modulus for materials having a CTE ranging from $70\text{--}80 \times 10^{-7} / ^\circ\text{C}$ measured from $20\text{ }^\circ\text{C}$ to $260\text{ }^\circ\text{C}$. Without intending to be bound by

any particular theory, it is believe these correlations were poor due to a limited volume of CTE and Young's modulus data over this range of glass compositions.

[00272] Embodiments described herein include methods for manufacturing glass articles, having adjustable CTEs and other properties, that may be used in electronic devices such as semiconductor devices, display devices, sensors, and the like. In some embodiments, the method includes melting a first glass composition in a melter and feeding a second glass composition may into the melter. This second glass composition includes the same combination of glass constituent components but at least one glass constituent component has a concentration that is different from the concentration of the same component in the first glass composition. Glass articles may be drawn from the melter while maintaining the contents of the melter in a molten state, including: (1) a first glass article that is formed from the first glass composition; (2) at least one intermediate glass article that is composed of neither the first glass composition nor the second glass composition and which may be drawn either simultaneously with the feeding of the second glass composition or at some different time; (3) and a final glass article that is composed of a composition that is different from the first glass composition and may be the same as or different from the second glass composition. The concentration of the at least one component in the at least one intermediate glass article may be between the concentration of the at least one component in the first glass composition and the concentration of the at least one component in the second glass composition. The first glass article may have a first set of values for a set of properties. The final glass article may have a second set of values for the same set of properties, the second set of values being different from the first set of values. The at least one intermediate glass article may have an intermediate set of values for the set of properties that is between the first set of values and the second set of values.. In the same or different embodiments, the method includes replacing an amount of a first alkaline earth component or a first alkali component having a first cation field strength in the molten base glass composition with an amount of a second alkaline earth component or a second alkali component having a second cation field strength that is different from the first cation field strength, such that glass compositions with various CTEs can be obtained by making minor adjustments to a base glass composition. Various embodiments may further advantageously provide glass compositions having desirable Young's modulus and 200 Poise temperatures, which may be predicted based on linear modeling.

[00273] The subject matter recited in the claims is not coextensive with and should not be interpreted to be coextensive with any embodiment, feature, or combination of features described or illustrated in this document. This is true even if only a single embodiment of the feature or combination of features is illustrated and described in this document.

[00274] It will be apparent to those skilled in the art that various modifications and variations can be made without departing from the spirit or scope of the claimed subject matter. Accordingly, the claimed subject matter is not to be restricted except in light of the attached claims and their equivalents.

What is claimed is:

1. A method comprising:

melting, in a melter, a first glass composition comprising a combination of glass constituent components;

feeding into the melter a second glass composition comprising the same combination of glass constituent components, wherein at least one glass constituent component of the second glass composition has a concentration that is different from a concentration of the same component of the first glass composition;

drawing at least three glass articles from the melter while maintaining the contents of the melter in a molten state, the at least three glass articles comprising:

a first glass article comprising the first glass composition;

at least one intermediate glass article comprising a glass composition that is neither the first glass composition nor the second glass composition; and

a final glass article comprising a glass composition different from the first glass composition;

wherein:

a concentration of the at least one glass constituent component in the at least one intermediate glass article is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition; and

the first glass article has a first set of values for a set of properties, the final glass article has a second set of values for the same set of properties, the second set of values being different from the first set of values, and the at least one intermediate glass article has an intermediate set of values for the set of properties that is between the first set of values and the second set of values.

2. The method of claim 1, wherein the final glass article comprises the second glass composition.

3. The method of any preceding claim, wherein the concentration of the at least one glass constituent component of the second glass composition is different from the concentration of the

at least one glass constituent component of the first glass composition by no more than 2 weight %.

4. The method of any preceding claim, wherein the at least one glass constituent component is selected from SiO_2 , Al_2O_3 , B_2O_3 , Na_2O , MgO , CaO , AlF_3 , and Sb_2O_3 .

5. The method of any preceding claim, wherein the at least one glass constituent component comprises AlF_3 .

6. The method of any preceding claim, wherein the first glass composition comprises from greater than or equal to 0.5 wt% to less than or equal to 1.5 wt% AlF_3 .

7. The method of any preceding claim, wherein the set of properties comprises one or more of a coefficient of thermal expansion ("CTE"), a Young's modulus, a density, a 200 Poise temperature, a surface quality, a refractive index, a resistivity, and an edge strength.

8. The method of claim 7, wherein the CTE of the first glass article is equal to or within $\pm 7.5 \times 10^{-7} / ^\circ\text{C}$ different from the CTE of the final glass article.

9. The method of claim 7 or claim 8, wherein the refractive index of the first glass article is less than or equal to ± 0.01 different from the refractive index of the final glass article.

10. The method of any one of claims 7-9, wherein a difference between the CTE of the at least one intermediate glass article and the CTE of the first glass article, as a percentage of the CTE of the first glass article, is greater than a difference between the Young's modulus of the at least one intermediate glass article and the Young's modulus of the first glass article, as a percentage of the Young's modulus of the first glass article.

11. The method of any preceding claim, wherein a viscosity of the composition within the melter varies by no more than 25 Poise during the drawing the at least three glass articles.

12. The method of any preceding claim, wherein a 200 Poise temperature of the glass mixture within the melter is less than or equal to 1500 °C.
13. The method of any preceding claim, wherein the at least three glass articles are in a shape of a boule.
14. The method of any preceding claim, wherein the feeding the second glass composition is simultaneous with the drawing the at least three glass articles.
15. The method of any preceding claim, wherein the at least one intermediate glass article comprises at least 3 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.
16. The method of any preceding claim, wherein the at least one intermediate glass article comprises at least 8 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.
17. The method of any preceding claim, wherein the at least one intermediate glass article comprises at least 18 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.
18. The method of any preceding claim, wherein the at least one intermediate glass article comprises at least 28 glass articles, each having a different concentration of the at least one glass constituent component that is between the concentration of the at least one glass constituent

component in the first glass composition and the concentration of the at least one glass constituent component in the second glass composition.

19. The method of any preceding claim, further comprising feeding into the melter a third glass composition comprising the same combination of glass constituent components, wherein at least one glass constituent component has a concentration that is different from a concentration of the same component of the first glass composition and the second glass composition; and

drawing at least a first additional glass article and a final additional glass article from the melter while maintaining the contents of the melter in a molten state, the first additional glass article having a first additional set of values for the set of properties and the final additional glass article having a final additional set of values for the set of properties.

20. The method of any preceding claim, wherein the set of properties comprises one or more of a coefficient of thermal expansion (“CTE”), a Young’s modulus, a density, a 200 Poise temperature, a surface quality, a refractive index, a resistivity, and an edge strength.

21. The method of claim 20, wherein the CTE of the first glass article is equal to or within $\pm 15 \times 10^{-7} / ^\circ\text{C}$ different from the CTE of the final additional glass article.

22. The method of claim 20 or claim 21, wherein a difference between the CTE of the first additional glass article and the CTE of the first glass article, as a percentage of the CTE of the first glass article, is greater than a difference between the Young’s modulus of the first additional glass article and the Young’s modulus of the first glass article, as a percentage of the Young’s modulus of the first glass article.

23. The method of any of claims 19-22, wherein a viscosity of the composition within the melter varies by no more than 25 Poise during the drawing the first glass article and the drawing the final additional glass article.

24. The method of any of claims 19-23, wherein a 200 Poise temperature of the glass mixture within the melter is less than or equal to 1500 °C.
25. The method of any preceding claim, wherein the first glass composition comprises an alkali boroaluminosilicate glass composition.
26. The method of any of claims 1-24, wherein the first glass composition comprises an alkaline earth boroaluminosilicate glass composition.
27. The method of any of claims 1-24, wherein the first glass composition comprises a zinc boroaluminosilicate glass composition.
28. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂;
greater than or equal to 1.5 wt% and less than or equal to 5.0 wt% Al₂O₃;
greater than or equal to 0 wt% and less than or equal to 2 wt% B₂O₃;
greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 10 wt% K₂O;
greater than or equal to 2 wt% and less than or equal to 10 wt% MgO;
greater than or equal to 0 wt% and less than or equal to 2 wt% CaO;
greater than or equal to 0 wt% and less than or equal to 2 wt% TiO₂; and
greater than or equal to 10 wt% and less than or equal to 15 wt% ZnO.
29. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 60 wt% and less than or equal to 65 wt% SiO₂;
greater than or equal to 10 wt% and less than or equal to 15 wt% Al₂O₃;
greater than or equal to 2 wt% and less than or equal to 4 wt% B₂O₃;
greater than or equal to 2 wt% and less than or equal to 5 wt% Li₂O;
greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O;
greater than or equal to 1 wt% and less than or equal to 3 wt% MgO; and
greater than or equal to 0 wt% and less than or equal to 3 wt% CaO.

30. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂;
greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃;
greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃;
greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 6 wt% MgO; and
greater than or equal to 7 wt% and less than or equal to 9 wt% CaO.
31. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 56 wt% and less than or equal to 66 wt% SiO₂;
greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al₂O₃;
greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li₂O;
greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 14 wt% K₂O;
greater than or equal to 0 wt% and less than or equal to 2 wt% MgO; and
greater than or equal to 0 wt% and less than or equal to 8 wt% CaO.
32. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂;
greater than or equal to 22 wt% and less than or equal to 27 wt% Al₂O₃;
greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃;
greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 8 wt% MgO; and
greater than or equal to 7 wt% and less than or equal to 12 wt% CaO.
33. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 35 wt% and less than or equal to 48 wt% SiO₂;
greater than or equal to 17 wt% and less than or equal to 20 wt% Al₂O₃;
greater than or equal to 0 wt% and less than or equal to 5 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 7 wt% K₂O;

- greater than or equal to 0 wt% and less than or equal to 4 wt% MgO;
greater than or equal to 0 wt% and less than or equal to 8.5 wt% CaO; and
greater than or equal to 25 wt% and less than or equal to 32 wt% La₂O₃.
34. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂;
greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃;
greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃;
greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 6 wt% MgO;
greater than or equal to 7 wt% and less than or equal to 9 wt% CaO;
greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and
greater than 0 wt% and less than or equal to 1.5 wt% AlF₃.
35. The method of any preceding claim, wherein the first glass composition comprises:
greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂;
greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃;
greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃;
greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 6 wt% MgO;
greater than or equal to 7 wt% and less than or equal to 9 wt% CaO;
greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and
greater than 0.5 wt% and less than or equal to 1.5 wt% AlF₃.
36. A glass article formed from a glass composition comprising:
greater than or equal to 56 wt% and less than or equal to 66 wt% SiO₂;
greater than or equal to 9.5 wt% and less than or equal to 12.0 wt% Al₂O₃;
greater than or equal to 3.0 wt% and less than or equal to 7.5 wt% Li₂O;
greater than or equal to 6 wt% and less than or equal to 18 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 14 wt% K₂O;
greater than or equal to 0 wt% and less than or equal to 2 wt% MgO; and

greater than or equal to 0 wt% and less than or equal to 8 wt% CaO.

37. A glass article formed from a glass composition comprising:
greater than or equal to 45 wt% and less than or equal to 55 wt% SiO₂;
greater than or equal to 20 wt% and less than or equal to 27 wt% Al₂O₃;
greater than or equal to 8 wt% and less than or equal to 10 wt% B₂O₃;
greater than or equal to 0 wt% and less than or equal to 8 wt% Na₂O;
greater than or equal to 0 wt% and less than or equal to 6 wt% MgO;
greater than or equal to 7 wt% and less than or equal to 9 wt% CaO;
greater than or equal to 0 wt% and less than or equal to 0.7 wt% Sb₂O₃; and
greater than 0 wt% and less than or equal to 1.5 wt% AlF₃.
38. A glass article formed by the method of any one of claims 1-35.

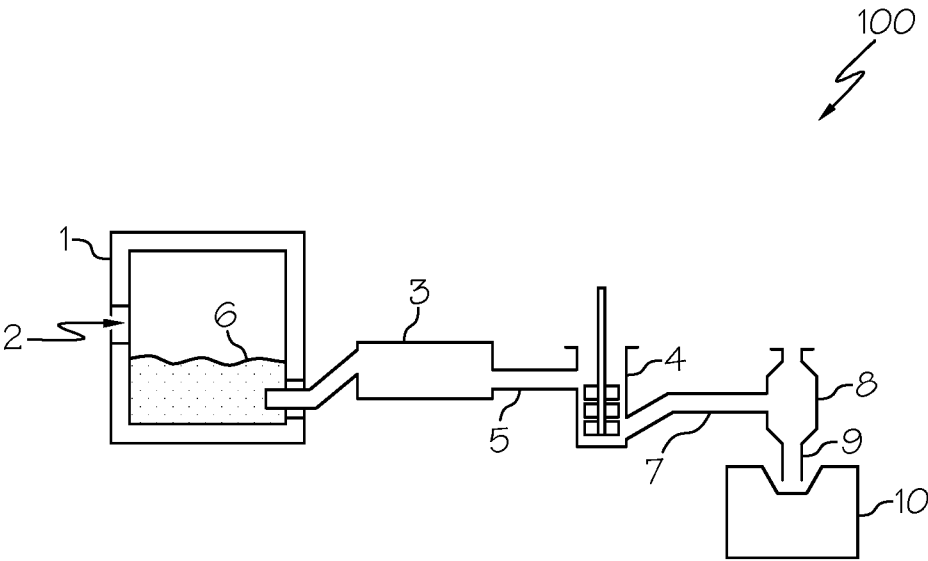


FIG. 1

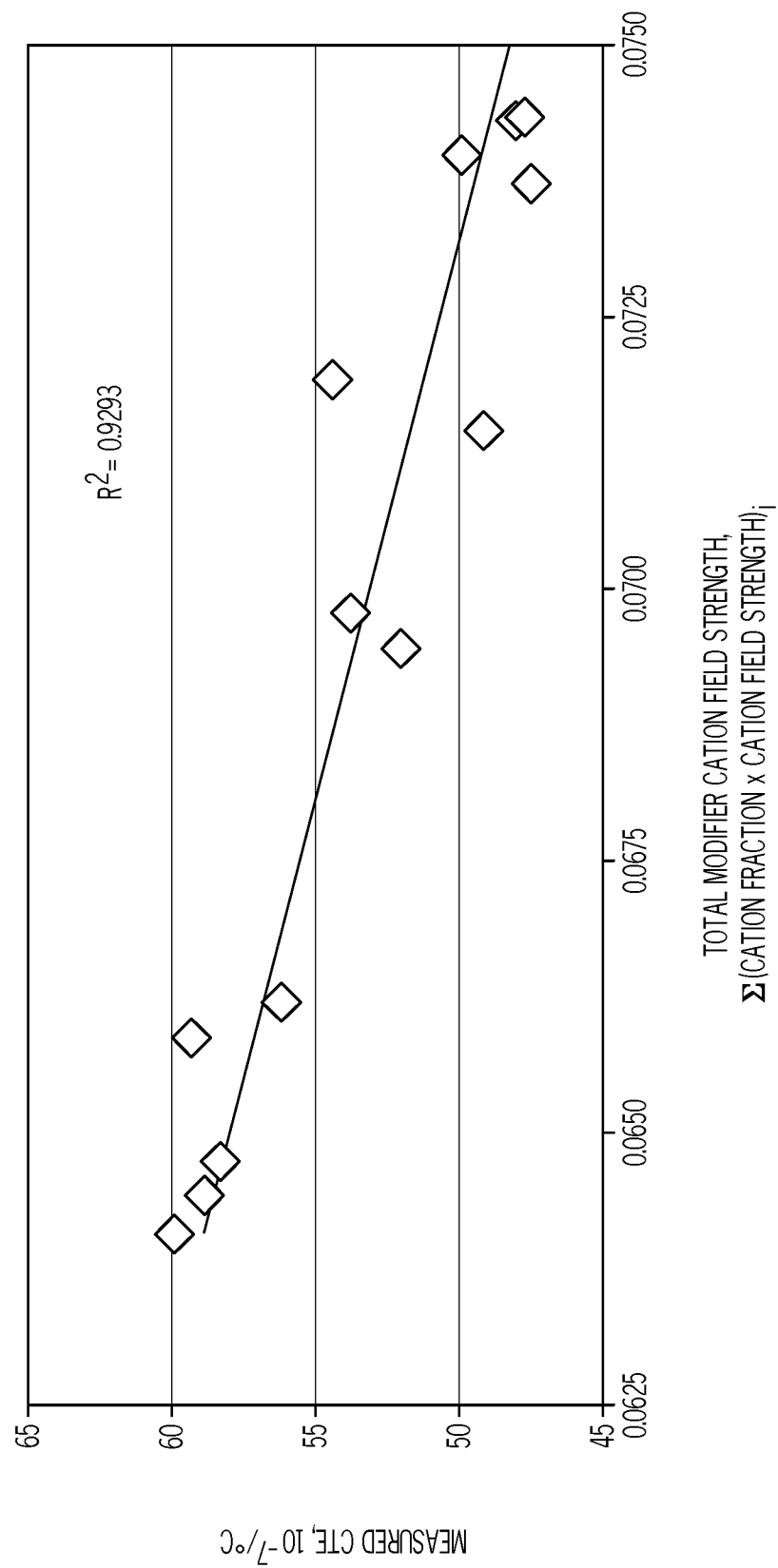


FIG. 2

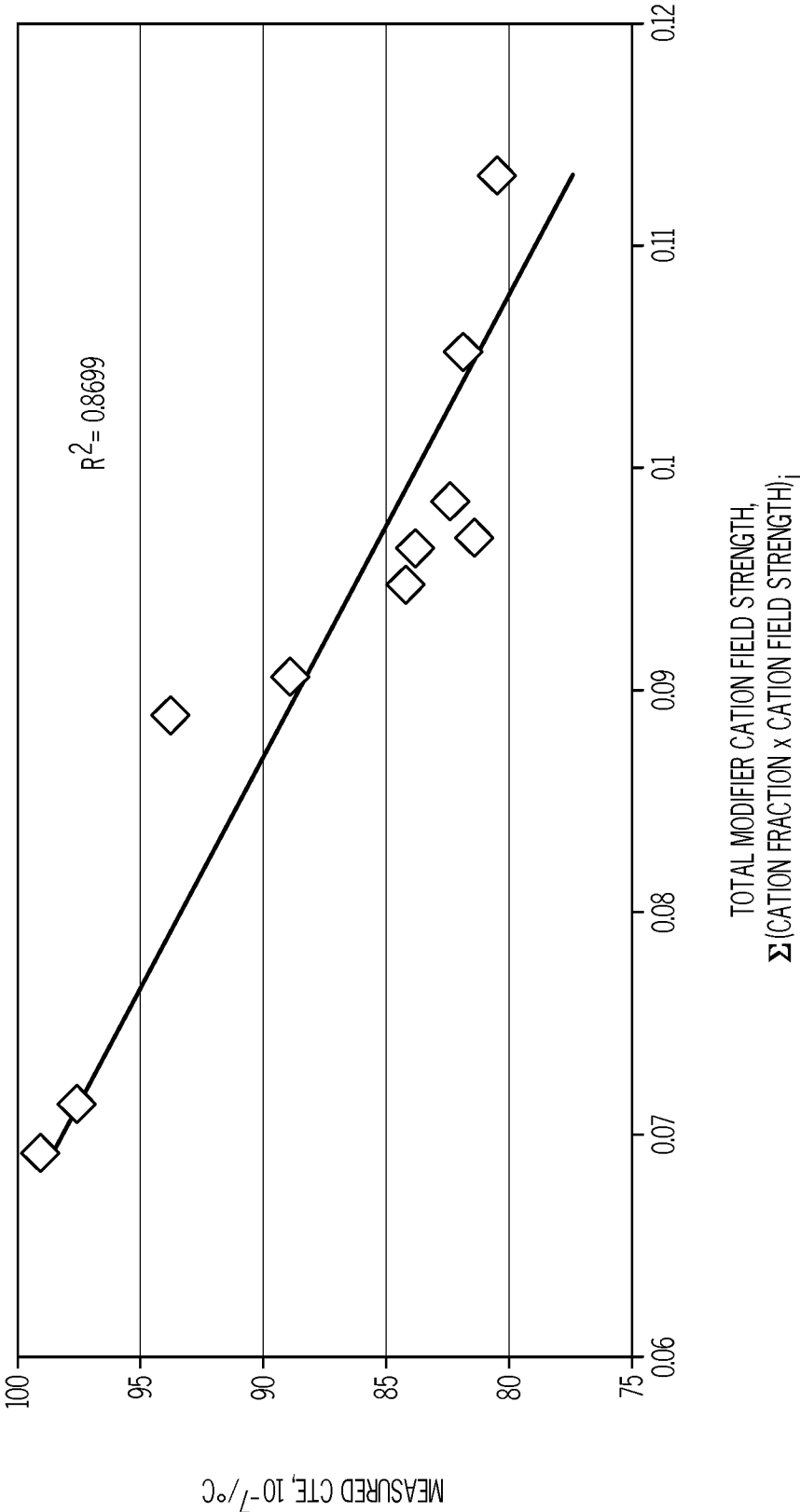


FIG. 3

4 / 27

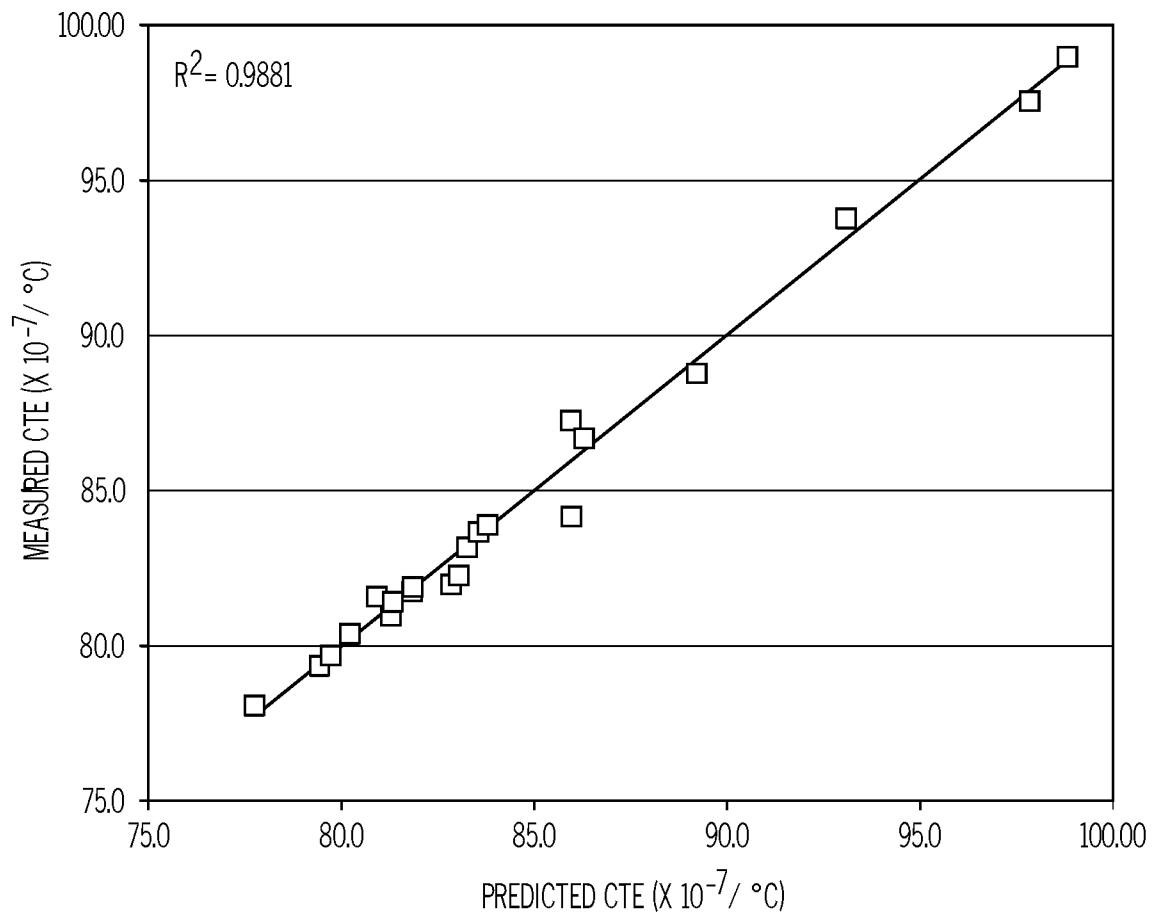


FIG. 4

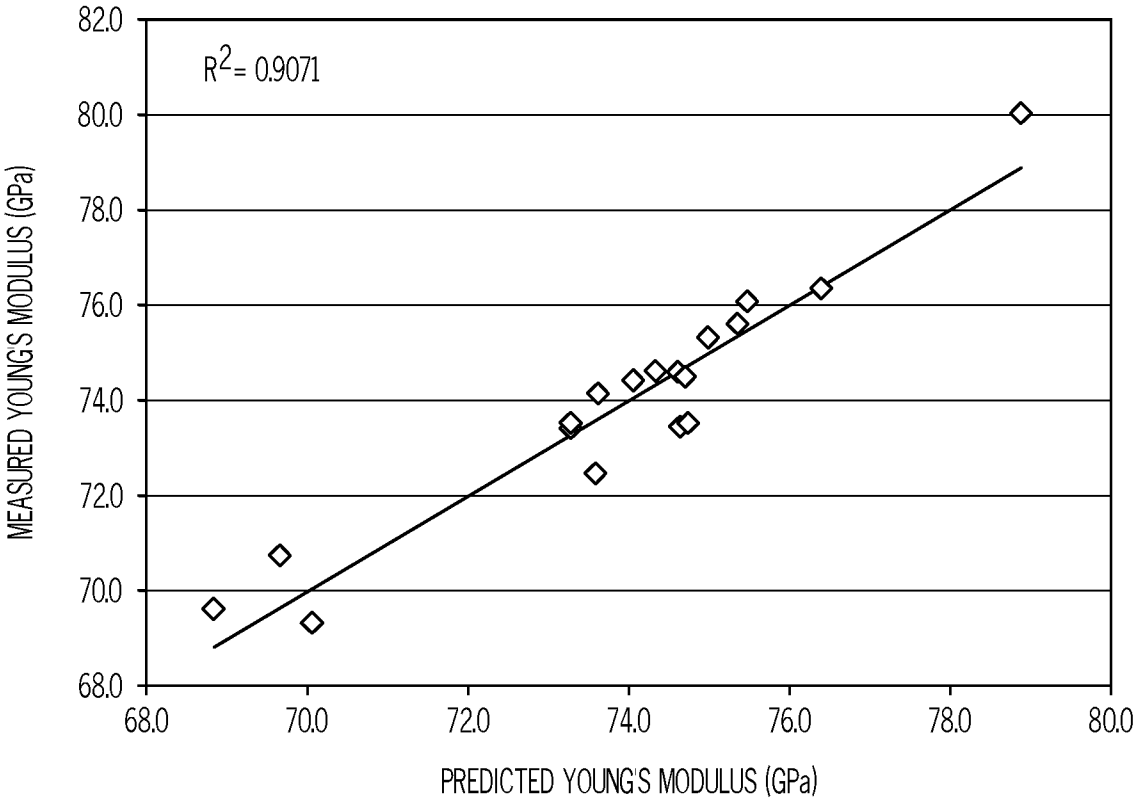


FIG. 5

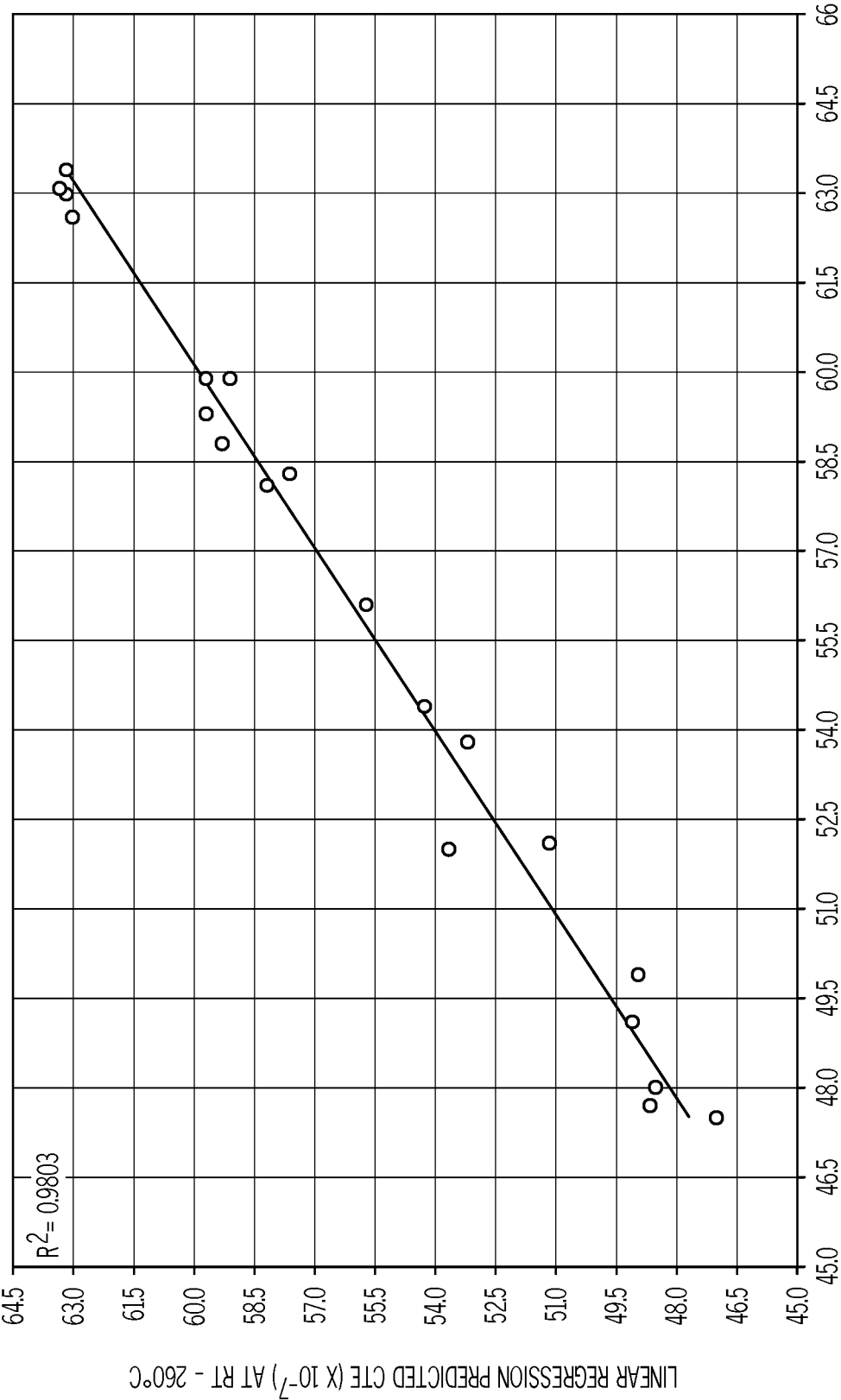


FIG. 6

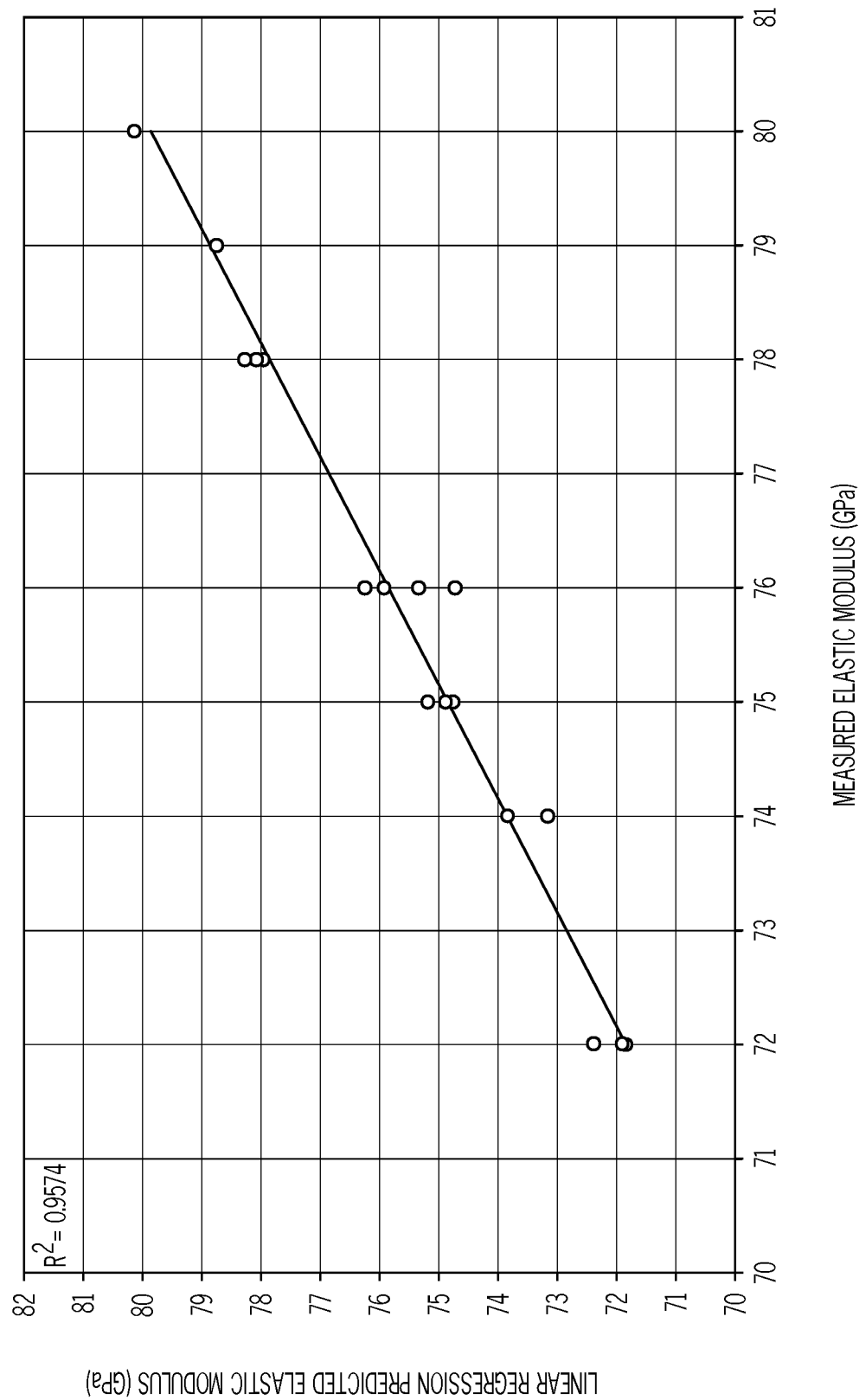


FIG. 7

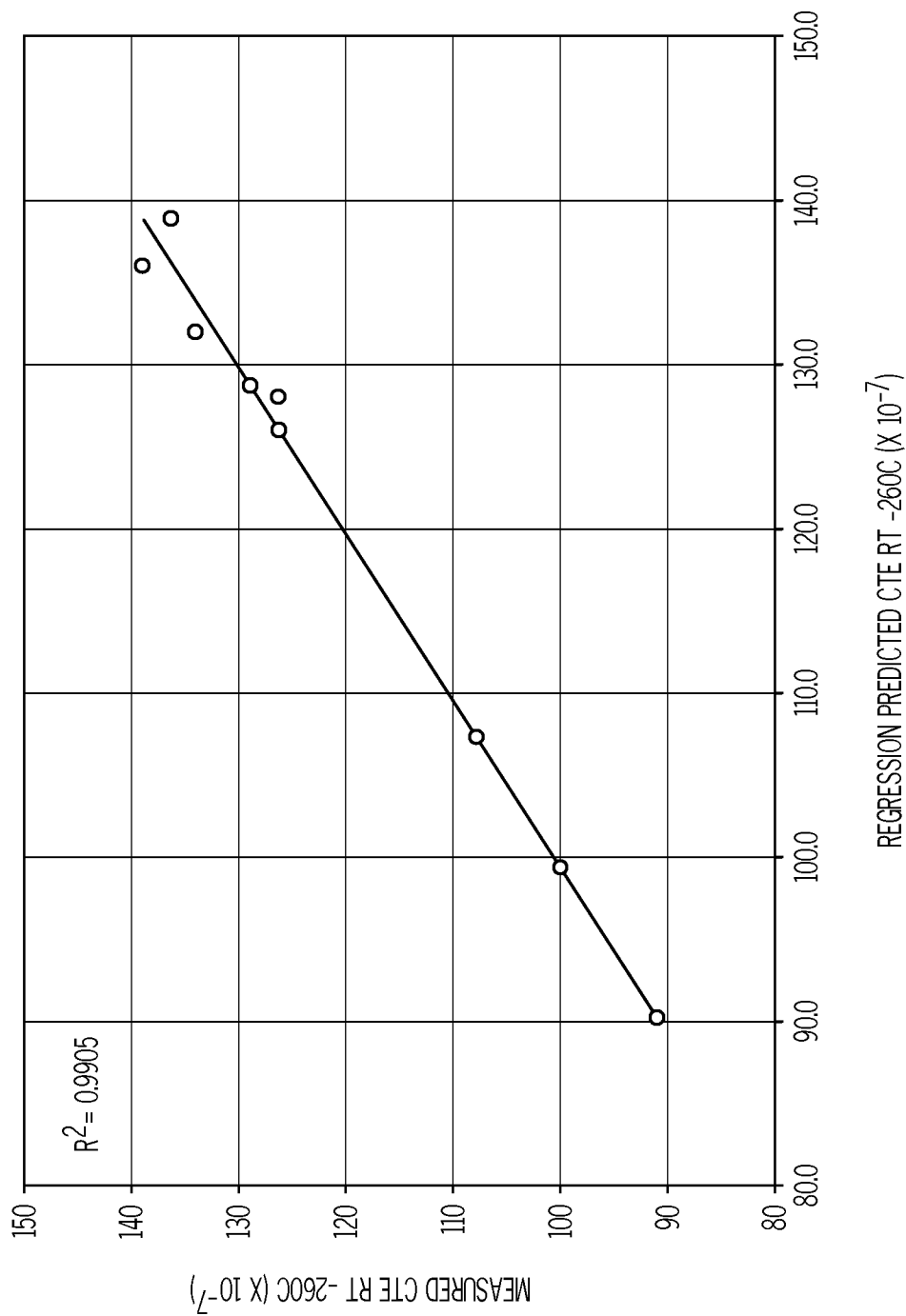


FIG. 8

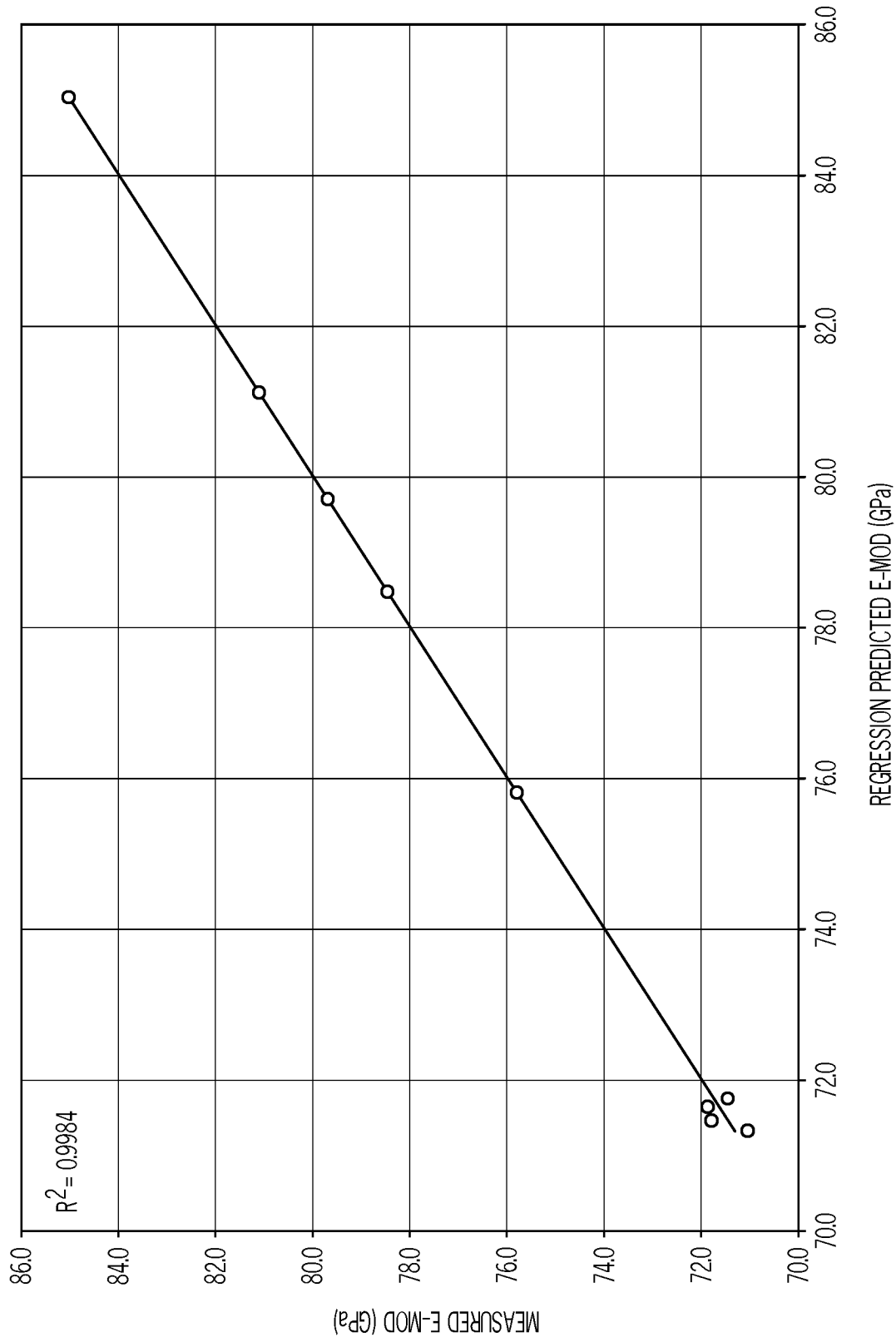


FIG. 9

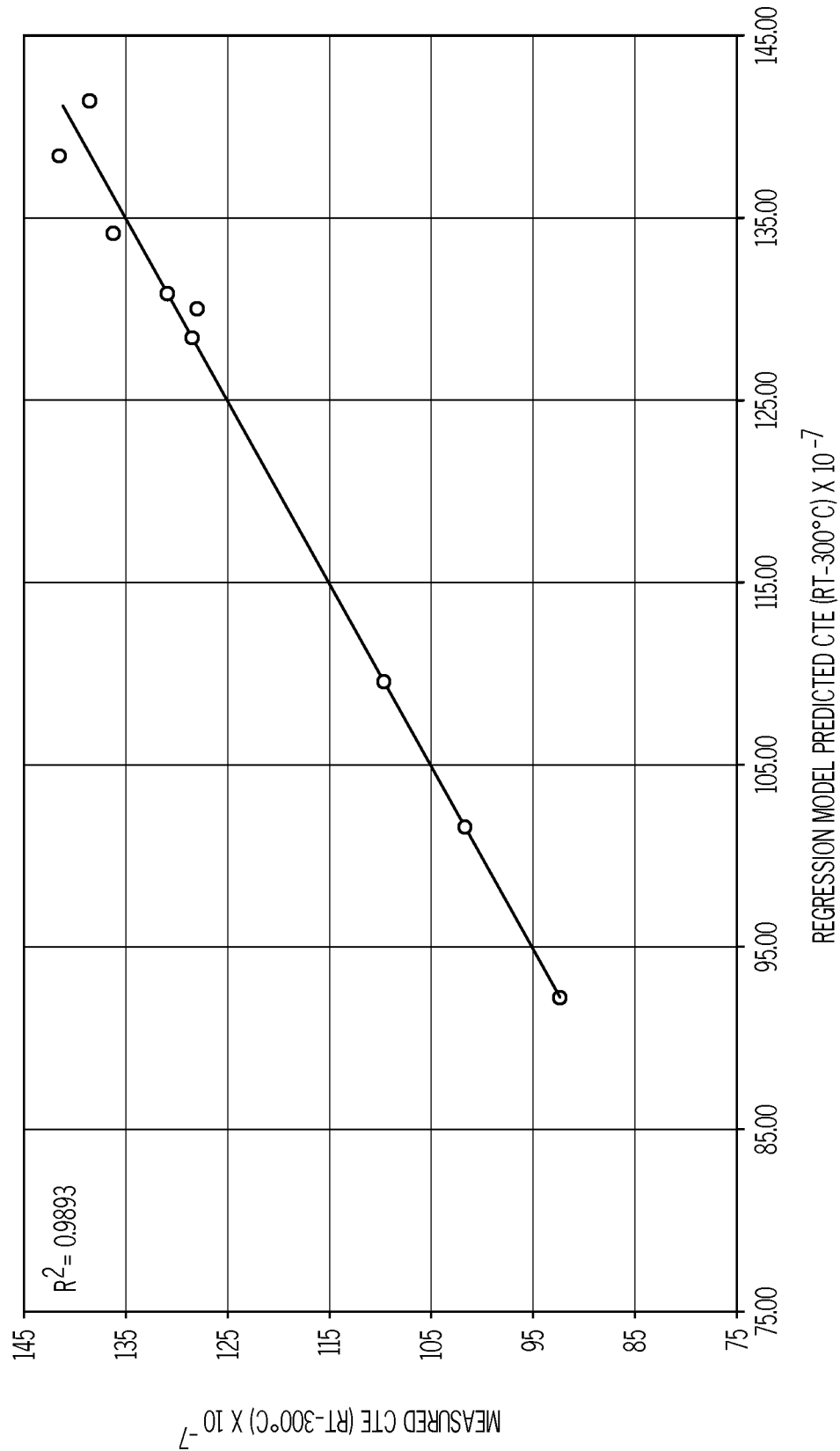


FIG. 10

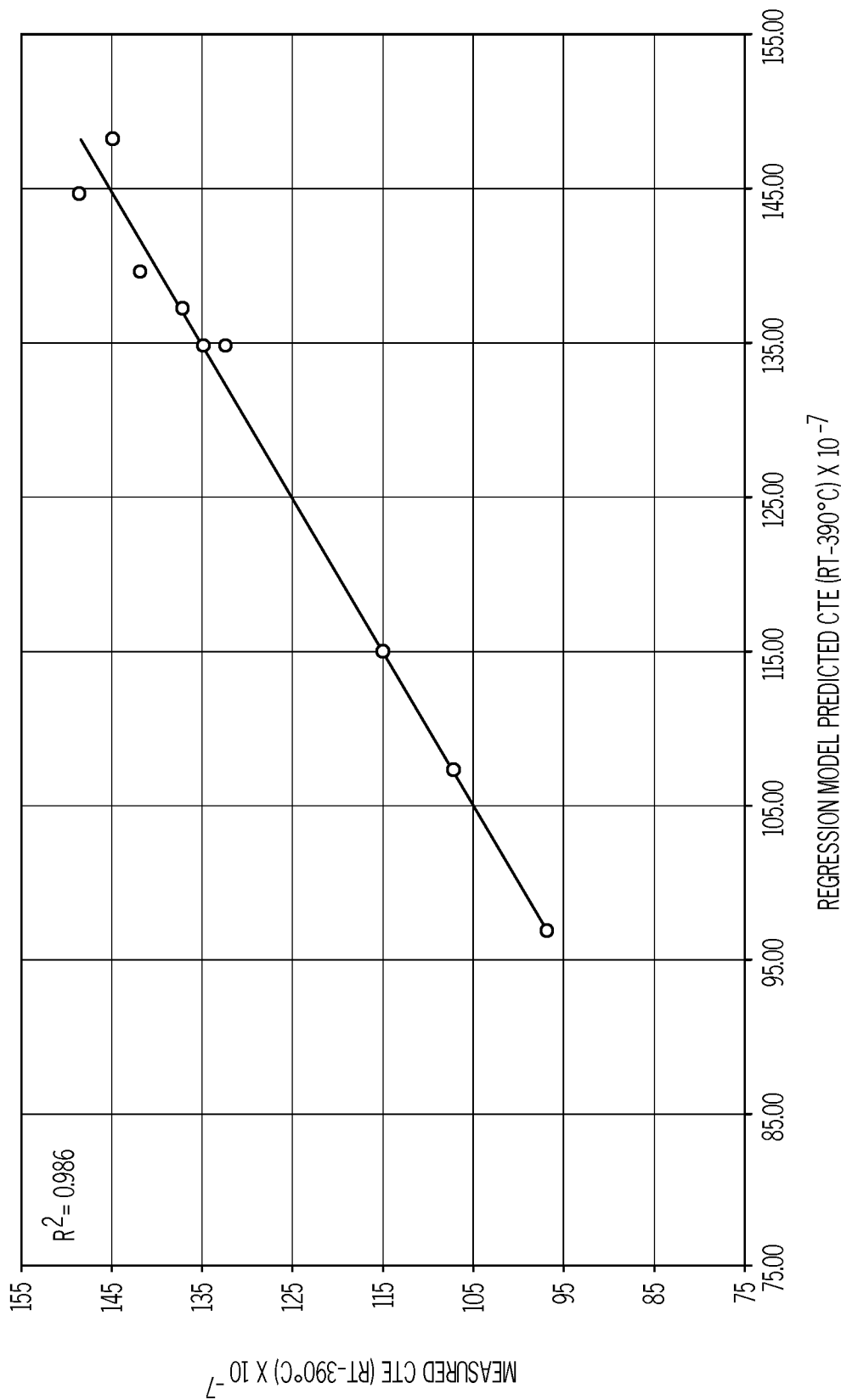


FIG. 11

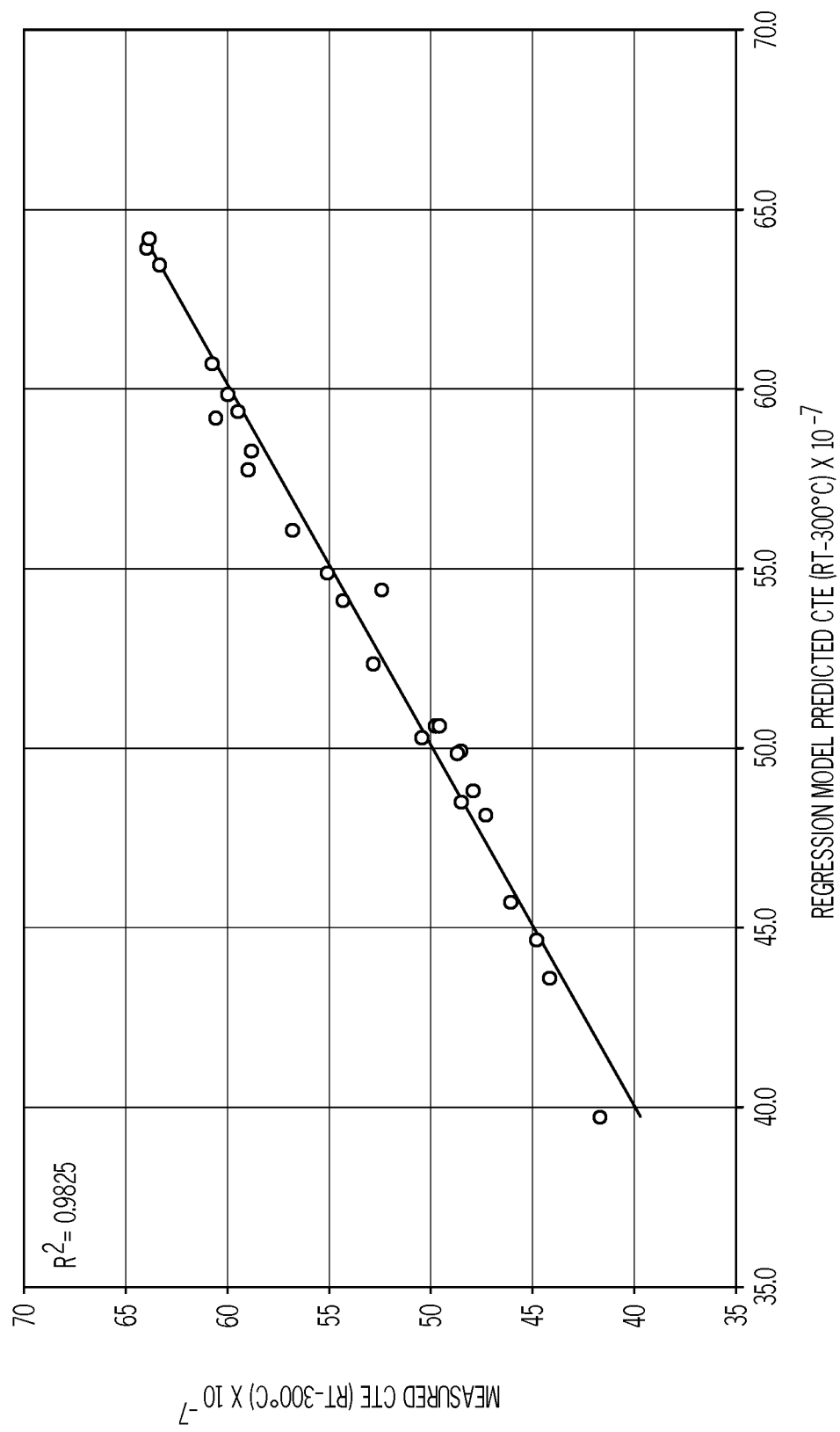


FIG. 12

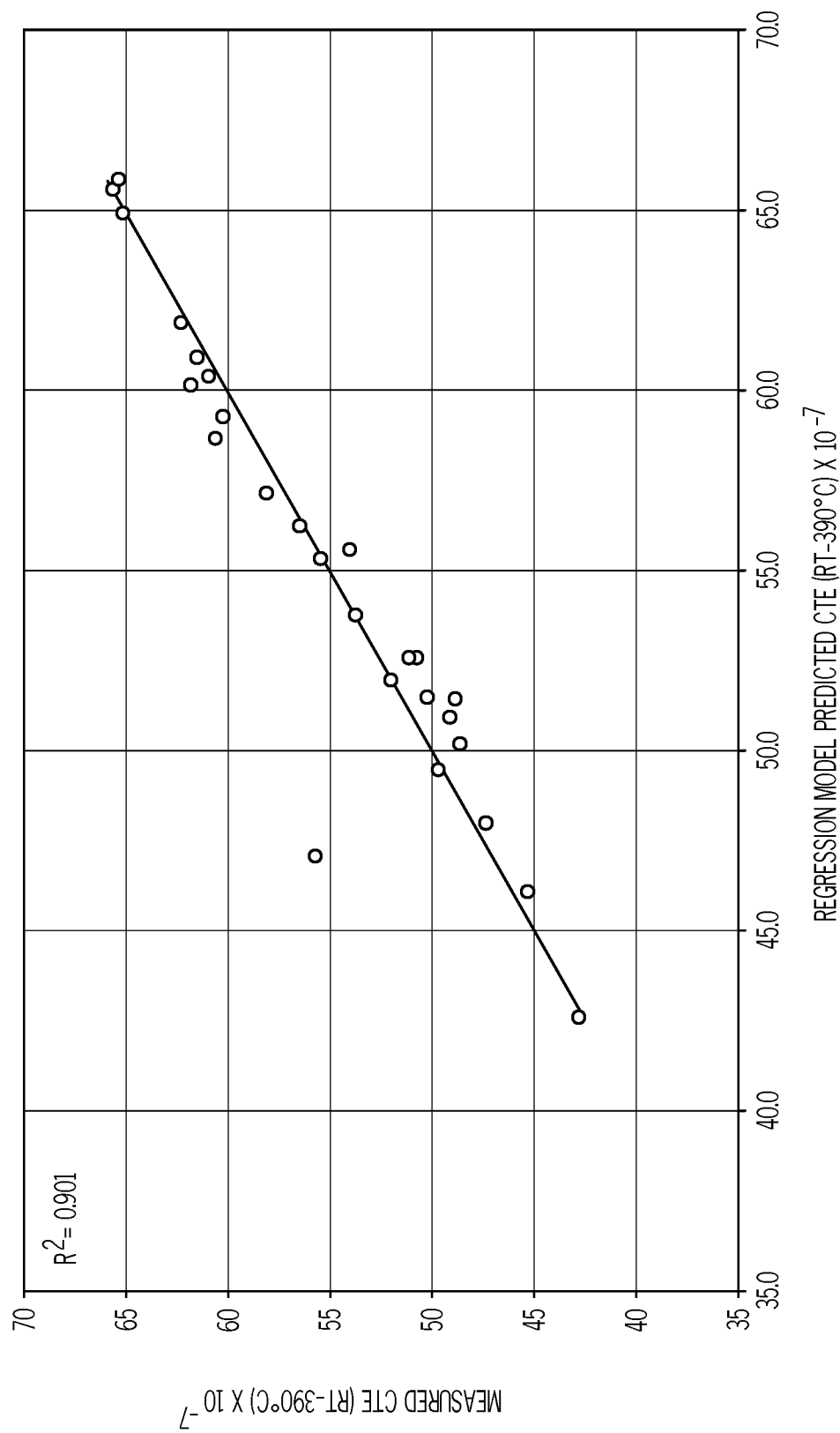


FIG. 13

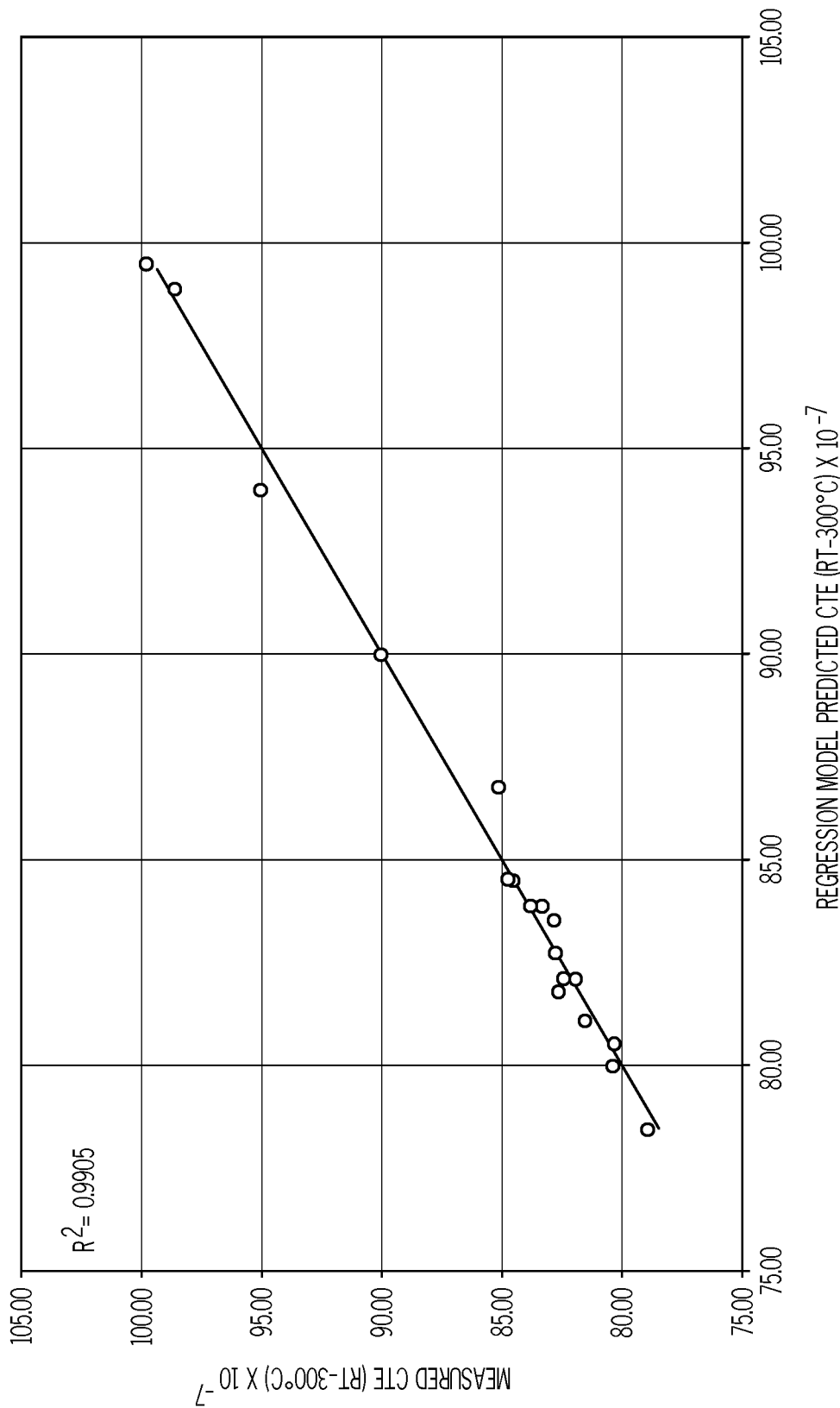


FIG. 14

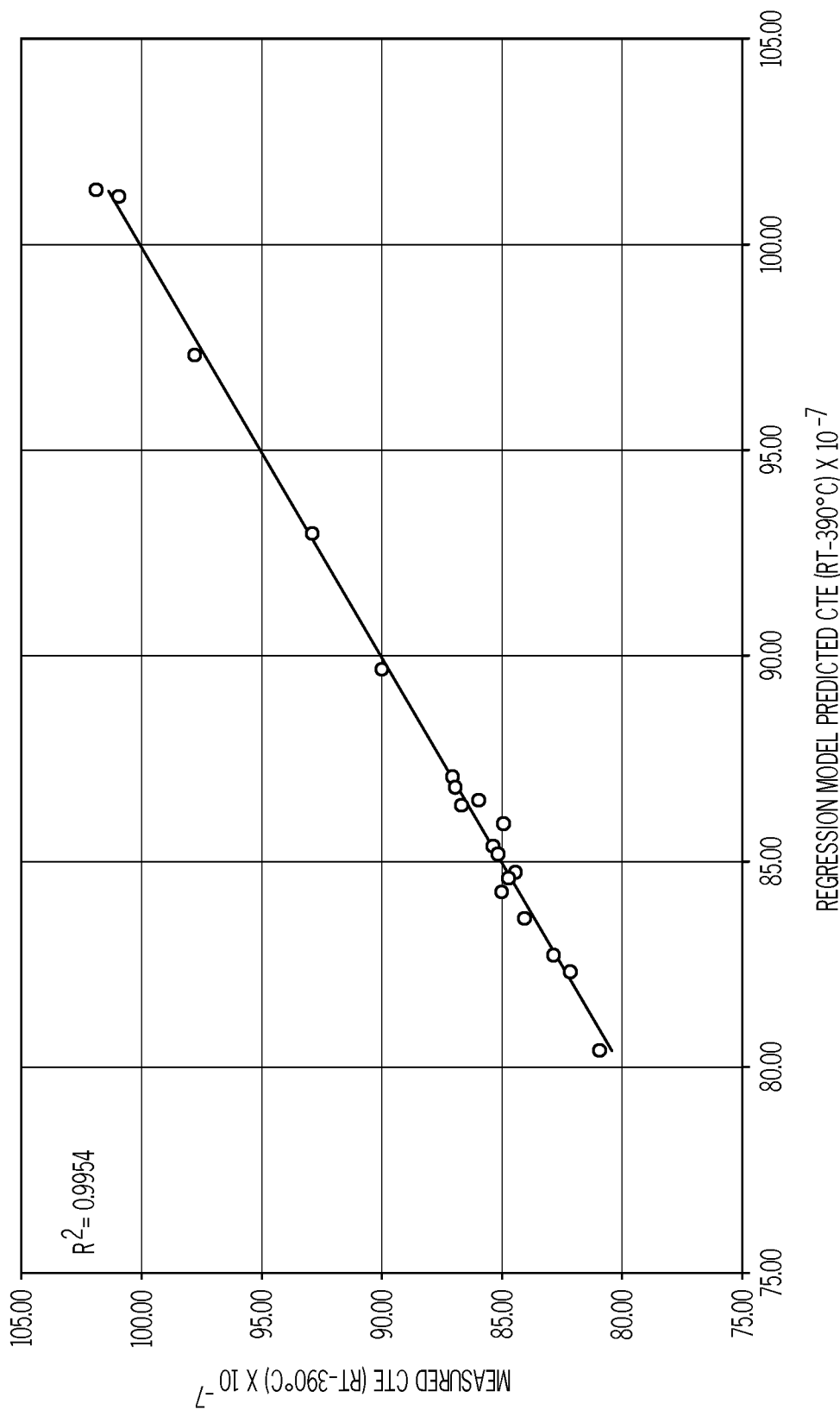


FIG. 15

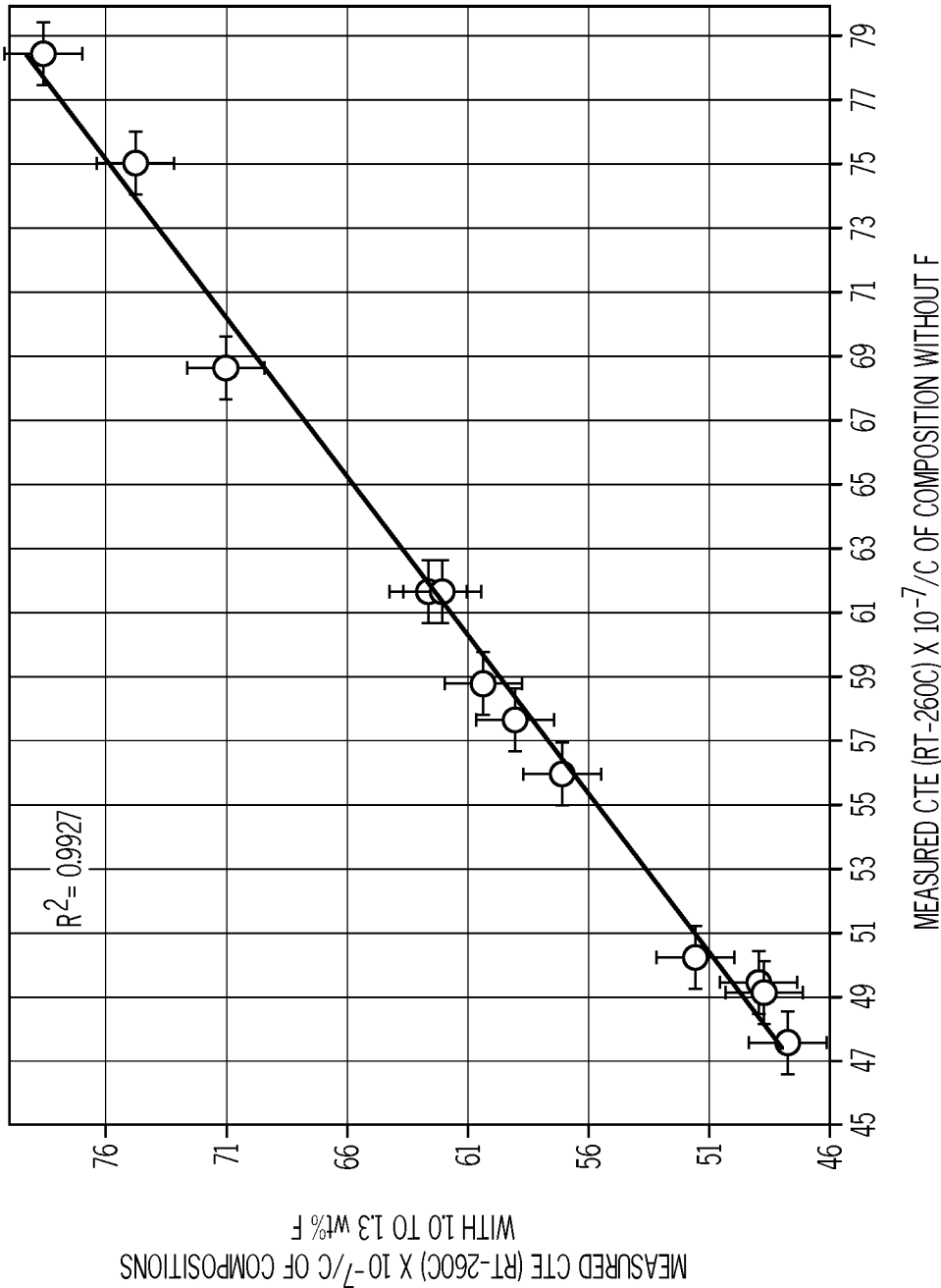


FIG. 16

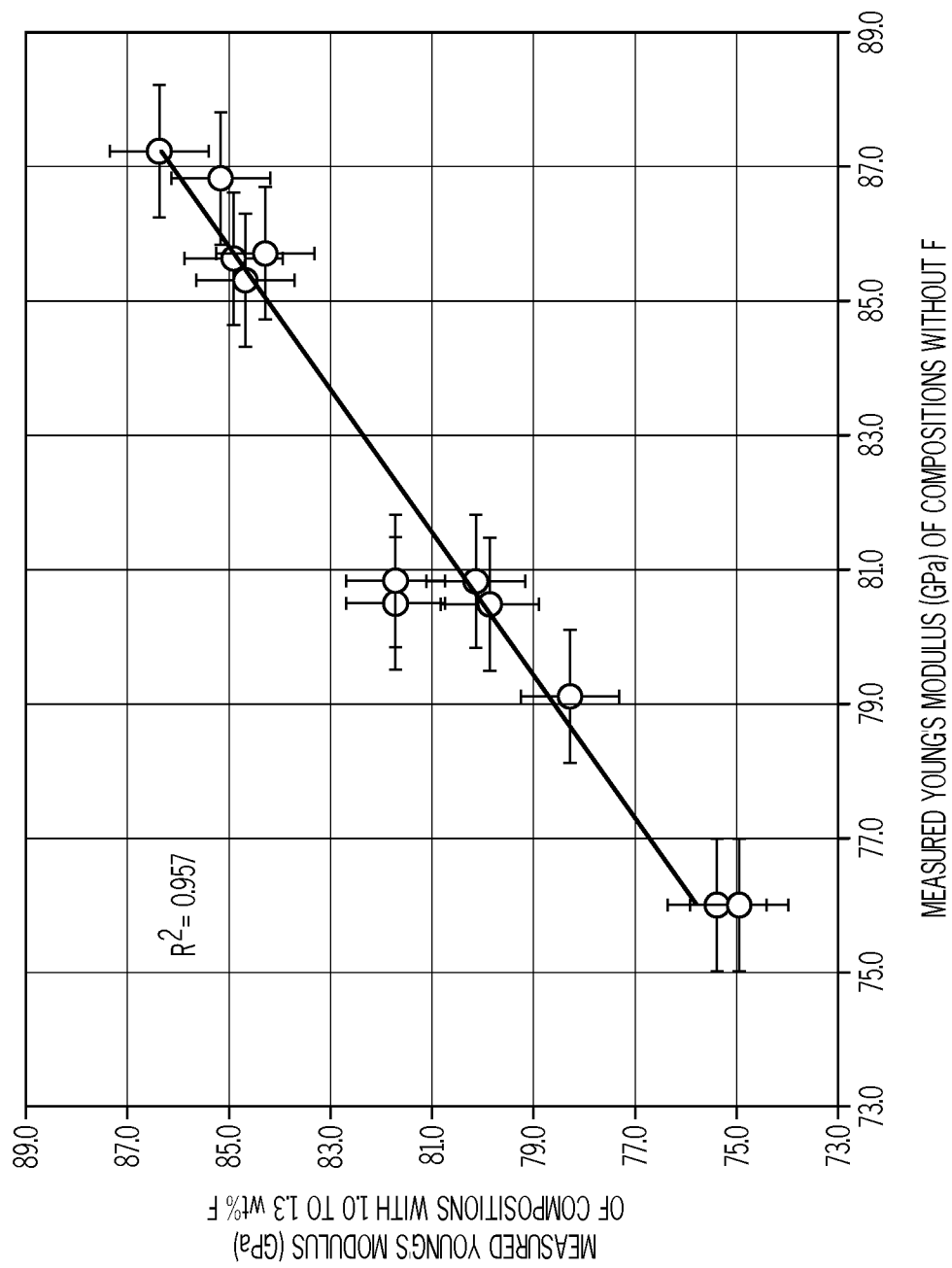


FIG. 17

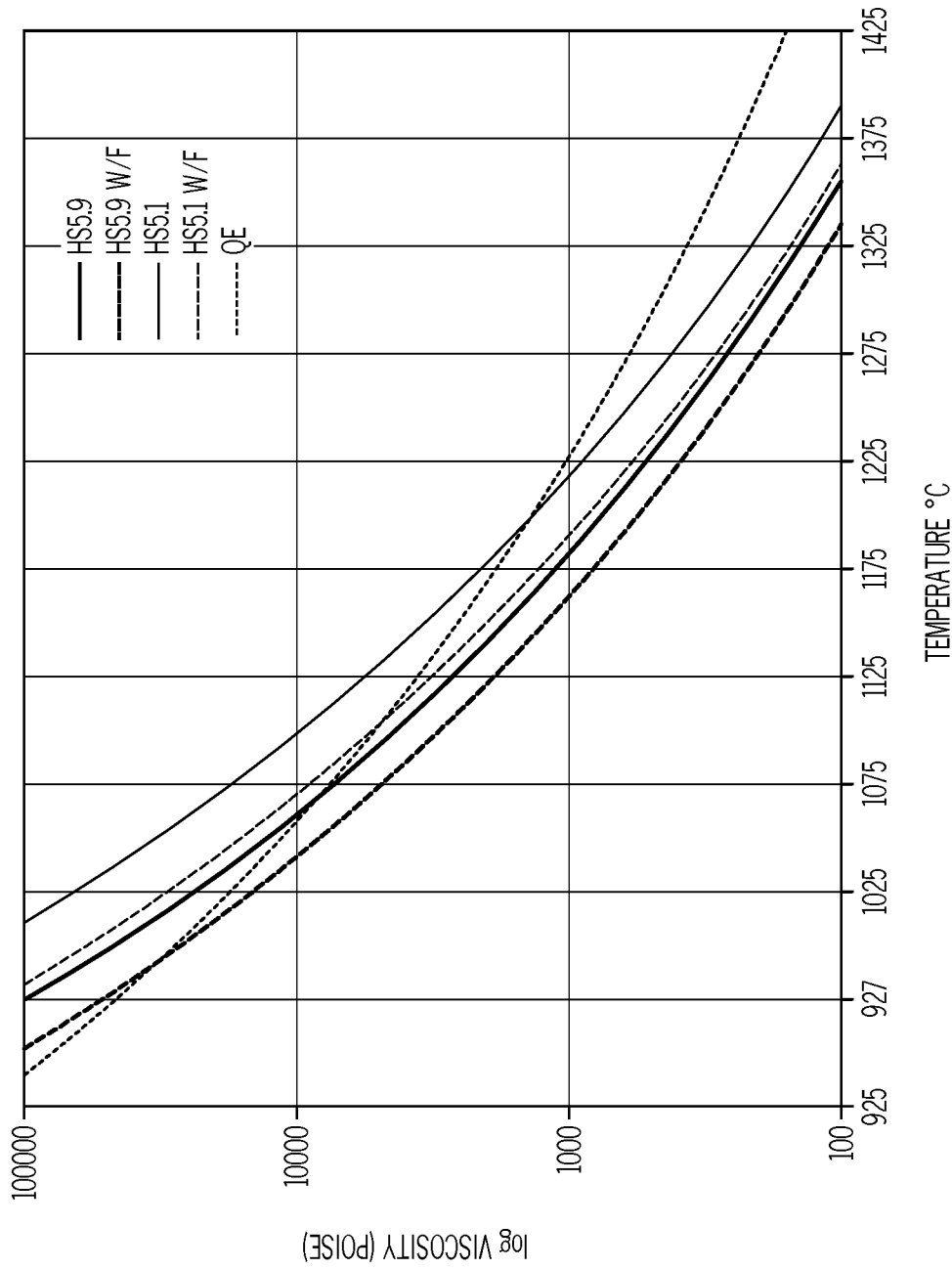


FIG. 18

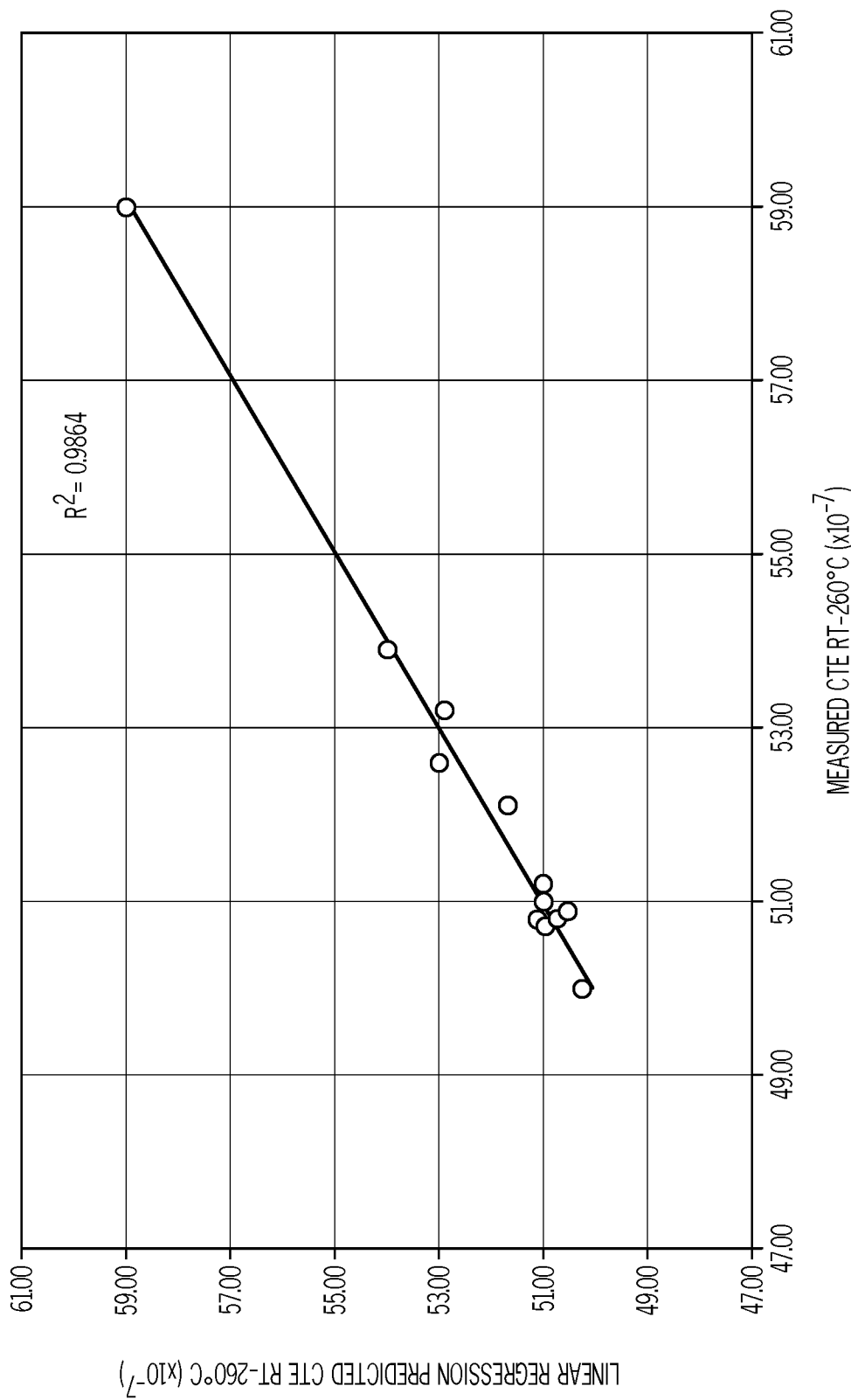


FIG. 19

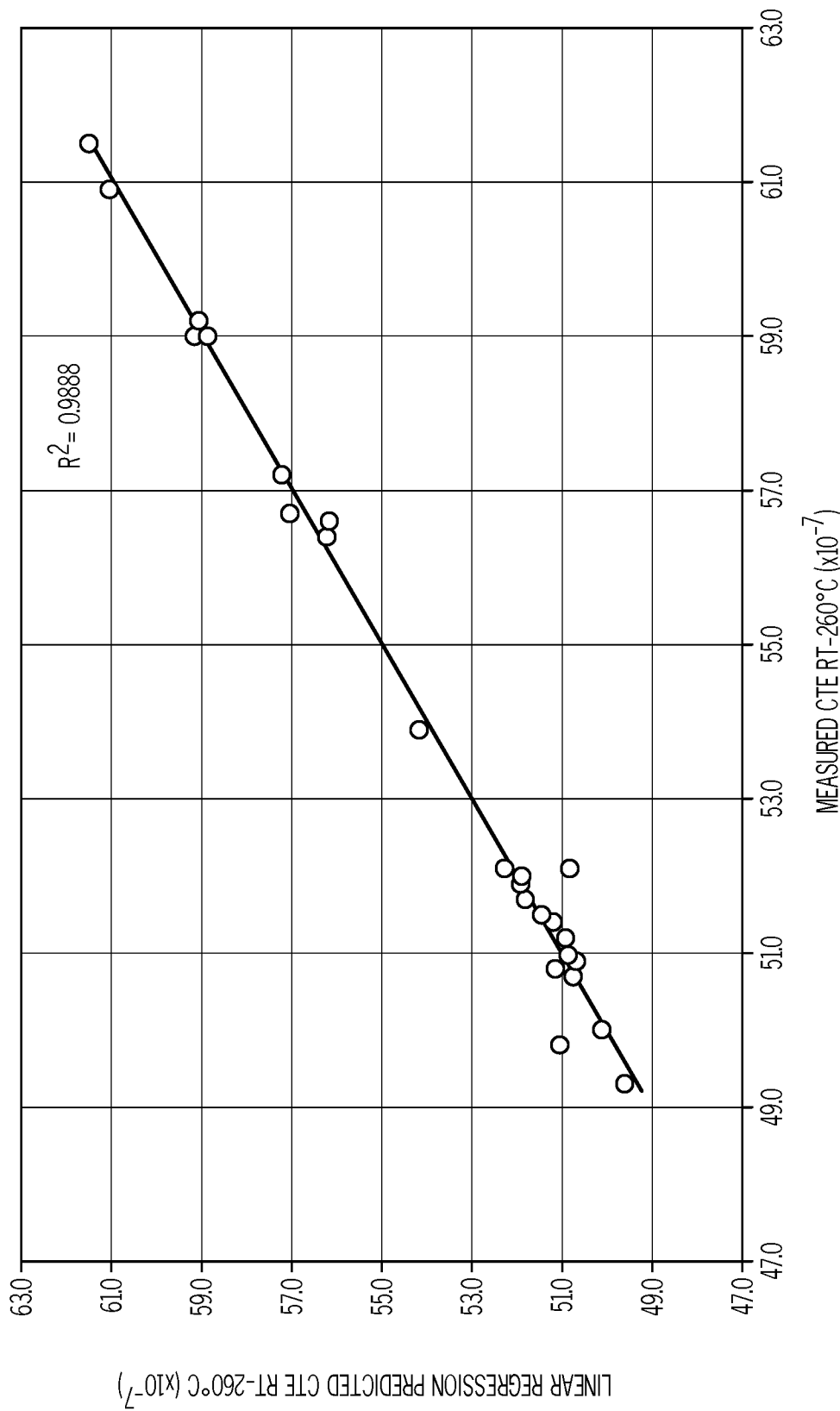


FIG. 20

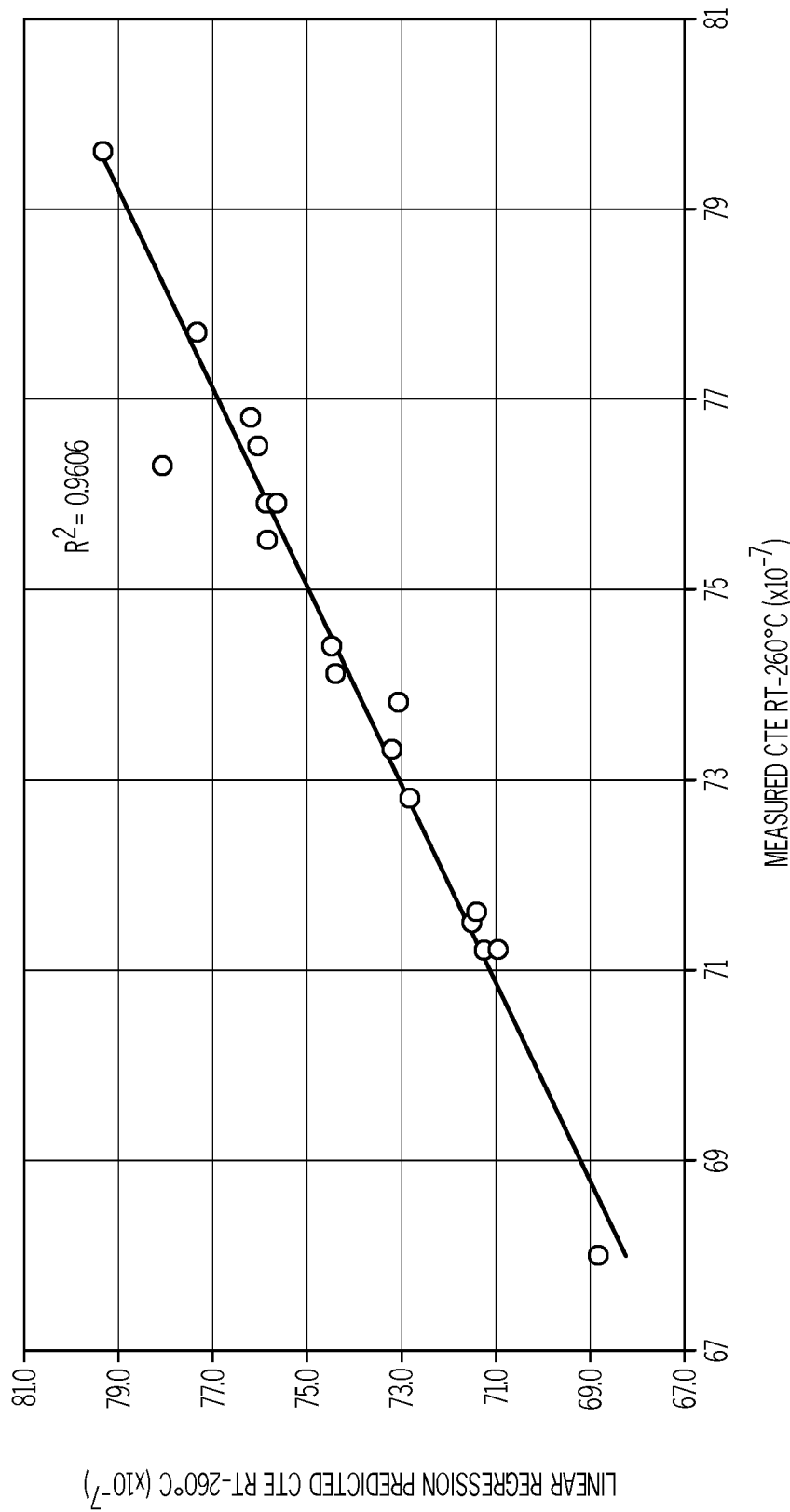


FIG. 21

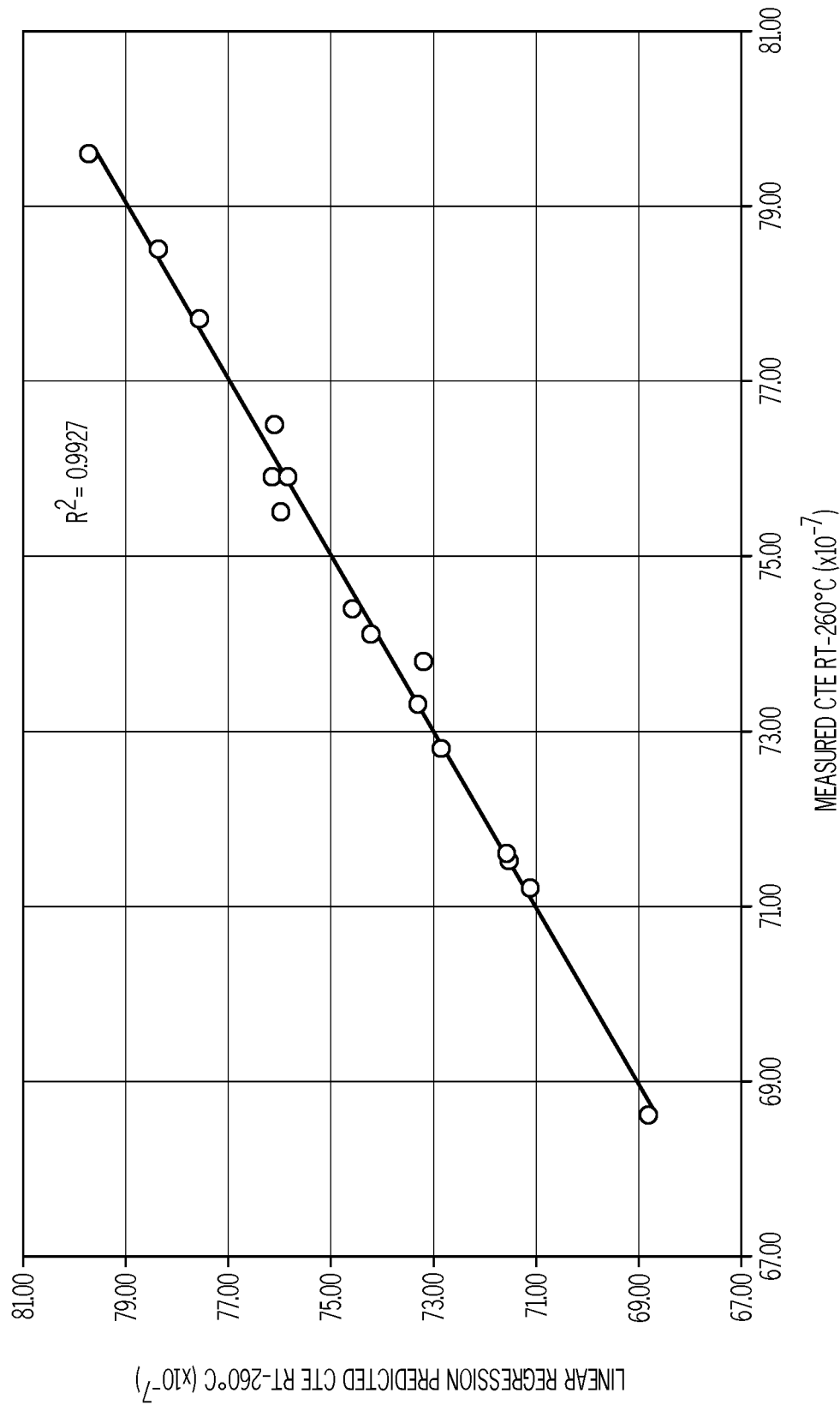


FIG. 22

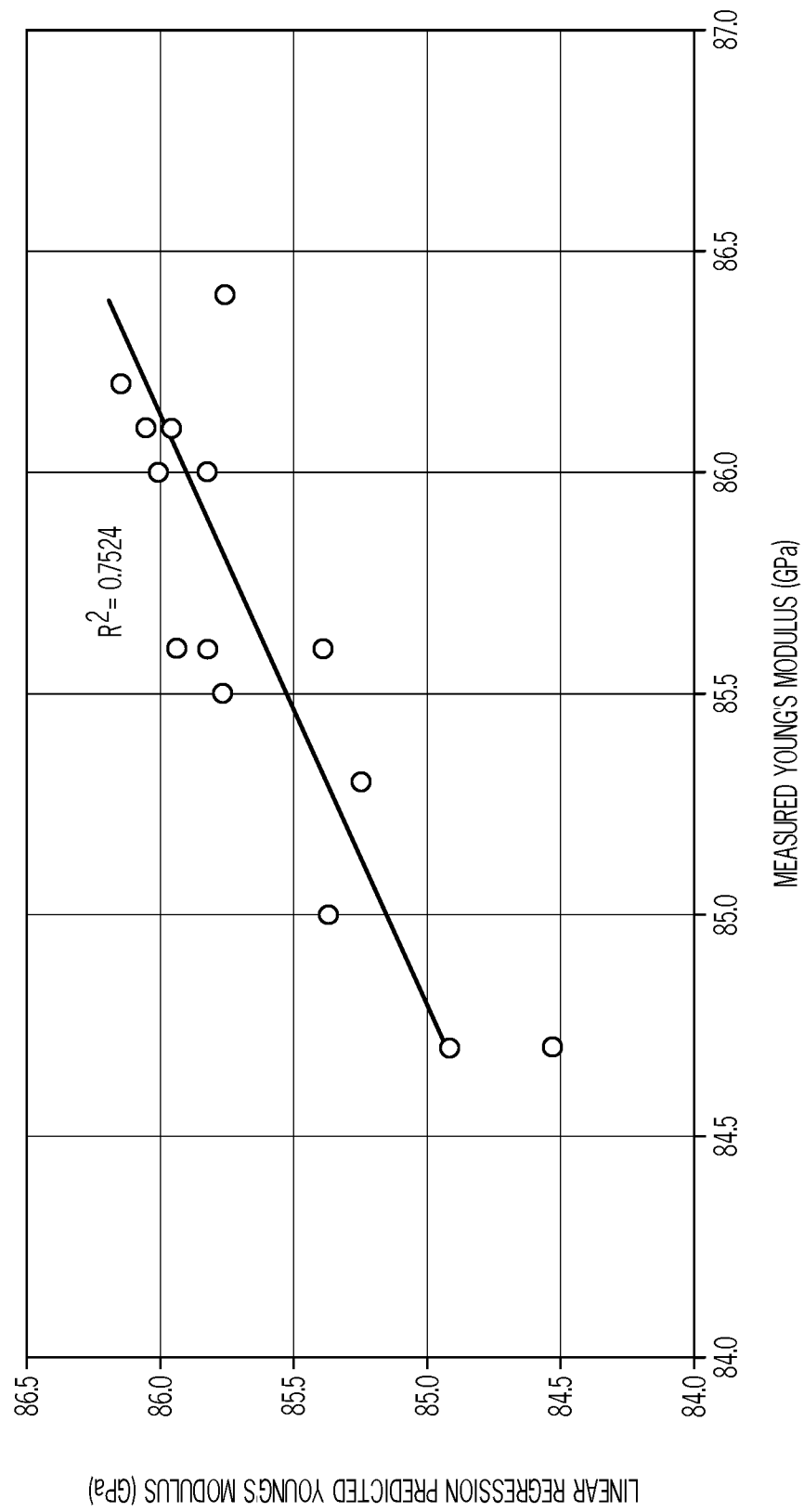


FIG. 23

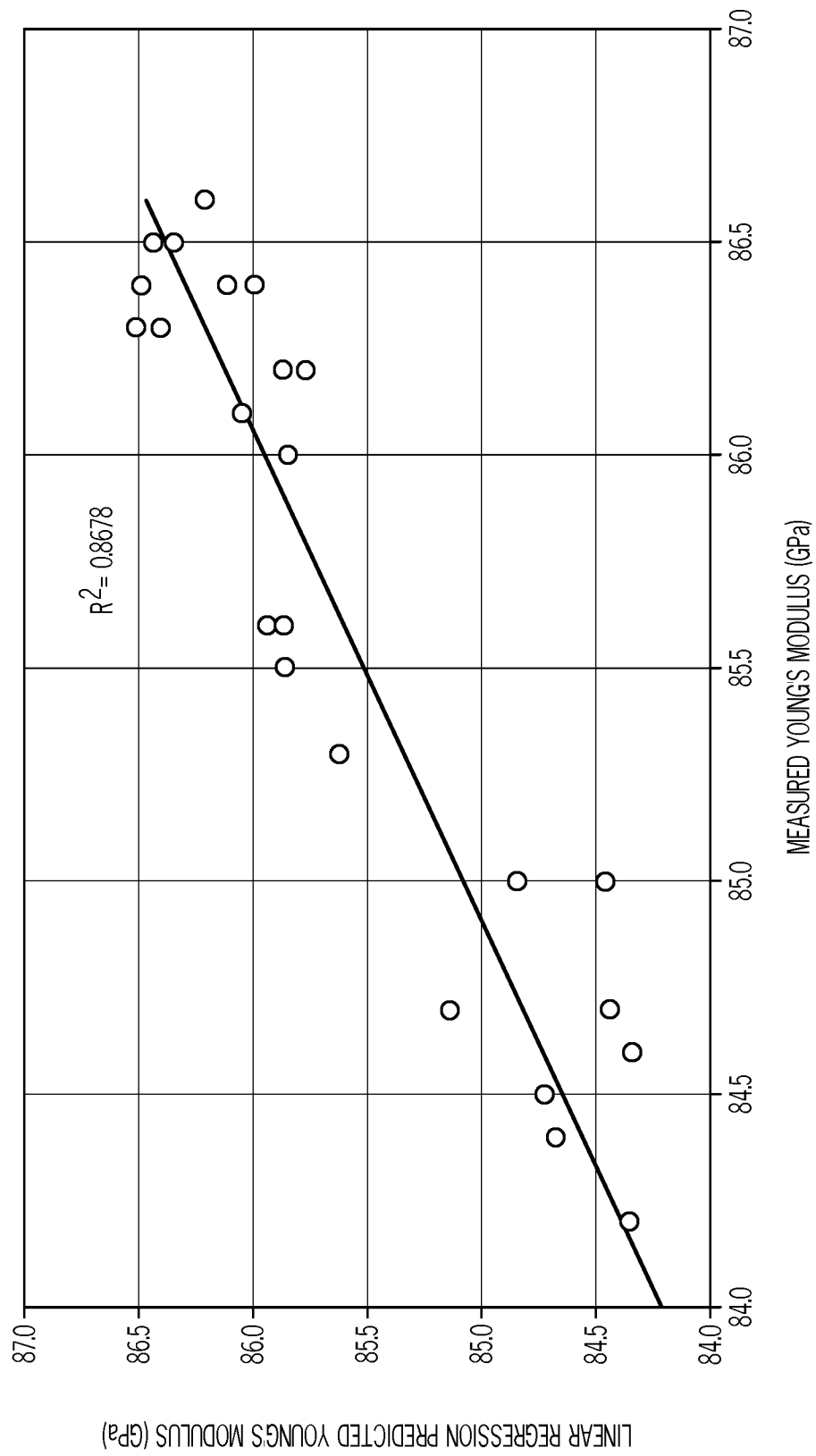


FIG. 24

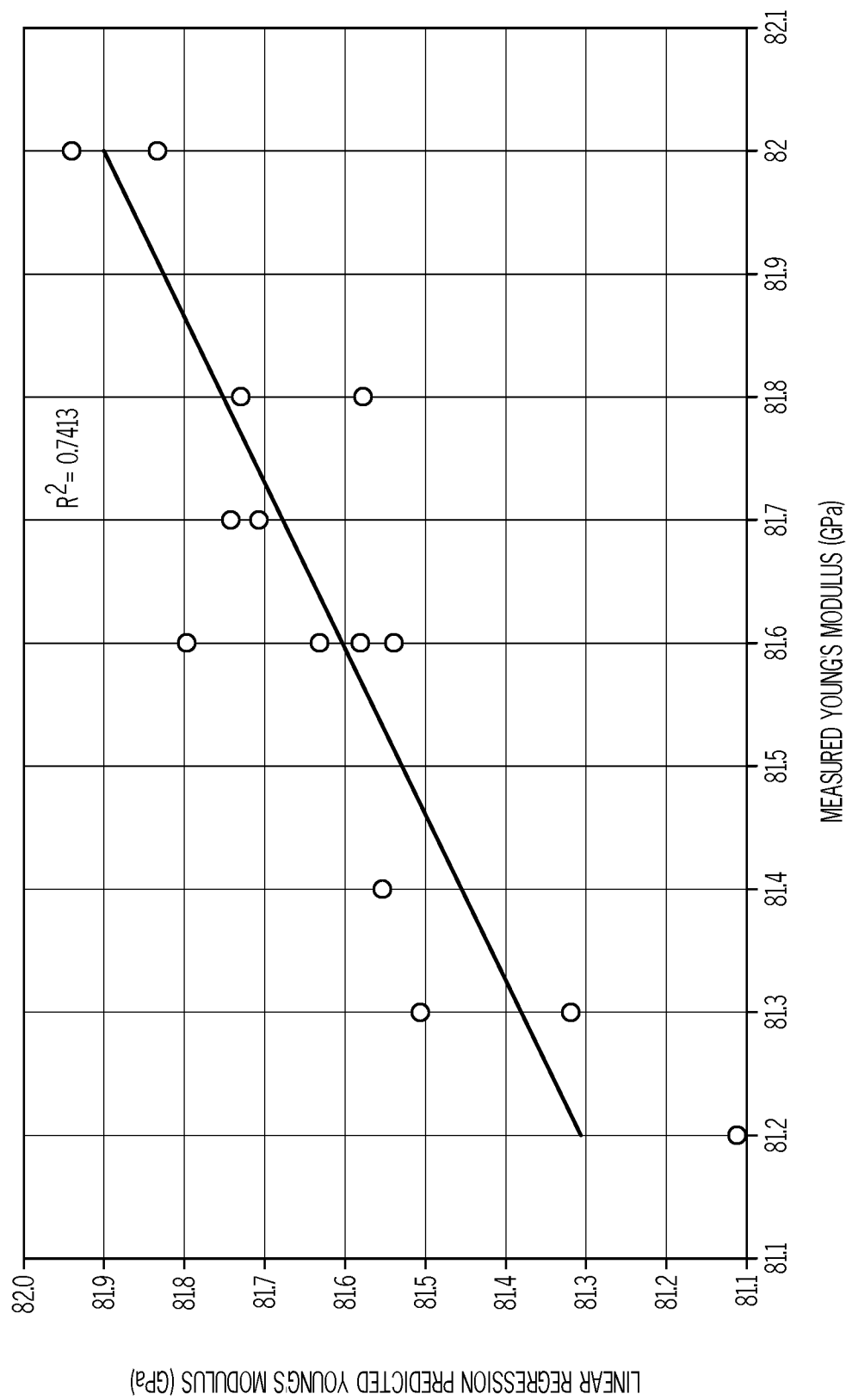


FIG. 25

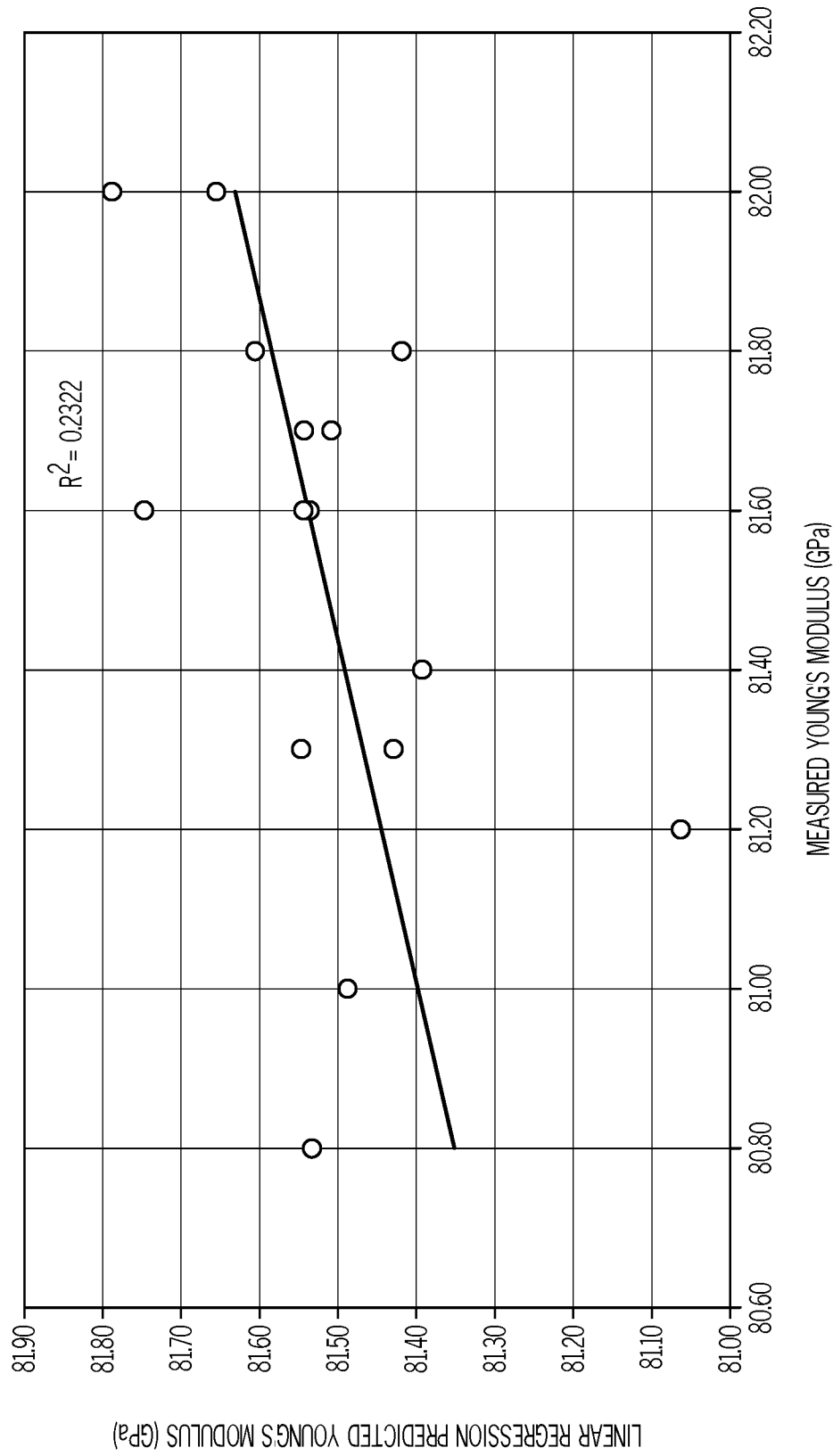


FIG. 26

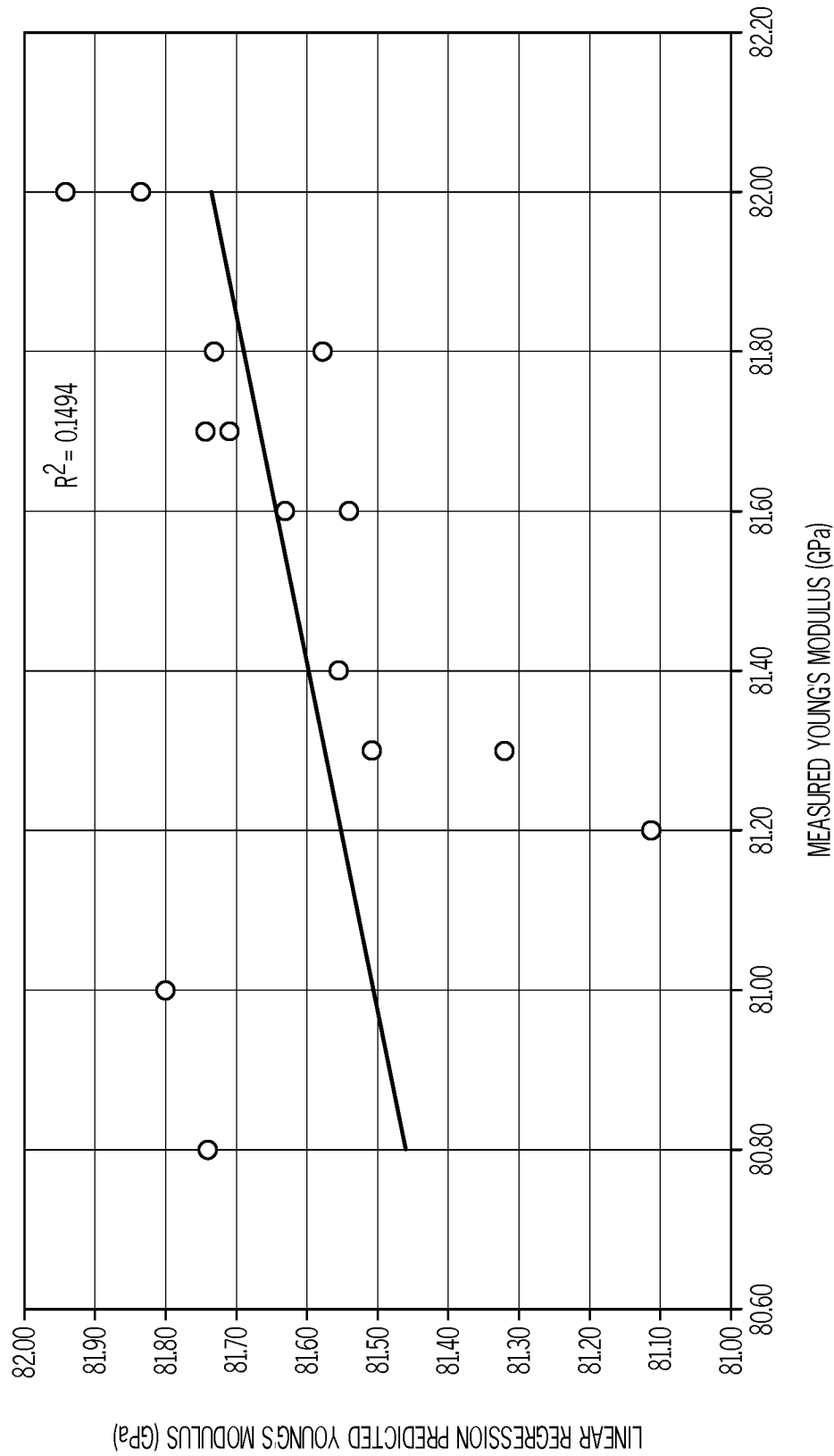


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/047112

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C03B1/00 C03B5/173	C03C3/087 C03C3/091 C03C3/095 C03C3/118
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) C03B 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 practicable, 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	US 2014/230490 A1 (ELLISON ADAM JAMES [US] ET AL) 21 August 2014 (2014-08-21) paragraphs [0104] - [0106]; tables 2, 3 -----	1-35,38
X	RU 2 206 524 C1 (IVANISHCHEV VJACHESLAV VASIL E; FOKIN ANDREJ VIKTOROVICH) 20 June 2003 (2003-06-20) claim 1 -----	1,38
X	WO 2012/093563 A1 (NITTO BOSEKI CO LTD [JP]; OGAWA KENTAROU [JP] ET AL.) 12 July 2012 (2012-07-12) claim 8 -----	1,38
X	US 3 915 684 A (SCHORNHORST JAMES R) 28 October 1975 (1975-10-28) claim 1 ----- -/--	1,38
☒ 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 application or patent 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 22 January 2020		Date of mailing of the international search report 04/02/2020
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 Flügel, Alexander

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2019/047112

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 851 326 A (LIBBEY OWENS FORD GLASS CO) 12 October 1960 (1960-10-12) claim 1 -----	1,38
X	US 3 784 386 A (ARAUJO R ET AL) 8 January 1974 (1974-01-08)	36
A	example 1; table 1 -----	37
X	US 5 972 460 A (TACHIWANA KAZUO [JP]) 26 October 1999 (1999-10-26) example 4 -----	36
X	JP H11 79782 A (TOYO GLASS CO LTD) 23 March 1999 (1999-03-23) example 1 -----	36
X	JP 2000 007372 A (ASAHI TECHNO GLASS CORP) 11 January 2000 (2000-01-11) example 4 -----	36
X	US 4 304 584 A (BORRELLI NICHOLAS F ET AL) 8 December 1981 (1981-12-08) example 12 -----	36
X	US 2008/213626 A1 (KOBAYASHI RYOJI [JP] ET AL) 4 September 2008 (2008-09-04) example 3 -----	36
X	US 2 748 006 A (KREIDL NORBERT J ET AL) 29 May 1956 (1956-05-29) example 3 -----	36

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2019/047112

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-35, 38

method for changing a glass composition in a glass melting furnace and glass article obtained by it

2. claim: 36

glass article with the composition of claim 36 incl. 56-66 wt% SiO₂

3. claim: 37

glass article with the composition of claim 37 incl. 45-55 wt% SiO₂

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/US2019/047112

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2014230490	A1	21-08-2014	CN 104364205 A 18-02-2015
		JP 6236058 B2 22-11-2017	
		JP 2015510864 A 13-04-2015	
		KR 20150031408 A 24-03-2015	
		TW 201339108 A 01-10-2013	
		US 2013233019 A1 12-09-2013	
		US 2014230490 A1 21-08-2014	
		WO 2013138147 A1 19-09-2013	
RU 2206524	C1	20-06-2003	NONE
WO 2012093563	A1	12-07-2012	JP 5849971 B2 03-02-2016
		JP WO2012093563 A1 09-06-2014	
		TW 201238926 A 01-10-2012	
		WO 2012093563 A1 12-07-2012	
US 3915684	A	28-10-1975	NONE
GB 851326	A	12-10-1960	NONE
US 3784386	A	08-01-1974	NONE
US 5972460	A	26-10-1999	NONE
JP H1179782	A	23-03-1999	JP 2987804 B2 06-12-1999
		JP H1179782 A 23-03-1999	
JP 2000007372	A	11-01-2000	NONE
US 4304584	A	08-12-1981	DE 3116082 A1 18-03-1982
		FR 2481259 A1 30-10-1981	
		GB 2075002 A 11-11-1981	
		JP S56169140 A 25-12-1981	
		US 4304584 A 08-12-1981	
US 2008213626	A1	04-09-2008	JP 2008171472 A 24-07-2008
		US 2008213626 A1 04-09-2008	
US 2748006	A	29-05-1956	NONE