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(54) **Title:** METHOD OF MAKING ARTICLES FROM GLASS AND GLASS CERAMIC ARTICLES SO PRODUCED

(57) **Abstract:** Method of making an article, the method comprising coalescing a plurality of the glass particles. The article may comprise glass, glass-ceramic, and/or crystalline ceramic. Examples of articles include kitchenware (e.g., plates), dental brackets, and reinforcing fibers, cutting tool inserts, abrasives, and structural components of gas engines, (e.g., valves and bearings).

METHOD OF MAKING ARTICLES FROM GLASS AND GLASS CERAMIC ARTICLES SO PRODUCED

Field of the Invention

The present invention relates to a method of making an article by coalescing a plurality of the glass particles. Examples of articles include kitchenware (e.g., plates), dental brackets, and reinforcing fibers, cutting tool inserts, abrasives, and structural components of gas engines, (e.g., valves and bearings).

Description of Related Art

A large number of glass and glass-ceramic compositions are known. The majority of oxide glass systems utilize well-known glass-formers such as SiO_2, B_2O_3, P_2O_5, GeO_2, TeO_2, As_2O_3, and V_2O_5 to aid in the formation of the glass. Some of the glass compositions formed with these glass-formers can be heat-treated to form glass-ceramics. The upper use temperature of glasses and glass-ceramics formed from such glass formers is generally less than 1200°C, typically about 700-800°C. The glass-ceramics tend to be more temperature resistant than the glass from which they are formed.

Although a large number of metal oxides can be obtained in an amorphous state by melting and rapidly quenching, most, because of the need for very high quench rates to provide amorphous rather than crystalline material, cannot be formed into bulk or complex shapes. Generally, such systems are very unstable against crystallization during subsequent reheating and therefore do not exhibit typical properties of glass such as viscous flow. On the other hand, glasses based on the known network forming oxides (e.g., SiO_2 and B_2O_3) are generally relatively stable against crystallization during reheating and, correspondingly, the "working" range where viscous flow occurs can be readily accessed. Formation of large articles from powders of known glass (e.g., SiO_2 and B_2O_3) via viscous sintering at temperatures above glass transition temperature is well known. For example, in the abrasive industry, grinding wheels are made using vitrified bond to secure the abrasive particles together.

It is desirable to provide large articles and/or complex shapes comprising non-traditional glass and glass-ceramics compositions.

Summary of the Invention

The present invention provides a method of making articles from glass. Optionally, the articles may be a composite of two or more different glass compositions or formulations. In some embodiments the glass is optionally heat-treated to at least partially crystallize the glass.

One embodiment of the present invention provides a method of making an article from glass comprising:

providing a substrate (e.g., ceramics, metals, intermetallics, and composites thereof) including an outer surface;

providing at least a first glass (e.g., sheets, particles (including microspheres), and fibers), wherein the first glass comprises at least two different metal oxides (i.e., the metal oxides do not have the same cation(s)), wherein the first glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the first glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the first glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5);

heating the first glass above the T_g such that at least a portion of the glass wets at least a portion of the outer surface of the substrate; and

cooling the glass to provide an article comprising ceramic comprising the glass attached to the at least a portion of the outer surface of the substrate. In some embodiments, the ceramic is glass. Optionally, the method can be practiced with a second, a third, or more, different glass, including glasses having, respectively, a T_g and T_x, and wherein the difference between each T_g and the T_x of a glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), one or more of the additional glasses optionally contain less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5%

by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). Preferably the glass, or if more than one glass is used, at least one of the glasses, comprises less than 40 percent (preferably, less than 35, 30, 25, 20, 15, 10, 5,or even 0) by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

Another embodiment of the present invention provides a method of making an article from glass comprising:

providing a substrate including an outer surface;

providing at least a first plurality of particles comprising glass (including glass particles), wherein the glass comprises at least two different metal oxides, wherein the glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5);

heating the glass above the T_g such that at least a portion of the glass of the first plurality of particles wets at least a portion of the outer surface of the substrate; and

cooling the glass to provide an article comprising ceramic comprising the glass attached to the at least a portion of the outer surface of the substrate. In some embodiments, the ceramic is glass. Optionally, the method can be practiced with a second, a third, or more, different pluralities of particles comprising (different) glasses, including glasses having, respectively, a T_g and T_x, and wherein the difference between each T_g and the T_x of a glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), one or more of the additional glasses optionally contain less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). Preferably the glass, or if more than one glass is used, at least one of the glasses, comprises less than 40 (preferably, less than 35, 30, 25, 20, 15, 10, 5,or even 0) percent by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

Another embodiment of the present invention provides a method of making an article comprising:

providing at least a first glass and second glass (e.g., sheets, particles (including microspheres), and fibers), wherein the first glass comprises at least two different metal oxides, wherein the first glass has a T_{g1} and T_{x1}, and wherein the difference between the T_{g1} and the T_{x1} is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the first glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5);

heating the first and second glasses above at least T_{g1} and at least the first glass coalescing with the second glass to provide the article. Optionally, the second glass has a T_{g2} and T_{x2}, wherein the difference between T_{g2} and T_{x2} is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K). Optionally, the second glass contains less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). Optionally, the method can be practiced with a third, a fourth, glass, etc. including glasses having, respectively, a T_g and T_x, and wherein the difference between each T_g and the T_x of a glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), one or more of the additional glasses optionally contain less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). The glasses may have the same composition, different composition, or combinations thereof. Preferably at least one of the glasses comprise less than 40 (preferably, less than 35, 30, 25, 20, 15, 10, 5,or even 0) percent by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

Another embodiment of the present invention provides a method of making an article comprising:

providing at least a first glass and second glass (e.g., sheets, particles (including microspheres), and fibers), wherein the first glass comprises at least two different metal oxides, wherein the first glass has a T_{g1} and T_{x1}, and wherein the difference between the T_{g1} and the T_{x1} is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the first glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5), and wherein the second glass comprises at least two different metal oxides, wherein the second glass has a T_{g2} and T_{x2}, and wherein the difference between the T_{g2} and the T_{x2} is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the second glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5);

heating the glasses above the higher of T_{g1} or T_{g2} and coalescing the first and second glasses to provide the article. Optionally, the method can be practices with a third, a fourth, glass, etc. including glasses having, respectively, a T_g and T_x, and wherein the difference between each T_g and the T_x of a glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), one or more of the additional glasses optionally contain less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). The glasses may have the same composition, different composition, or combinations thereof. Preferably at least one of the glasses comprise less than 40 (preferably, less than 35, 30, 25, 20, 15, 10, 5,or even 0) percent by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

Another embodiment of the present invention provides a method of making an article comprising:

providing at least a first plurality of particles comprising glass (including glass particles), wherein the glass comprises at least two different metal oxides, wherein the glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), the glass containing less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5);

heating the glass above the T_g and coalescing at least a portion of the first plurality of particles to provide the article. In some embodiments, the ceramic is glass. Optionally, the method can be practiced with a second, a third, or more, different pluralities of particles comprising (different) glasses, including glasses having, respectively, a T_g and T_x, and wherein the difference between each T_g and the T_x of a glass is at least 5K (or even, at least 10K, at least 15K, at least 20K, at least 25K, at least 30K,or at least 35K), one or more of the additional glasses optionally contain less than 20% by weight SiO_2 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, SiO_2), less than 20% by weight B_2O_3 (or even less than 15%, less than 10%, less than 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40% by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 1%, less than 5% by weight, or even zero percent, by weight, P_2O_5). Preferably the glass, or if more than one glass is used, at least one of the glasses, comprises less than 40 (preferably, less than 35, 30, 25, 20, 15, 10, 5,or even 0) percent by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

Desirably, the ratio of a T_g to T_l is at least 0.5. Examples of useful glass particles include those comprising REO-Al_2O_3-ZrO_2 and REO-Al_2O_3-ZrO_2–SiO_2 glasses. Other useful glasses may also include CaO-Al_2O_3, CaO-Al_2O_3-ZrO_2, BaO-TiO_2, La_2O_3-TiO_2, REO (i.e., rare earth oxide(s))-Al_2O_3 glasses.

Embodiments of the method according to the present invention, including for certain ceramic compositions, allow for the formation of article shapes and sizes that were obtainable from conventional methods. Coalescence of the glass is typically enhanced if the glass is under pressure during heating. In one embodiment, a charge of glass (e.g., particles (including beads), fibers, etc. is placed into a die and hot-pressing is performed at temperatures above glass transition where viscous flow of glass leads to coalescence into an article.

In this application:

"amorphous material" refers to material derived from a melt and/or a vapor phase that lacks any long range crystal structure as determined by X-ray diffraction and/or has an exothermic peak corresponding to the crystallization of the amorphous material as determined by a DTA (differential thermal analysis) as determined by the test described herein entitled "Differential Thermal Analysis";

"ceramic" includes amorphous material, glass, crystalline ceramic, glass-ceramic, and combinations thereof;

"glass" refers to amorphous material exhibiting a glass transition temperature;

"glass-ceramic" refers to ceramic comprising crystals formed by heat-treating amorphous material;

"rare earth oxides" refers to cerium oxide (e.g.,CeO_2), dysprosium oxide (e.g., Dy_2O_3), erbium oxide (e.g., Er_2O_3), europium oxide (e.g., Eu_2O_3), gadolinium (e.g., Gd_2O_3), holmium oxide (e.g., Ho_2O_3), lanthanum oxide (e.g., La_2O_3), lutetium oxide (e.g., Lu_2O_3), neodymium oxide (e.g., Nd_2O_3), praseodymium oxide (e.g., Pr_6O_{11}), samarium oxide (e.g., Sm_2O_3), terbium (e.g., Tb_2O_3), thorium oxide (e.g., Th_4O_7), thulium (e.g., Tm_2O_3), and ytterbium oxide (e.g., Yb_2O_3), and combinations thereof;

"REO" refers to rare earth oxide(s);

"T_g" refers to the glass transition temperature as determined in Example 1;

"T_l" refers to the glass melting point; and

"T_x" refers to crystallization onset temperature as determined in Example 1.

Further, it is understood herein that unless it is stated that a metal oxide (e.g., Al_2O_3, complex Al_2O_3·metal oxide, etc.) is crystalline, for example, in a glass-ceramic, it may be amorphous, crystalline, or portions amorphous and portions crystalline. For example if a glass-ceramic comprises Al_2O_3 and ZrO_2, the Al_2O_3 and ZrO_2 may each be in an amorphous state, crystalline state, or portions in an amorphous state and portions in a crystalline state, or even as a reaction product with another metal oxide(s) (e.g., unless it is stated that, for example, Al_2O_3 is present as crystalline Al_2O_3 or a specific crystalline phase of Al_2O_3 (e.g., alpha Al_2O_3), it may be present as crystalline Al_2O_3 and/or as part of one or more crystalline complex Al_2O_3·metal oxides. Further, it is understood that glass-ceramics formed by heating amorphous material not exhibiting a T_g may not actually comprise glass, but rather may comprise the crystals and amorphous material that does not exhibiting a T_g.

Optionally certain glass articles made according to the present invention can be heat-treated at least partially crystallize the glass to provide glass-ceramic.

Brief Description of the Drawing

FIG. 1 is a DTA curve of Example 1 material; and

FIGS. 2-6 are DTA curves of Examples 2, 5, 6, 7, and 9 materials, respectively.

Detailed Description

In general, ceramics according to the present invention can be made by heating (including in a flame) the appropriate metal oxide sources to form a melt, desirably a homogenous melt, and then rapidly cooling the melt to provide amorphous materials or ceramic comprising amorphous materials. Amorphous materials and ceramics comprising amorphous materials according to the present invention can be made, for example, by heating (including in a flame) the appropriate metal oxide sources to form a melt, desirably a homogenous melt, and then rapidly cooling the melt to provide amorphous material. Embodiments of amorphous materials can be made, for example, by melting the metal oxide sources in any suitable furnace (e.g., an inductive heated furnace, a gas-fired furnace, or an electrical furnace), or, for example, in a plasma. The resulting melt is cooled (e.g., discharging the melt into a cooling media (e.g., high velocity air jets, liquids, metal plates (including chilled metal plates), metal rolls (including chilled metal rolls), metal balls (including chilled metal balls), and the like)).

Embodiments of amorphous materials can also be obtained by other techniques, such as: laser spin melt with free fall cooling, Taylor wire technique, plasmatron technique, hammer and anvil technique, centrifugal quenching, air gun splat cooling, single roller and twin roller quenching, roller-plate quenching and pendant drop melt extraction (see, e.g., Rapid Solidification of Ceramics, Brockway et. al, Metals And Ceramics Information Center, A Department of Defense Information Analysis Center, Columbus, OH, January, 1984). Embodiments of amorphous materials may also be obtained by other techniques, such as: thermal (including flame or laser or plasma-assisted) pyrolysis of suitable precursors, physical vapor synthesis (PVS) of metal precursors and mechanochemical processing.

In one method, glass useful for the present invention can be made utilizing flame fusion as disclosed, for example, in U.S. Pat. No. 6,254,981 (Castle). In this method, the metal oxide sources materials are fed (e.g., in the form of particles, sometimes referred to as "feed particles") directly into a burner (e.g., a methane-air burner, an acetylene-oxygen burner, a hydrogen-oxygen burner, and like), and then quenched, for example, in water, cooling oil, air, or the like. Feed particles can be formed, for example, by grinding, agglomerating (e.g., spray-drying), melting, or sintering the metal oxide sources. The size of feed particles fed into the flame generally determines the size of the resulting glass particles/beads.

Examples of useful glass for carrying out the present invention include those comprising $CaO-Al_2O_3$, $CaO-Al_2O_3-ZrO_2$, $BaO-TiO_2$, $La_2O_3-TiO_2$, $REO-Al_2O_3$, $REO-Al_2O_3-ZrO_2$, $REO-Al_2O_3-ZrO_2-SiO_2$, and $SrO-Al_2O_3-ZrO_2$ glasses. Useful glass formulations include those at or near a eutectic composition. In addition to the $CaO-Al_2O_3$, $CaO-Al_2O_3-ZrO_2$, $BaO-TiO_2$, $La_2O_3-TiO_2$, $REO-Al_2O_3$, $REO-Al_2O_3-ZrO_2$, $REO-Al_2O_3-ZrO_2-SiO_2$, and $SrO-Al_2O_3-ZrO_2$ compositions disclosed herein, other compositions, including eutectic compositions, will be apparent to those skilled in the art after reviewing the present disclosure. For example, phase diagrams depicting various compositions, including eutectic compositions, are known in the art.

Surprisingly, it was found that ceramics of present invention could be obtained without limitations in dimensions. This was found to be possible through a coalescence step performed at temperatures above glass transition temperature. For instance, as evident from FIG. 1, glass useful in carry out the present invention undergoes glass transition (T_g) before significant crystallization occurs (T_x) as evidenced by the existence of endotherm (T_g) at lower temperature than exotherm (T_x). This allows for bulk fabrication of articles of any dimensions from relatively small pieces of glass. More specifically, for example, an article according to the present invention, can be provided by heating, for example, glass particles (including beads and microspheres), fibers, etc. useful in carrying out the present invention above the T_g such that the glass particles, etc. coalesce to form a shape and cooling the coalesced shape to provide the article. In certain embodiments, heating is conducted at at least one temperature in a range of about 725°C to about 1100°C.

Surprisingly, for certain embodiments according to the present invention, coalescence may be conducted at temperatures significantly higher than crystallization temperature (T_x). Although not wanting to be bound by theory, it s is believed the relatively slow kinetics of crystallization allow access to higher temperatures for viscous flow. Typically, the glass is under pressure during coalescence to aid the coalescence of the glass. In one embodiment, a charge of the glass particles, etc. is placed into a die and hot-pressing is performed at temperatures above glass transition where viscous flow of glass leads to coalescence into a relatively large part. Typically, the amorphous material is under pressure (e.g., greater than zero to 1 GPa or more) during coalescence to aid the coalescence of the amorphous material. It is also within the scope of the present invention to conduct additional coalescence to further improve desirable properties of the article. For example, hot-isostatic pressing may be conducted (e.g., at temperatures from about 900°C to about 1400°C) to remove residual porosity, increasing the density of the material. It is also within the scope of the present invention to coalesce glass via hot-isostatic pressing, hot extrusion, or other pressure assisted techniques.

Heat-treatment can be carried out in any of a variety of ways, including those known in the art for heat-treating glass to provide glass-ceramics. For example, heat-treatment can be conducted in batches, for example, using resistive, inductively or gas heated furnaces. Alternatively, for example, heat-treatment can be conducted continuously, for example, using rotary kilns. In the case of a rotary kiln, the material is fed directly into a kiln operating at the elevated temperature. The time at the elevated temperature may range from a few seconds (in some embodiments even less than 5 seconds) to a few minutes to several hours. The temperature may range anywhere from 900°C to 1600°C, typically between 1200°C to 1500°C. It is also within the scope of the present invention to perform some of the heat-treatment in batches (e.g., for the nucleation step) and another continuously (e.g., for the crystal growth step and to achieve the desired density). For the nucleation step, the temperature typically ranges between about 900°C to about 1100°C, in some embodiments, preferably in a range from about 925°C to about 1050°C. Likewise for the density step, the temperature typically is in a range from about 1100°C to about 1600°C, in some embodiments, preferably in a range from about 1200°C to about 1500°C. This heat treatment may occur, for example, by feeding the material directly into a furnace at the elevated temperature. Alternatively, for example, the material may be feed into a furnace at a much lower temperature (e.g., room temperature) and then heated to desired temperature at a predetermined heating rate.. It is within the scope of the present invention to conduct heat-treatment in an atmosphere other than air. In some cases it might be even desirable to heat-treat in a reducing atmosphere(s). Also, for, example, it may be desirable to heat-treat under gas pressure as in, for example, hot-isostatic press, or in gas pressure furnace.

Sources, including commercial sources, of metal oxides such as Al_2O_3, BaO, CaO, rare earth oxides (e.g., CeO_2, Dy_2O_3, Er_2O_3, Eu_2O_3, Gd_2O_3, Ho_2O_3, La_2O_3, Lu_2O_3, Nd_2O_3, Pr_6O_{11}, Sm_2O_3, Th_4O_7, Tm_2O_3, and Yb_2O_3, and combinations thereof), TiO_2, ZrO_2 are known in the art. For example sources of (on a theoretical oxide basis) Al_2O_3 include bauxite (including both natural occurring bauxite and synthetically produced bauxite), calcined bauxite, hydrated aluminas (e.g., boehmite, and gibbsite), aluminum, Bayer process alumina, aluminum ore, gamma alumina, alpha alumina, aluminum salts, aluminum nitrates, and combinations thereof. The Al_2O_3 source may contain, or only provide, Al_2O_3. Alternatively, the Al_2O_3 source may contain, or provide Al_2O_3, as well as one or more metal oxides other than Al_2O_3 (including materials of or containing complex $Al_2O_3 \cdot$ metal oxides (e.g., $Dy_3Al_5O_{12}$, $Y_3Al_5O_{12}$, $CeAl_{11}O_{18}$, etc.)).

Sources, including commercial sources, of rare earth oxides include rare earth oxide powders, rare earth metals, rare earth-containing ores (e.g., bastnasite and monazite), rare earth salts, rare earth nitrates, and rare earth carbonates. The rare earth oxide(s) source may contain, or only provide, rare earth oxide(s). Alternatively, the rare earth oxide(s) source may contain, or provide rare earth oxide(s), as well as one or more metal oxides other than rare earth oxide(s) (including materials of or containing complex rare earth oxide $\cdot$ other metal oxides (e.g., $Dy_3Al_5O_{12}$, $CeAl_{11}O_{18}$, etc.)).

Sources, including commercial sources, of (on a theoretical oxide basis) ZrO_2 include zirconium oxide powders, zircon sand, zirconium, zirconium-containing ores, and zirconium salts (e.g., zirconium carbonates, acetates, nitrates, chlorides, hydroxides, and combinations thereof). In addition, or alternatively, the ZrO_2 source may contain, or provide ZrO_2, as well as other metal oxides such as hafnia. Sources, including commercial sources, of (on a theoretical oxide basis) HfO_2 include hafnium oxide powders, hafnium, hafnium-containing ores, and hafnium salts. In addition, or alternatively, the HfO_2 source may contain, or provide HfO_2, as well as other metal oxides such as ZrO_2.

Sources, including commercial sources, of BaO include barium oxide powders, , barium -containing ores, barium salts, barium nitrates, and barium carbonates. The barium oxide source may contain, or only provide, barium oxide. Alternatively, the barium oxide source may contain, or provide barium oxide, as well as one or more metal oxides other than barium oxide (including materials of or containing complex barium oxide • other metal oxides).

Sources, including commercial sources, of CaO include calcium oxide powders and calcium-containing ores. The calcium oxide(s) source may contain, or only provide, calcium oxide. Alternatively, the calcium oxide source may contain, or provide calcium oxide, as well as one or more metal oxides other than calcium oxide (including materials of or containing complex calcium oxide • other metal oxides).

Sources, including commercial sources, of rare earth oxides include rare earth oxide powders, rare earth metals, rare earth-containing ores (e.g., bastnasite and monazite), rare earth salts, rare earth nitrates, and rare earth carbonates. The rare earth oxide(s) source may contain, or only provide, rare earth oxide(s). Alternatively, the rare earth oxide(s) source may contain, or provide rare earth oxide(s), as well as one or more metal oxides other than rare earth oxide(s) (including materials of or containing complex rare earth oxide • other metal oxides (e.g., $Dy_3Al_5O_{12}$, $CeAl_{11}O_{18}$, etc.)).

Sources, including commercial sources, of SiO_2 include silica powders, silicon metals, silicon-containing ores. The silicon oxide source may contain, or only provide, silicon oxide. Alternatively, the silicon oxide source may contain, or provide silicon oxide, as well as one or more metal oxides other than silicon oxide (including materials of or containing complex silicon oxide • other metal oxides).

Sources, including commercial sources, of SrO include strontium oxide powders, strontium carbonates, and strontium-containing ores. The strontium oxide source may contain, or only provide, strontium oxide. Alternatively, the strontium oxide source may contain, or provide strontium oxide, as well as one or more metal oxides other than strontium oxide (including materials of or containing complex strontium oxide • other metal oxides).

Sources, including commercial sources, of TiO_2 include titanium oxide powders, titanium metals and titanium -containing ores. The titanium oxide source may contain, or only provide, titanium oxide. Alternatively, the titanium oxide source may contain, or provide titanium oxide, as well as one or more metal oxides other than titanium oxide (including materials of or containing complex titanium oxide • other metal oxides).

Sources, including commercial sources, of (on a theoretical oxide basis) ZrO_2 include zirconium oxide powders, zircon sand, zirconium, zirconium-containing ores, and zirconium salts (e.g., zirconium carbonates, acetates, nitrates, chlorides, hydroxides, and combinations thereof). In addition, or alternatively, the ZrO_2 source may contain, or provide ZrO_2, as well as other metal oxides such as hafnia. Sources, including commercial sources, of (on a theoretical oxide basis) HfO_2 include hafnium oxide powders, hafnium, hafnium-containing ores, and hafnium salts. In addition, or alternatively, the HfO_2 source may contain, or provide HfO_2, as well as other metal oxides such as ZrO_2.

Optionally, ceramics according to the present invention further comprise additional metal oxides beyond those needed for the general composition. The addition of certain metal oxides may alter the properties and/or the crystalline structure or microstructure of ceramics made according to the present invention, as well as the processing of the raw materials and intermediates in making the ceramic. For example, oxide additions such as MgO, CaO, Li_2O, and Na_2O have been observed to alter both the T_g and T_x of glass. Although not wishing to be bound by theory, it is believed that such additions influence glass formation. Further, for example, such oxide additions may decrease the melting temperature of the overall system (i.e., drive the system toward lower melting eutectic), and ease of glass-formation. Complex eutectics in multi component systems (quaternary, etc.) may result in better glass–forming ability. The viscosity of the liquid melt and viscosity of the glass in its' "working" range may also be affected by the addition of metal oxides beyond those needed for the general composition.

In some instances, it may be preferred to incorporate limited amounts of metal oxides selected from the group consisting of: Na_2O, P_2O_5, SiO_2, TeO_2, V_2O_3, and combinations thereof. Sources, including commercial sources, include the oxides themselves, complex oxides, ores, carbonates, acetates, nitrates, chlorides, hydroxides, etc. These metal oxides may be added, for example, to modify a physical property of the resulting abrasive particles and/or improve processing. These metal oxides when used are typically are added from greater than 0 to 20% by weight, preferably greater than 0 to 5% by weight and more preferably greater than 0 to 2% by weight of the glass-ceramic depending, for example, upon the desired property.

Further other glass compositions which may be used in conjunction with the required glass(es) for carrying out the present invention include those conventional glasses that are well known in the art, including sources thereof.

For glasses that devitrify to form glass-ceramics, crystallization may also be affected by the additions of materials beyond those needed for the general composition. For example, certain metals, metal oxides (e.g., titanates and zirconates), and fluorides, for example, may act as nucleation agents resulting in beneficial heterogeneous nucleation of crystals. Also, addition of some oxides may change nature of metastable phases devitrifying from the glass upon reheating. In another aspect, for ceramics according to the present invention comprising crystalline ZrO_2, it may be desirable to add metal oxides (e.g., Y_2O_3, TiO_2, CaO, and MgO) that are known to stabilize tetragonal/cubic form of ZrO_2.

Examples of optional metal oxides (i.e., metal oxides beyond those needed for the general composition) may include, on a theoretical oxide basis, Al_2O_3, BaO, CaO, Cr_2O_3, CoO, Fe_2O_3, GeO_2, HfO_2, Li_2O, MgO, MnO, NiO, Na_2O, P_2O_5, rare earth oxides, Sc_2O_3, SiO_2, SrO, TeO_2, TiO_2, V_2O_3, Y_2O_3, ZnO, ZrO_2, and combinations thereof. Sources, including commercial sources, include the oxides themselves, complex oxides, ores, carbonates, acetates, nitrates, chlorides, hydroxides, etc. Further, for example, with regard to Y_2O_3, sources, including commercial sources, of (on a theoretical oxide basis) Y_2O_3 include yttrium oxide powders, yttrium, yttrium-containing ores, and yttrium salts (e.g., yttrium carbonates, nitrates, chlorides, hydroxides, and combinations thereof). The Y_2O_3 source may contain, or only provide, Y_2O_3. Alternatively, the Y_2O_3 source may contain, or provide Y_2O_3, as well as one or more metal oxides other than Y_2O_3 (including materials of or containing complex $Y_2O_3 \cdot$metal oxides (e.g., $Y_3Al_5O_{12}$)).

In some embodiments, it may be advantageous for at least a portion of a metal oxide source (in some embodiments, preferably, 10 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90,or even at least 95 percent by weight) to be obtained by adding particulate, metallic material comprising at least one of a metal (e.g., Al, Ca, Cu, Cr, Fe, Li, Mg, Ni, Ag, Ti, Zr, and combinations thereof), M, that has a negative enthalpy of oxide formation or an alloy thereof to the melt, or otherwise metal them with the other raw materials. Although not wanting to be bound by theory, it is believed that the heat resulting from the exothermic reaction associated with the oxidation of the metal is beneficial in the formation of a homogeneous melt and resulting amorphous material. For example, it is believed that the additional heat generated by the oxidation reaction within the raw material eliminates or minimizes insufficient heat transfer, and hence facilitates formation and homogeneity of the melt, particularly when forming amorphous particles with x, y, and z dimensions over 150 micrometers. It is also believed that the availability of the additional heat aids in driving various chemical reactions and physical processes (e.g., densification, and spherodization) to completion. Further, it is believed for some embodiments, the presence of the additional heat generated by the oxidation reaction actually enables the formation of a melt, which otherwise is difficult or otherwise not practical due to high melting point of the materials. Further, the presence of the additional heat generated by the oxidation reaction actually enables the formation of amorphous material that otherwise could not be made, or could not be made in the desired size range. Another advantage of the invention include, in forming the amorphous materials, that many of the chemical and physical processes such as melting, densification and spherodizing can be achieved in a short time, so that very high quench rates be can achieved. For additional details, see copending application having U.S. Serial No. ____________ (Attorney Docket No. 56931US007), filed the same date as the instant application.

The particular selection of metal oxide sources and other additives for making ceramics according to the present invention typically takes into account, for example, the desired composition and microstructure of the resulting ceramics, the desired degree of crystallinity, if any, the desired physical properties (e.g., hardness or toughness) of the resulting ceramics, avoiding or minimizing the presence of undesirable impurities, the desired characteristics of the resulting ceramics, and/or the particular process (including equipment and any purification of the raw materials before and/or during fusion and/or solidification) being used to prepare the ceramics.

The metal oxide sources and other additives can be in any form suitable to the process and equipment utilized for the present invention. The raw materials can be melted and quenched using techniques and equipment known in the art for making oxide glasses and amorphous metals. Desirable cooling rates include those of 50K/s and greater.

Cooling techniques known in the art include roll-chilling. Roll-chilling can be carried out, for example, by melting the metal oxide sources at a temperature typically 20-200°C higher than the melting point, and cooling/quenching the melt by spraying it under high pressure (e.g., using a gas such as air, argon, nitrogen or the like) onto a high-speed rotary roll(s). Typically, the rolls are made of metal and are water cooled. Metal book molds may also be useful for cooling/quenching the melt.

Other techniques for forming melts, cooling/quenching melts, and/or otherwise forming glass include vapor phase quenching, plasma spraying, melt-extraction, and gas atomization. Vapor phase quenching can be carried out, for example, by sputtering, wherein the metal alloys or metal oxide sources are formed into a sputtering target(s) which are used. The target is fixed at a predetermined position in a sputtering apparatus, and a substrate(s) to be coated is placed at a position opposing the target(s). Typical pressures of 10^{-3} torr of oxygen gas and Ar gas, discharge is generated between the target(s) and a substrate(s), and Ar or oxygen ions collide against the target to start reaction sputtering, thereby depositing a film of composition on the substrate. For additional details regarding plasma spraying, see, for example, copending application having U.S. Serial No. __________ (Attorney Docket No. 57980US002), filed the same date as the instant application.

Gas atomization involves melting feed particles to convert them to melt. A thin stream of such melt is atomized through contact with a disruptive air jet (i.e., the stream is divided into fine droplets). The resulting substantially discrete, generally ellipsoidal glass particles are then recovered. Melt-extraction can be carried out, for example, as disclosed in U.S. Pat. 5,605,870 (Strom-Olsen et al.). Containerless glass forming techniques utilizing laser beam heating as disclosed, for example, in PCT application having Publication No. WO 01/27046 A1, published April 4, 2001 may also be useful in making glass according to the present invention.

The cooling rate is believed to affect the properties of the quenched amorphous material. For instance, glass transition temperature, density and other properties of glass typically change with cooling rates.

Rapid cooling may also be conducted under controlled atmospheres, such as a reducing, neutral, or oxidizing environment to maintain and/or influence the desired oxidation states, etc. during cooling. The atmosphere can also influence glass formation by influencing crystallization kinetics from undercooled liquid. For example, larger undercooling of Al_2O_3 melts without crystallization has been reported in argon atmosphere as compared to that in air.

With regard to making particles, for example, the resulting ceramic (e.g., glass or ceramic comprising glass may be larger in size than that desired. The ceramic can be, and typically is, converted into smaller pieces using crushing and/or comminuting techniques known in the art, including roll crushing, canary milling, jaw crushing, hammer milling, ball milling, jet milling, impact crushing, and the like. In some instances, it is desired to have two or multiple crushing steps. For example, after the ceramic is formed (solidified), it may be in the form larger than desired. The first crushing step may involve crushing these relatively large masses or "chunks" to form smaller pieces. This crushing of these chunks may be accomplished with a hammer mill, impact crusher or jaw crusher. These smaller pieces may then be subsequently crushed to produce the desired particle size distribution. In order to produce the desired particle size distribution (sometimes referred to as grit size or grade), it may be necessary to perform multiple crushing steps. In general the crushing conditions are optimized to achieve the desired particle shape(s) and particle size distribution.

The shape of particles can depend, for example, on the composition of the glass, the geometry in which it was cooled, and the manner in which the glass is crushed (i.e., the crushing technique used), if the particles were formed by crushing.

Certain articles according to the present invention comprising glass can be heat-treated to increase or at least partially crystallize the glass (including crystallize the glass) to provide glass-ceramic. The heat-treatment of certain glasses to form glass-ceramics is well known in the art. The heating conditions to nucleate and grow glass-ceramics are known for a variety of glasses. Alternatively, one skilled in the art can determine the appropriate conditions from a Time-Temperature-Transformation (TTT) study of the glass using techniques known in the art. One skilled in the art, after reading the disclosure of the present invention should be able to provide TTT curves for glasses according to the present invention, determine the appropriate nucleation and/or crystal growth conditions to provide crystalline ceramics, glass-ceramics, and ceramic comprising glass according to the present invention.

Typically, glass-ceramics are stronger than the glasses from which they are formed. Hence, the strength of the material may be adjusted, for example, by the degree to which the glass is converted to crystalline ceramic phase(s). Alternatively, or in addition, the strength of the material may also be affected, for example, by the number of nucleation sites created, which may in turn be used to affect the number, and in turn the size of the crystals of the crystalline phase(s). For additional details regarding forming glass-ceramics, see, for example Glass–Ceramics, P.W. McMillan, Academic Press, Inc., 2^{nd} edition, 1979.

For example, during heat-treatment of a glass such as a glass comprising Al_2O_3, La_2O_3, and ZrO_2 formation of phases such as $La_2Zr_2O_7$, and, if ZrO_2 is present, cubic/tetragonal ZrO_2, in some cases monoclinic ZrO_2, have been observed at temperatures above about 900°C. Although not wanting to be bound by theory, it is believed that zirconia-related phases are the first phases to nucleate from the glass. For example, of Al_2O_3, $ReAlO_3$ (wherein Re is at least one rare earth cation), $ReAl_{11}O_{18}$, $Re_3Al_5O_{12}$, $Y_3Al_5O_{12}$, etc. phases are believed to generally occur at temperatures above about 925°C. Crystallite size during this nucleation step may be on the order of nanometers. For example, crystals as small as 10-15 nanometers have been observed. Longer heat-treating temperatures typically lead to the growth of crystallites and progression of crystallization. For at least some embodiments, heat-treatment at about 1300°C for about 1 hour provides a full crystallization.

Certain ceramic articles made according to the present invention contain less than less than 20 % by weight SiO_2 (or even less than 15%, less than 10 %, less than, 5% by weight, or even zero percent, by weight, SiO_2), less than 20 % by weight B_2O_3 (or even less than 15%, less than 10 %, less than, 5% by weight, or even zero percent, by weight, B_2O_3), and less than 40 % by weight P_2O_5 (or even less than 35%, less than 30%, less than 25%, less than 20%, less than 15%, less than 10 %, less than, 5% by weight, or even zero percent, by weight, P_2O_5), based on the total metal oxide weight of the ceramic.

The microstructure or phase composition (glassy/amorphous/crystalline) of a material can be determined in a number of ways. Various information can be obtained using optical microscopy, electron microscopy, differential thermal analysis (DTA), and x-ray diffraction (XRD), for example.

Using optical microscopy, amorphous material is typically predominantly transparent due to the lack of light scattering centers such as crystal boundaries, while crystalline material shows a crystalline structure and is opaque due to light scattering effects.

Using DTA, the material is classified as amorphous if the corresponding DTA trace of the material contains an exothermic crystallization event (T_x). If the same trace also contains an endothermic event (T_g) at a temperature lower than T_x it is considered to consist of a glass phase. If the DTA trace of the material contains no such events, it is considered to contain crystalline phases.

Differential thermal analysis (DTA) can be conducted using the following method. DTA runs can be made (using an instrument such as that obtained from Netzsch Instruments, Selb, Germany under the trade designation "NETZSCH STA 409 DTA/TGA") using a -140+170 mesh size fraction (i.e., the fraction collected between 105-micrometer opening size and 90-micrometer opening size screens). An amount of each screened sample (typically about 400 milligrams (mg)) is placed in a 100-microliter Al_2O_3 sample holder. Each sample is heated in static air at a rate of 10°C/minute from room temperature (about 25°C) to 1100°C.

Using powder x-ray diffraction, XRD, (using an x-ray diffractometer such as that obtained under the trade designation "PHILLIPS XRG 3100" from Phillips, Mahwah, NJ, with copper K α1 radiation of 1.54050 Angstrom) the phases present in a material can be determined by comparing the peaks present in the XRD trace of the crystallized material to XRD patterns of crystalline phases provided in JCPDS (Joint Committee on Powder Diffraction Standards) databases, published by International Center for Diffraction Data. Furthermore, an XRD can be used qualitatively to determine types of phases. The presence of a broad diffused intensity peak is taken as an indication of the amorphous nature of a material. The existence of both a broad peak and well-defined peaks is taken as an indication of existence of crystalline matter within an amorphous matrix. The initially formed amorphous material or ceramic (including glass prior to crystallization) may be larger in size than that desired. The amorphous material or ceramic can be converted into smaller pieces using crushing and/or comminuting techniques known in the art, including roll crushing, canary milling, jaw crushing, hammer milling, ball milling, jet milling, impact crushing, and the like. In some instances, it is desired to have two or multiple crushing steps. For example, after the ceramic is formed (solidified), it may be in the form of larger than desired. The first crushing step may involve crushing these relatively large masses or "chunks" to form smaller pieces. This crushing of these chunks may be accomplished with a hammer mill, impact crusher or jaw crusher. These smaller pieces may then be subsequently crushed to produce the desired particle size distribution. In order to produce the desired particle size distribution (sometimes referred to as grit size or grade), it may be necessary to perform multiple crushing steps. In general the crushing conditions are optimized to achieve the desired particle shape(s) and particle size distribution. Resulting particles that are of the desired size may be recrushed if they are too large, or "recycled" and used as a raw material for re-melting if they are too small..

The shape of particles can depend, for example, on the composition and/or microstructure of the ceramic, the geometry in which it was cooled, and the manner in which the ceramic is crushed (i.e., the crushing technique used). In general, where a "blocky" shape is preferred, more energy may be employed to achieve this shape. Conversely, where a "sharp" shape is preferred, less energy may be employed to achieve this shape. The crushing technique may also be changed to achieve different desired shapes. For some particles an average aspect ratio ranging from 1:1 to 5:1 is typically desired, and in some embodiments 1.25:1 to 3:1, or even 1.5:1 to 2.5:1.

Ceramic articles (including glass-ceramics) made according to the present invention may comprise at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystallites, wherein the crystallites have an average size of less than 1 micrometer. In another aspect, ceramic articles (including glass-ceramics) made according to the present invention may comprise less than at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystallites, wherein the crystallites have an average size of less than 0.5 micrometer. In another aspect, ceramics (including glass-ceramics) according to the present invention comprise less than at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystallites, wherein the crystallites have an average size of less than 0.3 micrometer. In another aspect, ceramic articles (including glass-ceramics) made according to the present invention may comprise less than at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystallites, wherein the crystallites have an average size of less than 0.15 micrometer. In another aspect, ceramic articles (including glass-ceramics) made according to the present invention may be free of at least one of eutectic microstructure features (i.e., is free of colonies and lamellar structure) or a non-cellular microstructure.

In another aspect, certain ceramic articles made according to the present invention may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, or even 100 percent by volume glass. In another aspect, certain ceramic articles made according to the present invention may comprise, for example, 100 or at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic.

Certain articles made according to the present invention comprise glass comprising CaO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the CaO and Al_2O_3, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising CaO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the CaO and Al_2O_3, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising CaO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises CaO and Al_2O_3, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the CaO and Al_2O_3, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising CaO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises CaO and Al_2O_3, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Certain articles made according to the present invention comprise glass comprising CaO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the CaO, Al_2O_3, and ZrO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising CaO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the CaO and Al_2O_3, and ZrO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising CaO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the CaO,

Al_2O_3, and ZrO_2, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the CaO, Al_2O_3, and ZrO_2, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising CaO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises CaO, Al_2O_3, and ZrO_2, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Certain articles made according to the present invention comprise glass comprising BaO and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the BaO andTiO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising BaO and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the BaO and TiO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising BaO and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the BaO and TiO_2, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the BaO and TiO_2, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising BaO and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises BaO and TiO_2, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Certain articles made according to the present invention comprise glass comprising La_2O_3 and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the La_2O_3 and TiO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising La_2O_3 and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the La_2O_3 and TiO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising La_2O_3 and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the La_2O_3 and TiO_2, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the La_2O_3 and TiO_2, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising La_2O_3 and TiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises La_2O_3 and TiO_2, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Certain articles made according to the present invention comprise glass comprising REO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the REO and Al_2O_3, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising REO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the REO and Al_2O_3, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising REO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the REO and Al_2O_3, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, the present invention provides glass-ceramic comprising REO and Al_2O_3, wherein, for example, glass-ceramic exhibits a microstructure comprising crystallites having an average crystallite size of less than 1 micrometer (typically, less than 500 nanometers, even less than 300, 200, or 150 nanometers; and in some embodiments, less than 100, 75, 50, 25, or 20 nanometers), and (b) is free of at least one of eutectic microstructure features or a non-cellular microstructure.. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the REO and Al_2O_3, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising REO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises REO and Al_2O_3, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Certain articles made according to the present invention comprise glass comprising REO and Al_2O_3, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the REO and Al_2O_3, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising REO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the REO and Al_2O_3 and ZrO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising REO, Al_2O_3, and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the REO and Al_2O_3 and ZrO_2, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, the present invention provides glass-ceramic comprising REO, Al_2O_3, and ZrO_2, wherein the glass-ceramic (a) exhibits a microstructure comprising crystallites having an average crystallite size of less than 1 micrometer (typically, less than

500 nanometers, even less than 300, 200, or 150 nanometers; and in some embodiments, less than 100, 75, 50, 25, or 20 nanometers), and (b) is free of at least one of eutectic microstructure features or a non-cellular microstructure. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the REO, Al_2O_3, and ZrO_2, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising REO and Al_2O_3 and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises REO, Al_2O_3, and ZrO_2, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising glass (e.g., at least 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume glass), the glass comprising REO, Al_2O_3, ZrO_2, and SiO_2 wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass collectively comprises the REO and Al_2O_3 and ZrO_2, based on the total weight of the glass.

In another aspect, certain articles made according to the present invention provides glass-ceramic comprising REO, Al_2O_3, ZrO_2, and SiO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the glass-ceramic collectively comprises the REO and Al_2O_3 and ZrO_2, based on the total weight of the glass-ceramic. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, or 95 percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, the present invention provides glass-ceramic comprising REO, Al_2O_3, ZrO_2, and SiO_2, wherein the glass-ceramic (a) exhibits a microstructure comprising crystallites having an average crystallite size of less than 1 micrometer (typically, less than 500 nanometers, even less than 300, 200, or 150 nanometers; and in some embodiments, less than 100, 75, 50, 25, or 20 nanometers), and (b) is free of at least one of eutectic microstructure features or a non-cellular microstructure. The glass-ceramic may comprise, for example, at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, percent by volume glass. The glass-ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, or 5 percent by volume crystalline ceramic.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the crystalline ceramic comprising, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the crystalline ceramic collectively comprises the REO, Al_2O_3, ZrO_2, and SiO_2, based on the total weight of the crystalline ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

In another aspect, certain articles made according to the present invention provides a ceramic comprising crystalline ceramic (e.g., at least 1, 2, 3, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85, 90, 95, 97, 98, 99, or even 100 percent by volume crystalline ceramic), the ceramic comprising REO and Al_2O_3 and ZrO_2, wherein at least 80 (85, 90, 95, 97, 98, 99, or even 100) percent by weight of the ceramic collectively comprises REO, Al_2O_3, ZrO_2, and SiO_2, based on the total weight of the ceramic. The ceramic may comprise, for example, at least 99, 98, 97, 95, 90, 85, 80, 75, 70, 65, 60, 55, 50, 45, 40, 35, 30, 25, 20, 15, 10, 5, 3, 2, or 1 percent by volume glass.

Crystalline phases that may be present in ceramics according to the present invention include alumina (e.g., alpha and transition aluminas), BaO, CaO, Cr_2O_3, CoO, Fe_2O_3, GeO_2, HfO_2, Li_2O, MgO, MnO, NiO, Na_2O, P_2O_5, REO, Sc_2O_3, SiO_2, SrO, TeO_2, TiO_2, V_2O_3, Y_2O_3, ZnO, ZrO_2, "complex metal oxides" (including "complex $Al_2O_3 \cdot$ metal oxide (e.g., complex $Al_2O_3 \cdot$ REO)), and combinations thereof.

Additional details regarding ceramics comprising Al_2O_3, at least one of REO or Y_2O_3, and at least one of ZrO_2 or HfO_2, including making, using, and properties, can be found in application having U.S. Serial Nos. 09/922,527, 09/922,528, and 09/922,530, filed August 2, 2001, and U.S. Serial Nos. __________ (Attorney Docket Nos. 56931US005, 56931US006, 56931US007, 56931US008, 56931US009, 56931US010, 57980US002, and 57981US002, filed the same date as the instant application.

Typically, and desirably, the (true) density, sometimes referred to as specific gravity, of ceramic according to the present invention is typically at least 70% of theoretical density. More desirably, the (true) density of ceramic according to the present invention is at least 75%, 80%, 85%, 90%,95%, 96%, 97%, 98%, 99%, 99.5% or 100% of theoretical density.

Examples of articles according of the present invention include kitchenware (e.g., plates), dental brackets, and reinforcing fibers, cutting tool inserts, abrasive materials, and structural components of gas engines, (e.g., valves and bearings). Other articles include those having a protective coating of ceramic on the outer surface of a body or other substrate. Further, for example, ceramic according to the present invention can be used as a matrix material. For example, ceramics according to the present invention can be used as a binder for ceramic materials and the like such as diamond, cubic-BN, Al_2O_3, ZrO_2, Si_3N_4, and SiC. Examples of useful articles comprising such materials include composite substrate coatings, cutting tool inserts abrasive agglomerates, and bonded abrasive articles such as vitrified wheels. The use of ceramics according to the present invention can be used as binders may, for example, increase the modulus, heat resistance, wear resistance, and/or strength of the composite article.

Advantages and embodiments of this invention are further illustrated by the following examples, but the particular materials and amounts thereof recited in these examples, as well as other conditions and details, should not be construed to unduly limit this invention. All parts and percentages are by weight unless otherwise indicated. Unless otherwise stated, all examples contained no significant amount of SiO_2, B_2O_3, P_2O_5, GeO_2, TeO_2, As_2O_3, and V_2O_5.

Examples

Example 1

A polyethylene bottle was charged with 27.5 grams of alumina particles (obtained under the trade designation "APA-0.5" from Condea Vista, Tucson, AZ), 22.5 grams of calcium oxide particles (obtained from Alfa Aesar, Ward Hill, MA) and 90 grams of isopropyl alcohol. About 200 grams of zirconia milling media (obtained from Tosoh Ceramics, Division of Bound Brook, NJ, under the trade designation "YTZ") were added to the bottle, and the mixture was milled at 120 revolutions per minute (rpm) for 24 hours. After the milling, the milling media were removed and the slurry was poured onto a glass ("PYREX") pan where it was dried using a heat-gun. The dried mixture was ground with a mortar and pestle and screened through a 70-mesh screen (212-micrometer opening size).

After grinding and screening, some of the particles were fed into a hydrogen/oxygen torch flame. The torch used to melt the particles, thereby generating melted glass beads, was a Bethlehem bench burner PM2D model B, obtained from Bethlehem Apparatus Co., Hellertown, PA, delivering hydrogen and oxygen at the following rates. For the inner ring, the hydrogen flow rate was 8 standard liters per minute (SLPM) and the oxygen flow rate was 3 SLPM. For the outer ring, the hydrogen flow rate was 23 (SLPM) and the oxygen flow rate was 9.8 SLPM. The dried and sized particles were fed directly into the torch flame, where they were melted and transported to an inclined stainless steel surface (approximately 51 centimeters (cm) (20 inches) wide with the slope angle of 45 degrees) with cold water running over (approximately 8 liters/minute) the surface to form beads.

Examples 2-9

Examples 2-9 glass beads were prepared as described in Example 1, except the raw materials and the amounts of raw materials used are listed in Table 1, below, and the milling of the raw materials was carried out in 90 (milliliters) ml of isopropyl alcohol with 200 grams of the zirconia media (obtained from Tosoh Ceramics, Division of Bound Brook, NJ, under the trade designation "YTZ") at 120 rpm for 24 hours. The sources of the raw materials used are listed in Table 2, below.

Table 1

Example	Weight percent of components	Batch amounts, g
2	CaO: 36 Al_2O_3: 44 ZrO_2: 20	CaO: 18 Al_2O_3: 22 ZrO_2: 10
3	La_2O_3: 45 TiO_2: 55	La_2O_3: 22.5 TiO_2: 27.5
4	La_2O_3: 36 TiO_2: 44 ZrO_2: 20	La_2O_3: 18 TiO_2: 22 ZrO_2: 10
5	BaO: 47.5 TiO_2: 52.5	BaO: 23.75 TiO_2: 26.25
6	La_2O_3: 48 Al_2O_3: 52	La_2O_3: 24 Al_2O_3: 26
7	La_2O_3: 40.9 Al_2O_3: 40.98 ZrO_2: 18.12	La_2O_3: 20.45 Al_2O_3: 20.49 ZrO_2: 9.06
8	La_2O_3: 43 Al_2O_3: 32 ZrO_2: 12 SiO_2: 13	La_2O_3: 21.5 Al_2O_3: 16 ZrO_2: 6 SiO_2: 6.5
9	SrO: 22.95 Al_2O_3: 62.05 ZrO_2: 15	SrO: 11.47 Al_2O_3: 31.25 ZrO_2: 7.5

Table 2

Raw Material	Source
Alumina particles (Al_2O_3)	Obtained from Condea Vista, Tucson, AZ under the trade designation "APA-0.5"
Calcium oxide particles (CaO)	Obtained from Alfa Aesar, Ward Hill, MA
Lanthanum oxide particles (La_2O_3)	Obtained from Molycorp Inc., Mountain Pass, CA
Silica particles (SiO_2)	Obtained from Alfa Aesar
Barium oxide particles (BaO)	Obtained from Aldrich Chemical Co.
Titanium dioxide particles (TiO_2)	Obtained from Kemira Inc., Savannah, GA
Strontium oxide particles (SrO)	Obtained from Alfa Aesar
Yttria-stabilized zirconium oxide particles (Y-PSZ)	Obtained from Zirconia Sales, Inc. of Marietta, GA under the trade designation "HSY-3"

Various properties/characteristics of some of Examples 1-9 materials were measured as follows. Powder X-ray diffraction (using an X-ray diffractometer (obtained under the trade designation "PHILLIPS XRG 3100" from PHILLIPS, Mahwah, NJ) with copper K $\alpha 1$ radiation of 1.54050 Angstrom)) was used to qualitatively measure phases present in example materials. The presence of a broad diffused intensity peak was taken as an indication of the amorphous nature of a material. The existence of both a broad peak and well-defined peaks was taken as an indication of existence of crystalline matter within an amorphous matrix. Phases detected in various examples are reported in Table 3, below.

Table 3

Example	Phases detected via X-ray diffraction	Color	T_g, °C	T_x, °C	Hot-pressing temp, °C
1	Amorphous*	Clear	850	987	985
2	Amorphous*	Clear	851	977	975
3	Amorphous*	Clear	799	875	880
4	Amorphous*	Clear	821	876	880
5	Amorphous*	Clear	724	760	815
6	Amorphous*	Clear	855	920	970
7	Amorphous*	Clear	839	932	965
8	Amorphous*	Clear	836	1002	970
9	Amorphous*	Clear	875	934	975

* glass, as the example has a T_g

For differential thermal analysis (DTA), a material was screened to retain glass beads within the 90-125 micrometer size range. DTA runs were made (using an instrument obtained from Netzsch Instruments, Selb, Germany under the trade designation "NETZSCH STA 409 DTA/TGA"). The amount of each screened sample placed in a 100-microliter Al_2O_3 sample holder was 400 milligrams. Each sample was heated in static air at a rate of 10°C/minute from room temperature (about 25°C) to 1200°C.

Referring to FIG. 1, line 375 is the plotted DTA data for the Example 1 material. Referring to FIG. 1 line 375, the material exhibited an endothermic event at a temperature around 799°C, as evidenced by the downward curve of line 375. It was believed that this event was due to the glass transition (T_g) of the material. At about 875°C, an exothermic event was observed as evidenced by the sharp peak in line 345. It was believed that this event was due to the crystallization (T_x) of the material. These T_g and T_x values for other examples are reported in Table 3, above.

FIGS 2-6 are the plotted DTA data for Examples 2, 5, 6, 7, and 9, respectively.

For each of Examples 1-9, about 25 grams of the glass beads were placed in a graphite die and hot-pressed using uniaxial pressing apparatus (obtained under the trade designation "HP-50", Thermal Technology Inc., Brea, CA). The hot-pressing was carried out in an argon atmosphere and 13.8 megapascals (MPa) (2000 pounds per square inch (2 ksi)) pressure. The hot-pressing temperature at which appreciable glass flow occurred, as indicated by the displacement control unit of the hot pressing equipment described above, are reported for Examples 1-9 in Table 3, above.

Various modifications and alterations of this invention will become apparent to those skilled in the art without departing from the scope and spirit of this invention, and it should be understood that this invention is not to be unduly limited to the illustrative embodiments set forth herein.

What is claimed is:

1. A method of making an article from glass comprising:

providing a substrate including an outer surface;

providing at least a first glass, wherein the first glass comprises at least two different metal oxides, wherein the first glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the first glass is at least 5K, the glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5;

heating the first glass above the T_g such that at least a portion of the glass wets at least a portion of the outer surface of the substrate; and

cooling the glass to provide an article comprising ceramic comprising the glass attached to the at least a portion of the outer surface of the substrate.

2. The method according to claim 1 wherein the difference between the T_g and the T_x is at least 25K.

3. The method according to claim 2 wherein the glass has a T_l, and wherein the ratio of the T_g to T_l is at least 0.5.

4. The method according to claim 3 wherein the first glass comprises less than 40 percent by weight glass collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

5. The method according to claim 3 wherein the glass is a REO-Al_2O_3 glass.

6. The method according to claim 5 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3 and REO, based on the total weight of the glass.

7. The method according to claim 1 wherein the glass is a REO-Al_2O_3-ZrO_2 glass.

8. The method according to claim 7 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3, REO, and ZrO_2, based on the total weight of the glass.

9. The method according to claim 1 wherein the article comprises glass, and wherein the method further comprises heat-treating the glass to provide glass-ceramic.

10. An article made according to the method of claim 9.

11. The method according to claim 1 wherein the difference between the T_g and the T_x is at least 35K.

12. An article made according to the method of claim 1.

13. A method of making an article from glass comprising:

providing a substrate including an outer surface;

providing at least a first plurality of particles comprising glass, wherein the glass comprises at least two different metal oxides, wherein the glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the glass is at least 5K, the glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5;

heating the glass above the T_g such that at least a portion of the glass of the first plurality of particles wets at least a portion of the outer surface of the substrate; and

cooling the glass to provide an article comprising ceramic comprising the glass attached to the at least a portion of the outer surface of the substrate.

14. The method according to claim 13 wherein the difference between the T_g and the T_x is at least 25K.

15. The method according to claim 14 wherein the glass has a T_l, and wherein the ratio of the T_g to T_l is at least 0.5.

16. The method according to claim 15 wherein the glass comprises less than 40 percent by weight collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

17. The method according to claim 15 wherein the glass is a REO-Al_2O_3 glass.

18. The method according to claim 17 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3 and REO, based on the total weight of the glass.

19. The method according to claim 13 wherein the glass is a REO-Al_2O_3-ZrO_2 glass.

20. The method according to claim 19 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3, REO, and ZrO_2, based on the total weight of the glass.

21. The method according to claim 13 wherein the article comprises glass, and wherein the method further comprises heat-treating the glass to provide glass-ceramic.

22. An article made according to the method of claim 21.

23. The method according to claim 13 wherein the difference between the T_g and the T_x is at least 35K.

24. An article made according to the method of claim 13.

25. A method of making an article comprising:

providing at least a first glass and second glass, wherein the first glass comprises at least two different metal oxides, wherein the first glass has a T_{g1} and T_{x1}, and wherein the difference between the T_{g1} and the T_{x1} is at least 5K, the first glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5;

heating the first and second glasses above at least T_{g1} and at least the first glass coalescing with the second glass to provide the article.

26. The method according to claim 25 wherein the difference between the T_{g1} and the T_{x1} is at least 25K.

27. The method according to claim 26 wherein the glass has a T_l, and wherein the ratio of the T_{g1} to T_{l1} is at least 0.5.

28. The method according to claim 27 wherein the first glass comprises less than 40 percent by weight collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

29. The method according to claim 28 wherein the glass is a REO-Al_2O_3 glass.

30. The method according to claim 29 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3 and REO, based on the total weight of the glass.

31. The method according to claim 25 wherein the glass is a REO-Al_2O_3-ZrO_2 glass.

32. The method according to claim 31 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3, REO, and ZrO_2, based on the total weight of the glass.

33. The method according to claim 25 wherein the article comprises glass, and wherein the method further comprises heat-treating the glass to provide glass-ceramic.

34. An article made according to the method of claim 33.

35. The method according to claim 25 wherein the difference between the T_{g1} and the T_{x1} is at least 35K.

36. An article made according to the method of claim 25.

37. A method of making an article comprising:

providing at least a first glass and second glass, wherein the first glass comprises at least two different metal oxides, wherein the first glass has a T_{g1} and T_{x1}, and wherein the difference between the T_{g1} and the T_{x1} is at least 5K, the first glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5, and wherein the second glass comprises at least two different metal oxides, wherein the second glass has a T_{g2} and T_{x2}, and wherein the difference between the T_{g2} and the T_{x2} is at least 5K, the second glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5;

heating the glasses above the higher of T_{g1} or T_{g2} and coalescing the first and second glasses to provide the article.

38. The method according to claim 37 wherein the difference between each of T_{g1} and T_{x1} and T_{g2} and T_{x2} is at least 25K.

39. The method according to claim 38 wherein the ratio of each of T_{g1} to T_{x1} and T_{g2} to T_{x2} is at least 0.5.

40. The method according to claim 39 wherein each of the first and second glasses comprise less than 40 percent by weight collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

41. The method according to claim 39 wherein the glass is a REO-Al_2O_3 glass.

42. The method according to claim 41 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3 and REO, based on the total weight of the glass.

43. The method according to claim 37 wherein the glass is a REO-Al_2O_3-ZrO_2 glass.

44. The method according to claim 43 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3, REO, and ZrO_2, based on the total weight of the glass.

45. The method according to claim 37 wherein the article comprises glass, and wherein the method further comprises heat-treating the glass to provide glass-ceramic.

46. An article made according to the method of claim 45.

47. The method according to claim 37 wherein the difference between the T_g and the T_x is at least 35K.

48. The method according to claim 37 wherein the first and second glasses have the same compositions.

49. The method according to claim 37 wherein the first and second glasses have different compositions.

50. An article made according to the method of claim 37.

51. A method of making an article comprising:

providing at least a first plurality of particles comprising glass, wherein the glass comprises at least two different metal oxides, wherein the glass has a T_g and T_x, and wherein the difference between the T_g and the T_x of the glass is at least 5K, the glass containing less than 20% by weight SiO_2, less than 20% by weight B_2O_3, and less than 40% by weight P_2O_5;

heating the glass above the T_g and coalescing at least a portion of the first plurality of particles to provide the article.

52. The method according to claim 51 wherein the difference between the T_g and the T_x is at least 25K.

53. The method according to claim 52 wherein the glass has a T_l, and wherein the ratio of the T_g to T_l is at least 0.5.

54. The method according to claim 53 wherein the glass comprises less than 40 percent by weight collectively SiO_2, B_2O_3, and P_2O_5, based on the total weight of the glass.

55. The method according to claim 53 wherein the glass is a REO-Al_2O_3 glass.

56. The method according to claim 55 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3 and REO, based on the total weight of the glass.

57. The method according to claim 53 wherein the glass is a REO-Al_2O_3-ZrO_2 glass.

58. The method according to claim 57 wherein the glass collectively comprises at least 80 percent by weight of the Al_2O_3, REO, and ZrO_2, based on the total weight of the glass.

59. The method according to claim 53 wherein the article comprises glass, and wherein the method further comprises heat-treating the glass to provide glass-ceramic.

60. An article made according to the method of claim 59.

61. The method according to claim 53 wherein the difference between the T_g and the T_x is at least 35K.

62. An article made according to the method of claim 53.

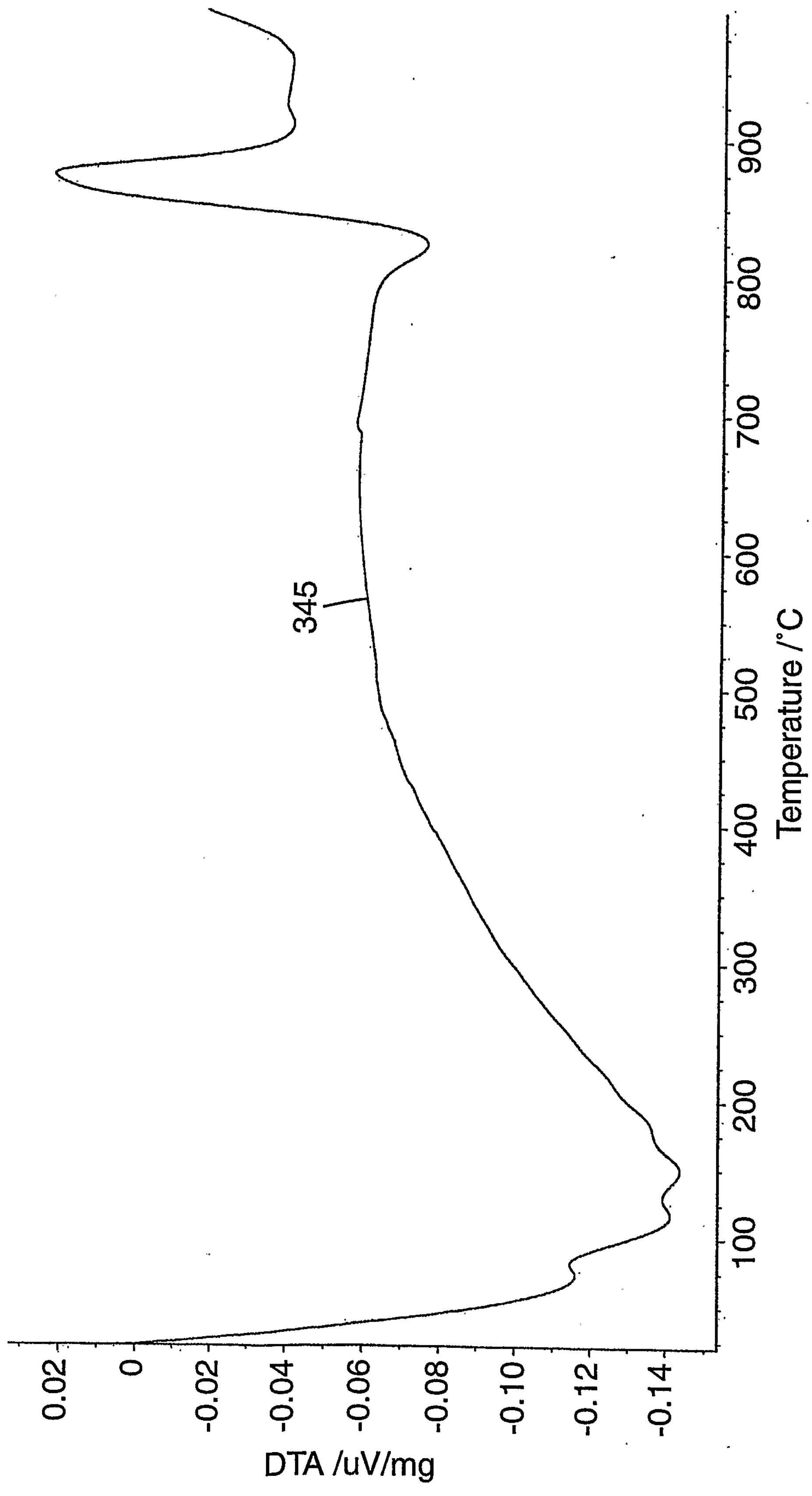
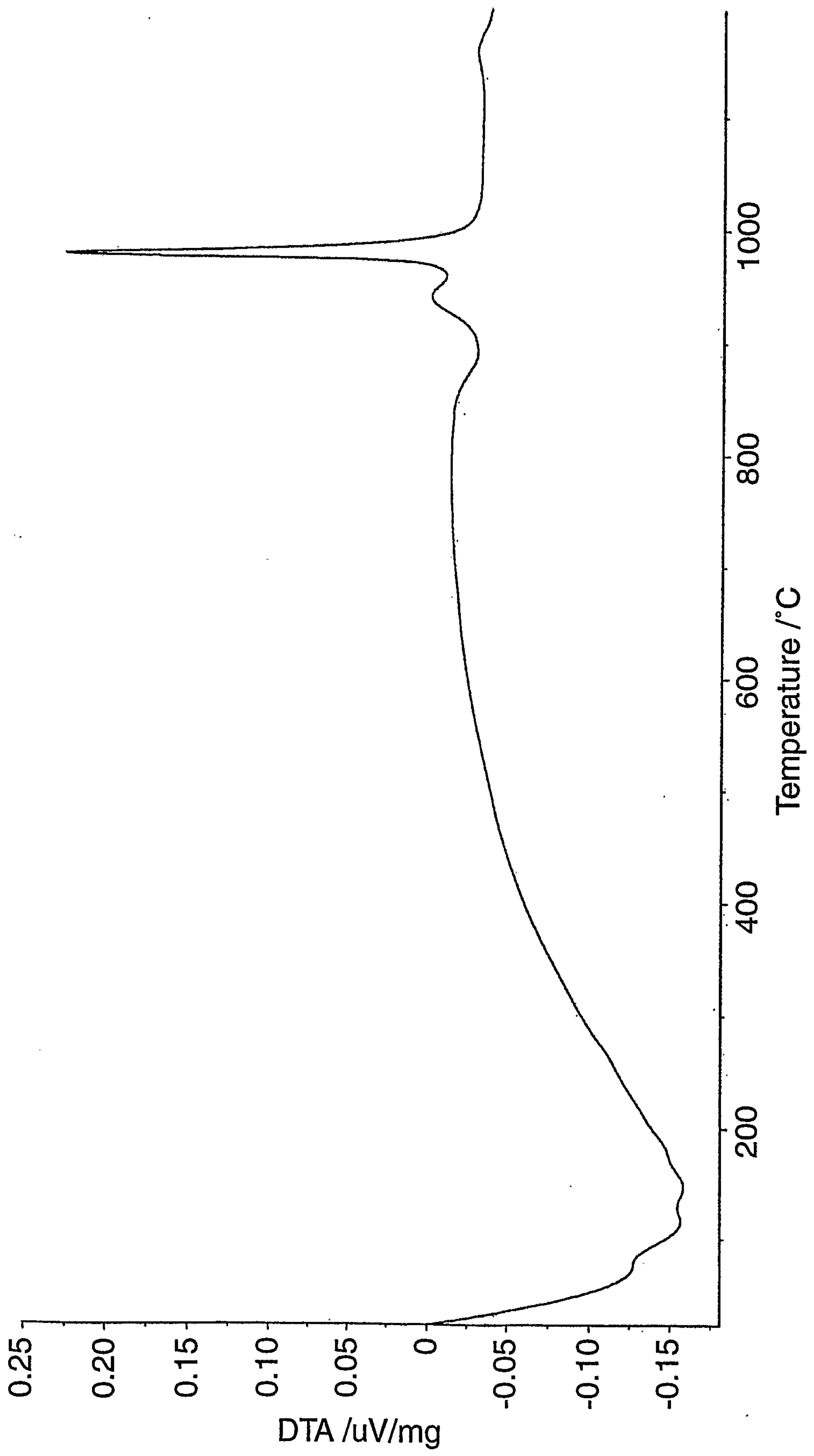

345
Temperature /°C
100
200
300
400
500
600
700
800
900
DTA /uV/mg
0.02
0
-0.02
-0.04
-0.06
-0.08
-0.10
-0.12
-0.14

FIG. 1


DTA /uV/mg
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0.20
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
Temperature /°C
200
400
600
800
1000

FIG. 2

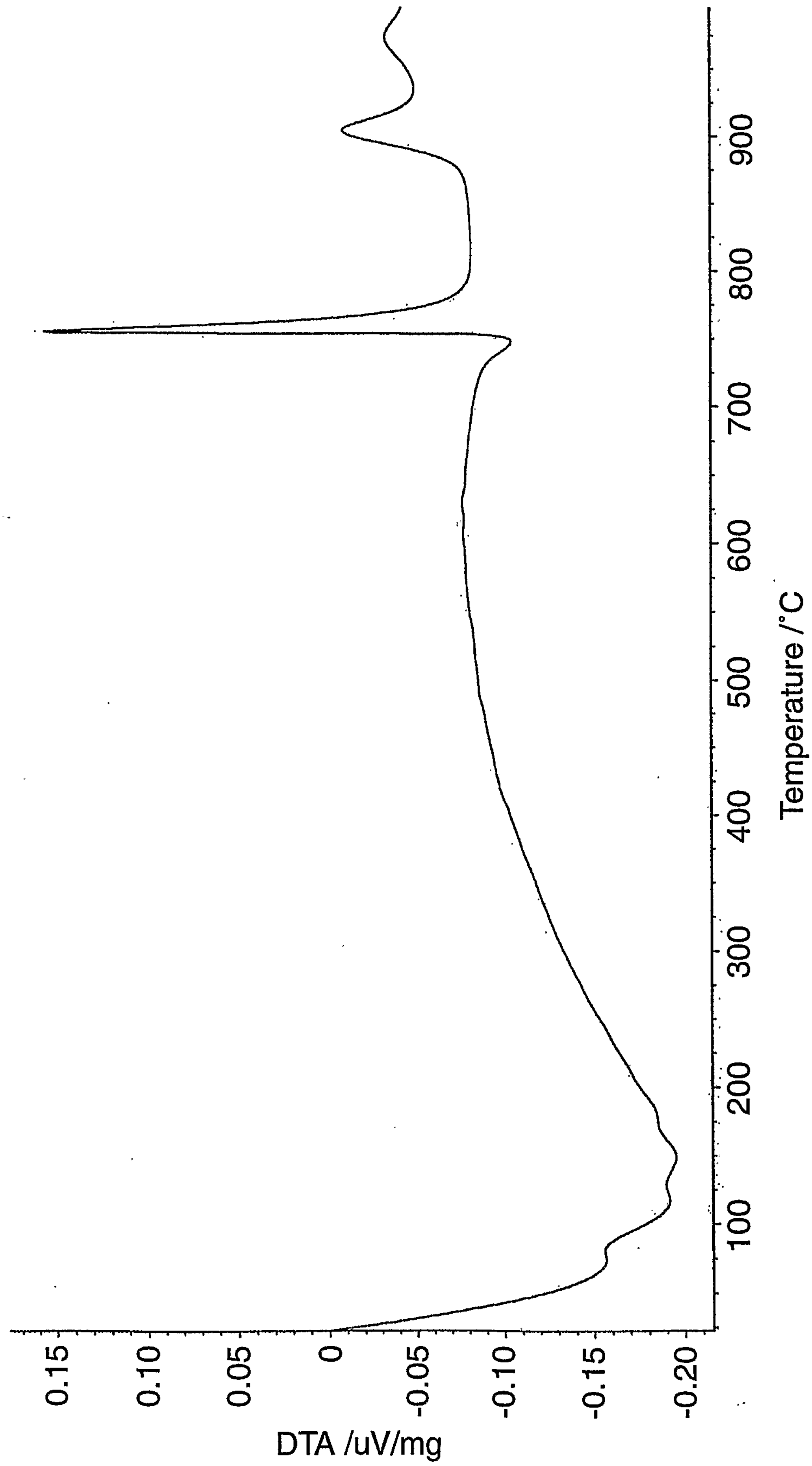
0.15
0.10
0.05
0
-0.05
-0.10
-0.15
-0.20
DTA /uV/mg
100
200
300
400
500
600
700
800
900
Temperature /°C

FIG. 3

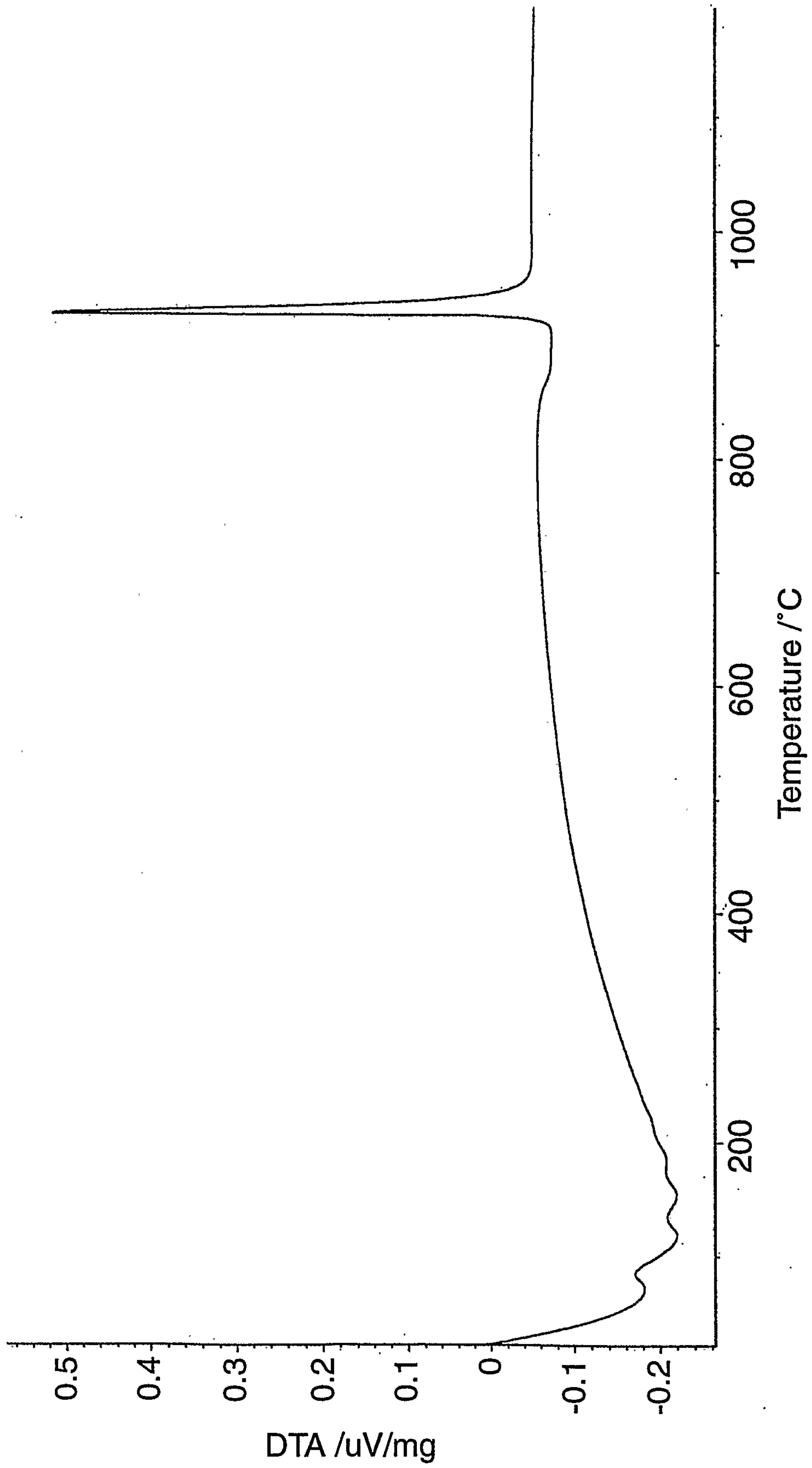
DTA /uV/mg
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
Temperature /°C
200
400
600
800
1000

FIG. 4

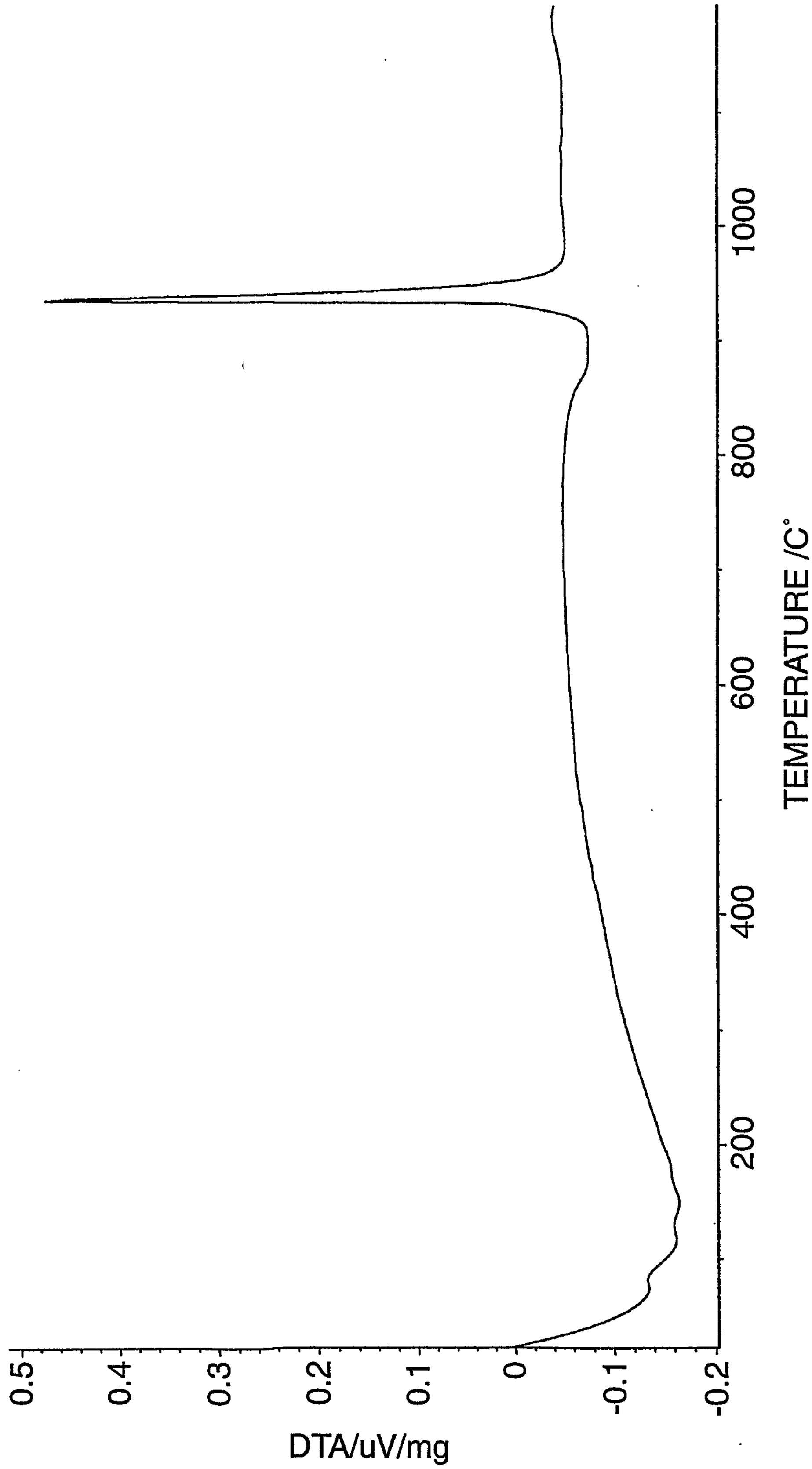
DTA/uV/mg
0.5
0.4
0.3
0.2
0.1
0
-0.1
-0.2
TEMPERATURE /C°
200
400
600
800
1000

FIG. 5

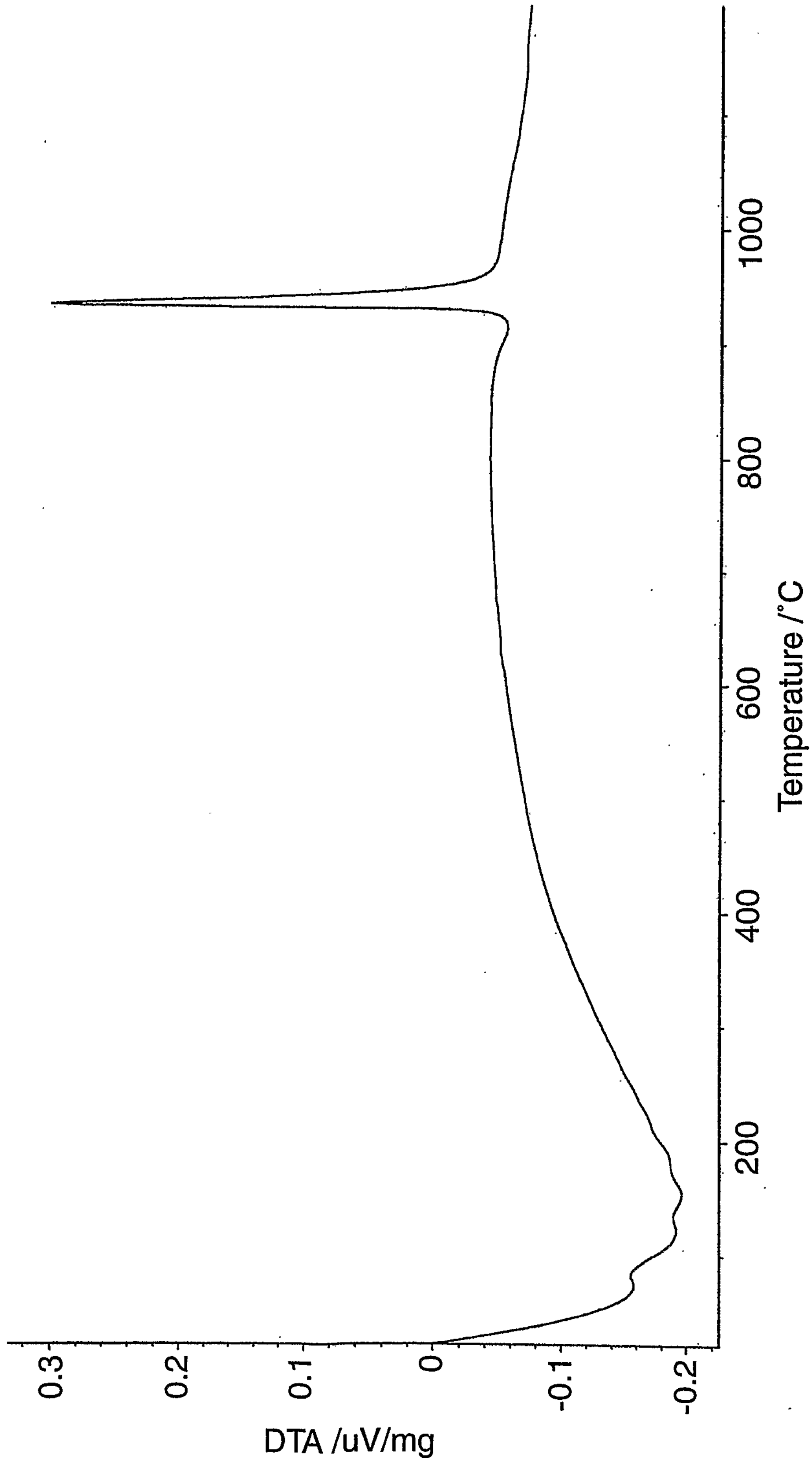

FIG. 6

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 02/24523

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C03B19/10 C03B19/06 C03B32/02 C03B32/00 C03C10/00

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)
IPC 7 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 practical, search terms used)

PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 02 08146 A (3M INNOVATIVE PROPERTIES CO) 31 January 2002 (2002-01-31) claims 1-99	1-62
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Y	WO 97 16385 A (3M CO) 9 May 1997 (1997-05-09) claim 1; examples 1-3	1-62
Y	US 3 881 282 A (WATSON G.R.) 6 May 1975 (1975-05-06) the whole document	1-62

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

° Special categories of cited documents:

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

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 January 2003	20/01/2003

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL – 2280 HV Rijswijk Tel. (+31–70) 340–2040, Tx. 31 651 epo nl, Fax: (+31–70) 340–3016	Stroud, J

1

Form PCT/ISA/210 (second sheet) (July 1992)

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	GB 1 260 933 A (PHILIPS ELECTRONIC & ASSOC IND LTD) 19 January 1972 (1972-01-19) the whole document	1-62
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A	US 4 756 746 A (KEMP P.B. ET AL.) 12 July 1988 (1988-07-12) claims 1-5	1-62
A	PATENT ABSTRACTS OF JAPAN vol. 013, no. 137 (C-582), 5 April 1989 (1989-04-05) & JP 63 303821 A (HITACHI CHEM CO LTD), 12 December 1988 (1988-12-12) abstract	1-62
A	PATENT ABSTRACTS OF JAPAN vol. 012, no. 426 (C-542), 10 November 1988 (1988-11-10) & JP 63 156024 A (KUBOTA LTD), 29 June 1988 (1988-06-29) abstract	1-62

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claims 1-62 relate to an extremely large number of possible articles and methods. In fact, the claims, of which 15 are independent, contain so many possibilities of a vague and speculative nature that a lack of clarity and conciseness within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible.

Moreover, present claims 1-62 relate to an extremely large number of possible methods and articles of composition and process steps far broader in scope than justified by the limited support and disclosure provided in the description. Support within the meaning of Article 6 PCT and disclosure within the meaning of Article 5 PCT is to be found, however, for only an extremely small proportion of the methods and articles claimed. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible.

Consequently, the search has been carried out for those parts of the claims which appear to be supported, disclosed, clear and concise, namely those parts relating to the methods and articles mentioned in the examples describing glass partilce or bead manufature by blowing through a burner and cooling or artilce manufacture by hot pressing powder, beads or fibres followed by thermal aftertreatment such as devitrifying and further restricted to glass or glass-ceramic forming compositions comprising alumina.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 02/24523

Box I Observations where certain claims were found unsearchable (Continuation of item 1 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:
see FURTHER INFORMATION sheet PCT/ISA/210

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 II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

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

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 fee, this Authority did not invite payment of any additional fee.

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.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/24523

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
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			CA	2236447	A1	09-05-1997
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			CN	1201444	A	09-12-1998
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			EP	0858435	A1	19-08-1998
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			FR	2009818	A5	13-02-1970
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			NO	121010	B	04-01-1971
			OA	3039	A	15-12-1970
			US	3926603	A	16-12-1975

Form PCT/ISA/210 (patent family annex) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/US 02/24523

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
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US 4756746	A	12-07-1988	DE	259844 T1	11-08-1988
			EP	0259844 A2	16-03-1988
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			JP	4044622 B	22-07-1992

Form PCT/ISA/210 (patent family annex) (July 1992)