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(54) **GLASS, GLASS CERAMIC, AND LAMINATED CERAMIC ELECTRONIC COMPONENT**

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(57) **ABSTRACT**

A glass that contains Si, B, Al, and Zn. The glass has SiO_2 at a content of 15% by weight to 65% by weight, B_2O_3 at a content of 11% by weight to 30% by weight, Al_2O_3, and ZnO, wherein a weight ratio of the SiO_2 to the B_2O_3 (SiO_2/B_2O_3) is 1.21 or higher, and a weight ratio of the Al_2O_3 to the ZnO (Al_2O_3/ZnO) is 0.75 to 1.64, and wherein an alkaline-earth metal is excluded as a material contained in the glass.

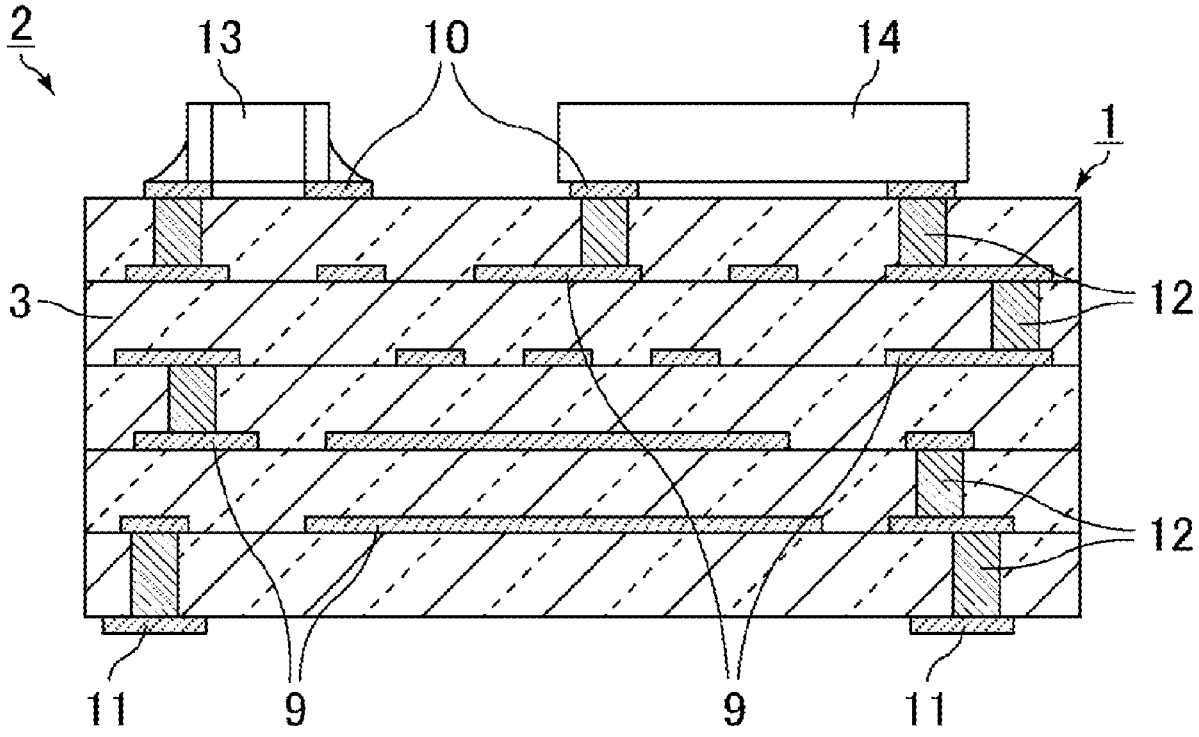


FIG.1

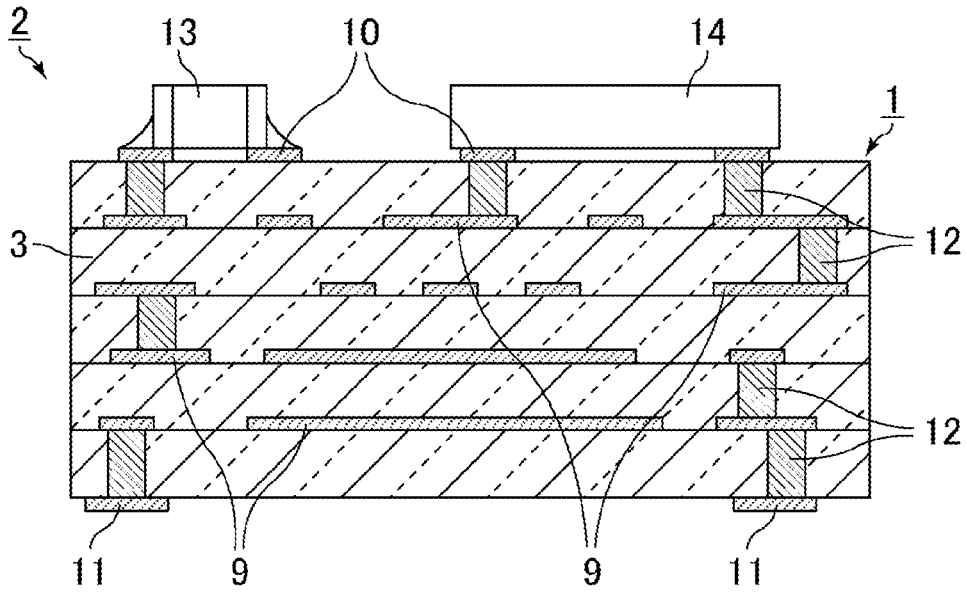
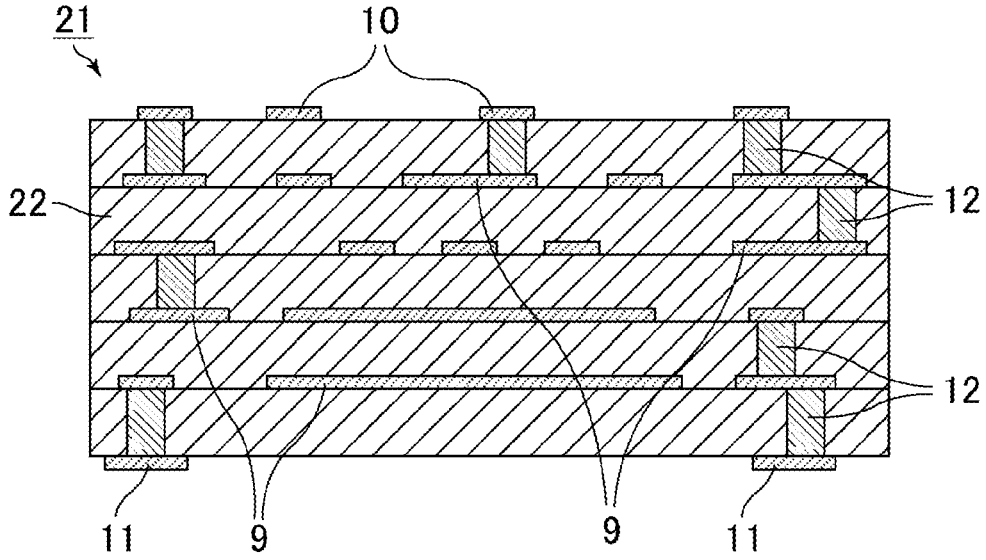


FIG.2



GLASS, GLASS CERAMIC, AND LAMINATED CERAMIC ELECTRONIC COMPONENT

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] The present application is a continuation of International application No. PCT/JP2021/022433, filed Jun. 14, 2021, which claims priority to Japanese Patent Application No. 2020-104657, filed Jun. 17, 2020, Japanese Patent Application No. 2020-104658, filed Jun. 17, 2020, Japanese Patent Application No. 2020-192650, filed Nov. 19, 2020, and Japanese Patent Application No. 2020-192651, filed Nov. 19, 2020, the entire contents of each of which are incorporated herein by reference.

FIELD OF THE INVENTION

[0002] The present invention relates to glass, glass ceramics, and multilayer ceramic electronic components.

BACKGROUND OF THE INVENTION

[0003] Known ceramic materials for ceramic multilayer circuit boards include low temperature fireable glass ceramic materials.

[0004] For example, Patent Literature 1 discloses a glass composition for low temperature fired substrates, having a basic composition of RO-Al_2O_3—B_2O_3—SiO_2, wherein RO is one or two or more of MgO, CaO, SrO, BaO, and ZnO, RO and Al_2O_3 are each within a range of 1 to 25 mol %, and the mol % ratio SiO_2/B_2O_3 is 1.3 or lower; and a glass ceramic containing the glass composition for low temperature fired substrates containing an aggregate.

[0005] Patent Literature 1: JP 2004-26529 A

SUMMARY OF THE INVENTION

[0006] The glass ceramic disclosed in Patent Literature 1 can achieve an excellent dielectric loss of 20×10^{-4} or lower at 3 GHz.

[0007] However, the glass composition for low temperature fired substrates disclosed in Patent Literature 1 has a SiO_2/B_2O_3 mol % ratio of 1.3 or lower, i.e., a high boron (B) content. Such a boron-rich glass composition causes an unstable boron content. Specifically, boron may be dissolved into a solvent during mixing grinding or may be evaporated during firing. If the boron content is reduced as a result of dissolution or evaporation, the viscosity of the glass may be low during firing, causing insufficient sintering. Glass from which boron is released due to dissolution or evaporation is chemically unstable and have poor resistance to moisture and to plating solutions, potentially causing poor quality.

[0008] The above situation thus causes a demand for a glass material having a low boron content and a low dielectric loss.

[0009] The present invention is made to solve the above issues and aims to provide a glass having a low boron content and a low dielectric loss.

[0010] The glass of the present invention contains Si, B, Al, and Zn. Specifically, the glass has SiO_2 at a content of 15% by weight to 65% by weight, B_2O_3 at a content of 11% by weight to 30% by weight, Al_2O_3, and ZnO, wherein a weight ratio of the SiO_2 to the B_2O_3 (SiO_2/B_2O_3) is 1.21 or higher, and a weight ratio of the Al_2O_3 to the ZnO (Al_2O_3/ZnO) is 0.75 to 1.64, and wherein an alkaline-earth metal is excluded as a material contained in the glass.

[0011] The glass ceramic of the present invention contains 45% by weight to 100% by weight of the glass of the present invention.

[0012] The multilayer ceramic electronic component of the present invention includes multiple glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention.

[0013] The present invention can provide a glass having a low boron content, a low permittivity, and a low dielectric loss, a glass ceramic containing the glass, and a multilayer ceramic electronic component including multiple glass ceramic layers each of which is a sintered article of the glass ceramic.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] FIG. **1** is a schematic cross-sectional view of an example of the multilayer ceramic electronic component of the present invention.

[0015] FIG. **2** is a schematic cross-sectional view of a multilayer green sheet (non-fired) produced in the course of production of the multilayer ceramic electronic component illustrated in FIG. **1**.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0016] The glass, glass ceramic, and multilayer ceramic electronic component of the present invention are described hereinbelow. The present invention is not limited to the following structures and may be suitably modified without departing from the gist of the present invention. Combinations of two or more preferred structures described in the following are also within the scope of the present invention.

[0017] <Glass>

[0018] The glass of the present invention contains Si, B, Al, and Zn, and has a SiO_2 content of 15% by weight to 65% by weight, a B_2O_3 content of 11% by weight to 30% by weight, a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of 1.21 or higher, and a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of 0.75 to 1.64, and wherein an alkaline-earth metal is excluded as a material contained in the glass.

[0019] B_2O_3 in the glass contributes to a low viscosity of the glass and thus allows a sintered article of the glass ceramic to be dense.

[0020] The glass of the present invention has a B_2O_3 content of 11% by weight to 30% by weight and a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of 1.21 or higher, which means that the proportion of B_2O_3 in the whole glass is small. This therefore less easily causes release of boron from the glass due to dissolution or evaporation and eventually less easily causes issues such as insufficient sintering and poor resistance to plating solutions. The glass of the present invention preferably has a B_2O_3 content of 15% by weight to 30% by weight.

[0021] The glass of the present invention has a SiO_2 content of 15% by weight to 65% by weight, preferably 20% by weight to 60% by weight.

[0022] A SiO_2 content of 15% by weight to 65% by weight contributes to a low permittivity of a sintered glass ceramic containing the glass of the present invention. This resultantly leads to, for example, reduction in the stray capacity due to electrical signals with higher frequencies.

[0023] A SiO_2 content of higher than 65% by weight causes issues such as difficulty in sintering at 1000° C. or lower and less precipitation of $ZnAl_2O_4$ crystals. In contrast, since the SiO_2 content is 65% by weight or less in the present invention, these issues do not occur.

[0024] A SiO_2 content of lower than 15% by weight causes too low a viscosity to achieve vitrification.

[0025] The weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) is 1.21 or higher. A weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) within this range less easily causes release of boron from the glass due to dissolution or evaporation.

[0026] The weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) is preferably 5.91 or lower, more preferably 4 or lower.

[0027] A weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of lower than 1.21 means too much B_2O_3 relative to SiO_2, which easily causes dissolution or evaporation of boron.

[0028] Al_2O_3 in the glass contributes to improved chemical stability of the glass.

[0029] Zn in the glass forms $ZnAl_2O_4$ together with Al.

[0030] The glass of the present invention contains Al and Zn. Al and Zn contained in the glass precipitate in the form of $ZnAl_2O_4$ crystals, which contribute to a low loss, in the glass.

[0031] A weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of 0.75 to 1.64 or lower allows the glass to have a $ZnAl_2O_4$ content within a preferred range.

[0032] A weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of lower than 0.75 means too much ZnO and causes a low Q value, which is the reciprocal of the dielectric loss. In contrast, a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of higher than 1.64 means too much Al_2O_3 and causes a high viscosity of the glass, resulting in a failure in providing a dense sintered article.

[0033] The weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) may be 0.75 or higher and 1.63 or lower.

[0034] The glass of the present invention may further contain a sub-component.

[0035] The glass of the present invention may contain Li as a sub-component. The Li_2O content is preferably 0.05% by weight to 1% by weight.

[0036] Li_2O in the glass contributes to a low viscosity of the glass. Li_2O contained in the glass leads to improved sinterability.

[0037] A predetermined amount of Li_2O can lead to good sinterability and a low dielectric loss even when a glass ceramic containing the glass of the present invention contains 40% by weight or more of an aggregate.

[0038] The glass of the present invention may further contain a different sub-component in addition to the Li-containing sub-component.

[0039] The different sub-component preferably includes at least one metal selected from the group consisting of an alkali metal, and a different metal from that of a main component of the glass.

[0040] The alkali metal preferably includes at least one selected from the group consisting of Na and K.

[0041] The different metal preferably includes at least one selected from the group consisting of Ti, Zr, and Sn.

[0042] The sum of the amounts of the sub-components is preferably 0.05% by weight to 5% by weight, more preferably 0.1% by weight to 5% by weight of the weight of the whole glass. The sum of the amounts of the sub-components means the sum of the amount of the Li-containing sub-component and the amount of the different component. A predetermined amount of the sub-components can promote crystallization of the glass and contribute to a low dielectric loss.

[0043] <Glass Ceramic>

[0044] The glass ceramic of the present invention contains 45% by weight to 100% by weight of the glass of the present invention.

[0045] The glass ceramic of the present invention contains 45% by weight or more of the glass of the present invention and can therefore achieve a low permittivity and a low dielectric loss. Also, the glass ceramic of the present invention contains 45% by weight or more of the glass of the present invention and therefore less suffers issues such as insufficient sintering due to dissolution or evaporation of boron and poor resistance to plating solutions.

[0046] The glass ceramic of the present invention preferably contains 50% by weight to 100% by weight of the glass of the present invention.

[0047] The glass ceramic of the present invention is a low temperature co-fired ceramic (LTCC) material. The "low temperature co-fired ceramic material" herein means a glass ceramic material sinterable at a firing temperature of 1000° C. or lower.

[0048] The glass ceramic of the present invention may further contain an aggregate.

[0049] The aggregate may include at least one compound selected from the group consisting of SiO_2, TiO_2, ZnO_2, ZrO_2, Al_2O_3, and BaO.

[0050] In the case where the glass ceramic of the present invention contains an aggregate, the glass content is preferably 45% by weight to less than 100% by weight, more preferably 50% by weight to less than 100% by weight.

[0051] SiO_2 as an aggregate is preferably in the form of quartz and/or amorphous silica.

[0052] Quartz can contribute to a high coefficient of thermal expansion of a sintered glass ceramic. The coefficient of thermal expansion of the glass is about 6 ppm/K, while the coefficient of thermal expansion of the quartz is about 15 ppm/K. Thus, the presence of quartz in the glass ceramic may lead to a high coefficient of thermal expansion after sintering. This may generate a compression stress in the course of cooling after sintering, resulting in a high mechanical strength (e.g., flexural strength), as well as high reliability in mounting the product on a mounting board (e.g., a resin board).

[0053] Al_2O_3 and ZrO_2 as aggregates can prevent precipitation of cristobalite crystals during sintering of the glass ceramic. The cristobalite crystal is a type of SiO_2 crystal and exhibits a phase transition at about 280° C. Thus, precipitation of cristobalite crystals in the course of sintering of the glass ceramic may greatly change the volume in a high-temperature environment, causing poor reliability. From this viewpoint, the glass ceramic is preferably free from cristobalite crystals. The expression "free from cristobalite crystals" herein means that the amount of cristobalite crystals is not higher than the detection limit. The presence or absence of precipitation of cristobalite crystals is confirmed by crystal structure analysis such as X-ray diffraction (XRD).

[0054] Al_2O_3 and ZrO_2 as aggregates can also contribute to a low dielectric loss, high coefficient of thermal expansion, and high mechanical strength of a sintered glass ceramic.

[0055] TiO_2 as an aggregate has a high temperature coefficient of relative permittivity (TCC) with the minus sign and thus enables control of TCC of the glass ceramic.

[0056] ZnO as an aggregate can lead to improved sinterability and can compensate for volatile ZnO components in the glass.

[0057] BaO as an aggregate can exhibit an effect as a sintering aid.

[0058] BaO may be added in the form of a compound containing Ba and O, such as $BaCO_3$, $BaZrO_3$, or Si—B—Ba—O glass.

[0059] For the glass ceramic, the glass and the aggregate can be distinguished by analyzing the electron diffraction pattern using a transmission electron microscope (TEM).

[0060] The amount of the aggregate can be determined by dividing the weight of the elements defining the aggregate excluding oxygen in the form of oxide by the weight of the whole glass ceramic. Accordingly, when $BaZrO_3$ is contained as an aggregate, both BaO and ZrO_2 are contained as aggregates.

[0061] <Multilayer Ceramic Electronic Component>

[0062] The multilayer ceramic electronic component of the present invention includes multiple glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention.

[0063] Examples of the multilayer ceramic electronic component of the present invention include a laminate including multiple glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention, and an electronic component including a multilayer ceramic substrate that includes the laminate and a chip component mounted on the multilayer ceramic substrate.

[0064] The multilayer ceramic electronic component of the present invention includes multiple glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention, and thus has a low permittivity and a low dielectric loss.

[0065] The laminate including multiple glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention may be used for a ceramic multilayer substrate for communications and a multilayer dielectric filter, for example.

[0066] Each glass ceramic layer preferably has a coefficient of thermal expansion of 6 ppm/K or higher.

[0067] Each glass ceramic layer preferably has a relative permittivity of 5.5 or lower.

[0068] Each glass ceramic layer preferably has a Q value of 1000 or higher.

[0069] Each glass ceramic layer preferably has a temperature characteristic of relative permittivity (TCC) of −60 ppm/K or higher and +60 ppm/K or lower.

[0070] FIG. **1** is a schematic cross-sectional view of an example of the multilayer ceramic electronic component of the present invention. As illustrated in FIG. **1**, an electronic component **2** includes a laminate **1** including a stack of multiple (five in FIG. **1**) glass ceramic layers **3** and chip components **13** and **14** mounted on the laminate **1**. The laminate **1** is also a multilayer ceramic substrate.

[0071] Each of the glass ceramic layers **3** is a sintered article of the glass ceramic of the present invention. Thus, the laminate **1** including the stack of multiple glass ceramic layers **3** and the electronic component **2** including a multilayer ceramic substrate that includes the laminate **1** and the chip components **13** and **14** mounted on the multilayer ceramic substrate (laminate **1**) are each the multilayer ceramic electronic component of the present invention. The compositions of the multiple glass ceramic layers **3** may be the same as or different from each other, and are preferably the same as each other.

[0072] The laminate **1** may further include a conductive layer. For example, the conductive layer defines a passive element such as a capacitor or an inductor or defines a connection line that provides an electrical connection between elements. Examples of the conductive layer include conductive layers **9**, **10**, and **11** as well as via hole conductive layers **12**, as illustrated in FIG. **1**.

[0073] The conductive layers **9**, **10**, and **11** as well as the via hole conductive layers **12** preferably contain Ag or Cu as a main component. Use of such a low-resistance metal can prevent occurrence of signal propagation delay due to electrical signals with higher frequencies. The constituent material of each glass ceramic layer **3** used is the glass ceramic of the present invention, i.e., a low temperature co-fired ceramic material, and thus can be co-fired with Ag or Cu.

[0074] The conductive layers **9** are provided inside the laminate **1**. Specifically, the conductive layers **9** are provided at interfaces of glass ceramic layers **3**.

[0075] The conductive layers **10** are provided on one main surface of the laminate **1**.

[0076] The conductive layers **11** are provided on the other main surface of the laminate **1**.

[0077] The via hole conductive layers **12** are each provided to penetrate a glass ceramic layer **3** and play a role of electrically connecting conductive layers **9** of different levels, electrically connecting conductive layers **9** and **10**, or electrically connecting conductive layers **9** and **11**.

[0078] The laminate **1** may be produced as follows, for example.

[0079] (A) Preparation of Glass

[0080] SiO_2, B_2O_3, Al_2O_3, and ZnO as well as a subcomponent to be optionally added are mixed such that the SiO_2 content is 15% by weight to 65% by weight, the B_2O_3 content is 11% by weight to 30% by weight, the weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) is 1.21 or higher, and the weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) is 0.75 to 1.64. Thereby, the glass of the present invention is prepared. The SiO_2 content in the glass is preferably 20% by weight to 60% by weight. The B_2O_3 content in the glass is preferably 15% by weight to 30% by weight.

[0081] (B) Preparation of Glass Ceramic

[0082] The glass of the present invention is optionally mixed with an aggregate as appropriate whereby the glass ceramic of the present invention is prepared.

[0083] The glass ceramic of the present invention is prepared such that it contains 45% by weight to 100% by weight of the glass of the present invention.

[0084] (C) Production of Green Sheet

[0085] The glass ceramic of the present invention is mixed with components such as a binder and a plasticizer, whereby ceramic slurry is prepared. The ceramic slurry is applied in a pattern to a base film (e.g., a polyethylene terephthalate (PET) film) and dried, whereby a green sheet is produced.

[0086] (D) Production of Multilayer Green Sheet

[0087] The green sheets are stacked, whereby a multilayer green sheet (non-fired) is produced. FIG. **2** is a schematic cross-sectional view of a multilayer green sheet (non-fired) produced in the course of production of the multilayer ceramic electronic component illustrated in FIG. **1**. As

illustrated in FIG. **2**, a multilayer green sheet **21** includes a stack of multiple (five in FIG. **2**) green sheets **22**. The green sheets **22** are to be the glass ceramic layers **3** after firing. The multilayer green sheet **21** may be provided with conductive layers including the conductive layers **9**, **10**, and **11** as well as the via hole conductive layers **12**. The conductive layers may be formed by a technique such as screen printing or photolithography using a conductive paste containing Ag or Cu.

[0088] (E) Firing of Multilayer Green Sheet

[0089] The multilayer green sheet **21** is fired. As a result, the multilayer ceramic substrate **1** as illustrated in FIG. **1** is obtained.

[0090] The firing temperature for the multilayer green sheet **21** may be any temperature at which the glass ceramic of the present invention defining the green sheets **22** can be sintered, and may be 1000° C. or lower.

[0091] The firing atmosphere for the multilayer green sheet **21** may be any atmosphere, and is preferably the air atmosphere in the case where an oxidation-resistive material such as Ag is used for the conductive layers **9**, **10**, and **11** as well as the via hole conductive layers **12**, or preferably an oxygen-poor atmosphere such as a nitrogen atmosphere in the case where an easily oxidative material such as Cu is used therefor. The firing atmosphere for the multilayer green sheet **21** may be a reduced atmosphere.

[0092] The multilayer green sheet **21** may be fired while sandwiched between restraining green sheets. The restraining green sheets each contain as a main component an inorganic material (e.g., Al_2O_3) that is substantially unsinterable at the sintering temperature for the glass ceramic of the present invention defining the green sheets **22**. Thus, the restraining green sheets do not shrink during firing of the multilayer green sheet **21** but act to reduce shrinkage of the multilayer green sheet **21** in the main surface direction. They can resultantly lead to improved dimensional accuracy of the resulting laminate **1** (particularly the conductive layers **9**, **10**, and **11** as well as the via hole conductive layers **12**).

[0093] The laminate **1** may be provided with the chip components **13** and **14** each electrically connected with a conductive layer **10**. Thereby, the electronic component **2** including the laminate **1** is fabricated.

[0094] Examples of the chip components **13** and **14** include an LC filter, a capacitor, and an inductor.

[0095] The electronic component **2** may be mounted on a board (e.g., motherboard) so as to be electrically connected therewith via the conductive layers **11**.

Examples

[0096] The following provides examples that more specifically disclose the glass, glass ceramic, and multilayer ceramic electronic component of the present invention. The present invention is not limited to these examples.

[0097] (A) Preparation of Glass

[0098] Glasses G1 to G41 (each in the form of powder) having the respective compositions shown in Table 1 were prepared by the following method. First, glass material powders were mixed and put into a Pt-Rh crucible, and then melted at 1650° C. for six hours or longer in the air atmosphere. The resulting melt was rapidly cooled, whereby cullet was produced. The cullet was coarsely pulverized and put into a container together with an organic solvent and PSZ balls (diameter: 5 mm). The contents were then mixed using a ball mill. The pulverization duration in the mixing with the ball mill was adjusted so that a glass powder having a central particle size of 1.5 μm was obtained. The "central particle size" herein means the central particle size D_{50} measured by laser diffraction-scattering analysis.

TABLE 1

Glass No.	SiO_2 [wt %]	B_2O_3 [wt %]	Al_2O_3 [wt %]	ZnO [wt %]	TiO_2 [wt %]	ZrO_2 [wt %]	SnO_2 [wt %]	SrO [wt %]	CaO [wt %]	BaO [wt %]	Li_2O [wt %]	SiO_2/B_2O_3 weight ratio	Al_2O_3/ZnO weight ratio
G1	60.0	30.0	5.2	4.8	—	—	—	—	—	—	—	2.00	1.08
G2	59.4	18.8	10.9	10.9	—	—	—	—	—	—	—	3.16	1.00
G3	60.0	15.0	12.5	12.5	—	—	—	—	—	—	—	4.00	1.00
G4	55.0	20.0	12.5	12.5	—	—	—	—	—	—	—	2.75	1.00
G5	50.0	30.0	10.3	9.7	—	—	—	—	—	—	—	1.67	1.06
G6	50.0	15.0	17.5	17.5	—	—	—	—	—	—	—	3.33	1.00
G7	42.0	29.0	15.0	14.0	—	—	—	—	—	—	—	1.45	1.07
G8	40.0	20.0	20.6	19.4	—	—	—	—	—	—	—	2.00	1.06
G9	40.0	15.0	22.5	22.5	—	—	—	—	—	—	—	2.67	1.00
G10	29.0	24.0	24.2	22.8	—	—	—	—	—	—	—	1.21	1.06
G11	30.0	20.0	25.8	24.2	—	—	—	—	—	—	—	1.50	1.07
G12	30.0	15.0	28.4	26.6	—	—	—	—	—	—	—	2.00	1.07
G13	20.0	15.0	33.6	31.4	—	—	—	—	—	—	—	1.33	1.07
G14	42.9	28.6	14.4	13.6	0.5	—	—	—	—	—	—	1.50	1.06
G15	41.0	27.3	13.8	13.0	5.0	—	—	—	—	—	—	1.50	1.06
G16	41.6	28.6	14.9	13.9	—	1.0	—	—	—	—	—	1.45	1.07
G17	39.9	27.4	14.3	13.4	—	5.0	—	—	—	—	—	1.46	1.07
G18	41.6	28.6	14.9	13.9	—	—	1.0	—	—	—	—	1.45	1.07
G19	39.9	27.4	14.3	13.4	—	—	5.0	—	—	—	—	1.46	1.07
G20	43.2	19.2	16.8	16.8	—	1.0	—	3.0	—	—	—	2.25	1.00
G21	42.8	19.0	16.6	16.6	—	—	—	5.0	—	—	—	2.25	1.00
G22	42.3	18.8	16.5	16.5	—	1.0	—	—	5.0	—	—	2.25	1.00
G23	42.6	19.0	16.7	16.7	—	—	—	—	—	5.0	—	2.24	1.00
G24	49.1	24.6	11.3	15.0	—	—	—	—	—	—	—	2.00	0.75
G25	42.9	24.1	20.5	12.5	—	—	—	—	—	—	—	1.78	1.64
G26	45.0	35.0	10.3	9.7	—	—	—	—	—	—	—	1.29	1.06
G27	30.0	10.0	30.9	29.1	—	—	—	—	—	—	—	3.00	1.06
G28	42.9	24.1	13.5	19.5	—	—	—	—	—	—	—	1.78	0.69
G29	42.9	24.1	21.8	11.2	—	—	—	—	—	—	—	1.78	1.95

TABLE 1-continued

Glass No.	SiO_2 [wt %]	B_2O_3 [wt %]	Al_2O_3 [wt %]	ZnO [wt %]	TiO_2 [wt %]	ZrO_2 [wt %]	SnO_2 [wt %]	SrO [wt %]	CaO [wt %]	BaO [wt %]	Li_2O [wt %]	SiO_2/B_2O_3 weight ratio	Al_2O_3/ZnO weight ratio
G30	65.0	20.0	7.8	7.2	—	—	—	—	—	—	—	3.25	1.08
G31	15.0	20.0	33.6	31.4	—	—	—	—	—	—	—	0.75	1.07
G32	30.0	30.0	20.6	19.4	—	—	—	—	—	—	—	1.00	1.06
G33	45.0	15.0	20.0	20.0	—	—	—	—	—	—	—	3.00	1.00
G34	45.0	14.95	20.0	20.0	—	—	—	—	—	—	0.05	3.01	1.00
G35	45.0	14.0	20.0	20.0	—	—	—	—	—	—	1.0	3.21	1.00
G36	45.0	12.0	20.0	20.0	—	—	—	—	—	—	3.0	3.75	1.00
G37	65.0	30.0	2.5	2.5	—	—	—	—	—	—	—	2.17	1.00
G38	60.0	11.0	14.5	14.5	—	—	—	—	—	—	—	5.45	1.00
G39	40.0	11.0	24.5	24.5	—	—	—	—	—	—	—	3.64	1.00
G40	15.0	12.0	36.5	36.5	—	—	—	—	—	—	—	1.25	1.00
G41	75.0	15.0	5.0	5.0	—	—	—	—	—	—	—	5.00	1.00

[0099] The glasses G26 to G29, G31, G32, and G41 each are not the glass of the present invention.

[0100] The glass G26 has a B_2O_3 content of higher than 30% by weight.

[0101] The glass G27 has a B_2O_3 content of lower than 11% by weight.

[0102] The glass G28 has a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of lower than 0.75.

[0103] The glass G29 has a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of higher than 1.64.

[0104] The glass G31 has a SiO_2 content within a range of 15% by weight to 65% by weight and a B_2O_3 content of 11% by weight to 30% by weight, but has a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of lower than 1.21.

[0105] The glass G32 has a SiO_2 content within a range of 15% by weight to 65% by weight and a B_2O_3 content of 11% by weight to 30% by weight, but has a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of lower than 1.21.

[0106] The glass G41 has a SiO_2 content of higher than 65% by weight.

[0107] (B) Preparation of Glass Ceramic

[0108] Next, based on each composition shown in Table 2, the glass of the present invention optionally combined with aggregates was put into ethanol and mixed using a ball mill. Thereby, a glass ceramic was prepared. SiO_2 among the aggregates is quartz.

[0109] (C) Production of Green Sheet

[0110] One of the glass ceramics, a binder solution of polyvinyl butyral dissolved in ethanol, and a dioctyl phthalate (DOP) solution serving as a plasticizer were mixed, whereby ceramic slurry was prepared. The ceramic slurry was then applied in a pattern to a polyethylene terephthalate film using a doctor blade and dried at 40° C. Thereby, one of 25-μm-thick green sheets S1 to S33 and S35 to S47 was produced.

[0111] For the glass G31, the ceramic slurry was gelated and thus not subjected to the steps after production of green sheet.

[0112] (D) Production of Multilayer Green Sheet

[0113] Each of the green sheets S1 to S33 and S35 to S47 was cut to provide 78 mm×58 mm rectangles and 30 pieces thereof were stacked. The stack was put into a mold and compressed using a press, and then cut off at its side portions so as to have a 50-mm-square dimensions in a plan view. Thereby, respective multilayer green sheets were produced.

[0114] (E) Firing of Multilayer Green Sheet

[0115] The multilayer green sheets were fired at 980° C. for 60 minutes in a reduced atmosphere. The resulting fired articles were laminates L1 to L33 and L35 to L47 each including multiple glass ceramic layers each of which is a sintered article of the glass ceramic.

[0116] <Measurement of Relative Permittivity and Dielectric Loss>

[0117] For each of the resulting laminates L1 to L33 and L35 to L47, the thickness was measured and the relative permittivity and dielectric loss under 6 GHz conditions were measured by the perturbation method. The reciprocal of the measured dielectric loss was taken as the Q value. The results are shown in Table 2.

[0118] A relative permittivity of 5.5 or lower was evaluated as good. A Q value of 1000 or higher was evaluated as good. As stated in the Note of Example 2, the laminates L6, L29, L30, L32, L35, and L47 were insufficiently sintered.

[0119] The measurement devices and the measurement conditions were as follows.

[0120] Network analyzer: 8757D available from Keysight Technologies

[0121] Signal generator: 83751 synthesized sweeper available from Keysight Technologies

[0122] Resonator: self-made jig (resonance frequency: 6 GHz)

[0123] Before the measurement, the network analyzer and the signal generator were connected and the cable loss was measured. The resonator was calibrated using a reference substrate (quartz, permittivity: 3.73, Q value: 4545 at 6 GHz, thickness: 0.636 mm).

TABLE 2

Laminate No.	Glass No.	Glass Amount [wt %]	Aggregates SiO_2 [wt %]	Aggregates TiO_2 [wt %]	Aggregates ZnO [wt %]	Aggregates ZrO_2 [wt %]	Aggregates BaO [wt %]	Relative permittivity	Q value [at 6 GHz]	Note
L1	G1	90	7	2	1	—	—	4.21	1360	
L2	G2	90	7	2	1	—	—	4.45	1279	

TABLE 2-continued

Laminate No.	Glass No.	Glass Amount [wt %]	Aggregates SiO_2 [wt %]	TiO_2 [wt %]	ZnO [wt %]	ZrO_2 [wt %]	BaO [wt %]	Relative permittivity	Q value [at 6 GHz]	Note
L3	G3	90	7	2	1	—	—	4.42	1714	
L4	G3	100	—	—	—	—	—	4.64	1980	
L5	G4	90	6.7	—	0.3	3	—	4.31	1510	
L6	G4	40	48	2	2	—	8	4.02	870	Insufficient sintering
L7	G5	90	7	2	1	—	—	4.50	2218	
L8	G6	90	7	2	1	—	—	4.64	2762	
L9	G7	90	7	2	1	—	—	4.72	2099	
L10	G7	50	32	10	—	—	8	5.30	1450	
L11	G8	90	7	2	1	—	—	4.73	2054	
L12	G9	90	7	2	1	—	—	4.88	1628	
L13	G10	90	7	2	1	—	—	4.95	1350	
L14	G11	90	7	2	1	—	—	5.08	1401	
L15	G12	90	7	2	1	—	—	4.92	2074	
L16	G13	90	7	2	1	—	—	5.43	2258	
L17	G14	90	7	2	1	—	—	4.72	2633	
L18	G15	90	7	2	1	—	—	5.39	2353	
L19	G16	90	7	2	1	—	—	4.69	2272	
L20	G17	90	7	2	1	—	—	4.99	2300	
L21	G18	90	7	2	1	—	—	4.66	2115	
L22	G19	90	7	2	1	—	—	5.20	1980	
L23	G20	90	7	2	1	—	—	5.07	1033	
L24	G21	90	7	2	1	—	—	5.43	1054	
L25	G22	90	7	2	1	—	—	5.35	1110	
L26	G23	90	7	2	1	—	—	5.41	1311	
L27	G24	90	7	2	1	—	—	4.55	1220	
L28	G25	90	7	2	1	—	—	4.10	1666	
L29	G26	90	7	2	1	—	—	3.82	988	Insufficient sintering
L30	G27	90	7	2	1	—	—	3.15	3624	Insufficient sintering
L31	G28	90	7	2	1	—	—	4.89	836	Low Q value
L32	G29	90	7	2	1	—	—	3.29	855	Insufficient sintering
L33	G30	90	7	2	1	—	—	4.12	1194	
L34	G31	—	—	—	—	—	—	—	—	Slurry gelated
L35	G32	90	7	2	1	—	—	4.43	1992	Insufficient sintering
L36	G33	90	7	2	1	—	—	4.60	2200	
L37	G34	65	32	2	1	—	—	4.31	1400	
L38	G34	55	42	2	1	—	—	4.27	1300	
L39	G35	55	42	2	1	—	—	4.33	1100	
L40	G35	45	52	2	1	—	—	4.21	1000	
L41	G36	40	57	2	1	—	—	4.10	600	Low Q value
L42	G3	70	21	1	8	—	—	4.70	1680	
L43	G37	90	7	2	1	—	—	4.14	1294	
L44	G38	90	7	2	1	—	—	4.57	1855	
L45	G39	90	7	2	1	—	—	4.89	1920	
L46	G40	90	7	2	1	—	—	5.45	1745	
L47	G41	90	7	2	1	—	—	3.56	912	Insufficient sintering

[0124] The results in Table 2 demonstrate that the laminates each including the glass ceramic layers each of which is a sintered article of the glass ceramic of the present invention had a low relative permittivity and a high Q value (a low dielectric loss) although they each were formed from a glass having a B_2O_3 content of 30% by weight or less. Further, the laminates suffered no issues due to dissolution or evaporation of boron.

[0125] The laminate L6 suffered sintering defects presumably because it contained less than 45% by weight of the glass G4.

[0126] The laminate L29 suffered issues such as dissolution and evaporation of boron during production presumably because it was formed from the glass G26 having a B_2O_3 content of higher than 30% by weight.

[0127] The laminate L30 suffered sintering defects presumably because it was formed from the glass G27 having a B_2O_3 content of less than 11% by weight and thus the viscosity of the glass was not sufficiently low.

[0128] The laminate L32 failed to provide a dense sintered article presumably because it was formed from the glass G29 having a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of higher than 1.64 and too much Al_2O_3 caused a high viscosity of the glass.

[0129] The laminate L47 suffered insufficient progress of sintering at 980° C. presumably because it was formed from the glass G41 having a SiO_2 content of higher than 65% by weight.

[0130] The glass G31 failed to provide a laminate because it had a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of lower than 1.21 and thus the ceramic slurry was gelated by heating at 980° C.

[0131] The laminate L35 suffered issues such as dissolution and evaporation of boron during production presumably because it was formed from the glass G32 having a weight ratio of SiO_2 to B_2O_3 (SiO_2/B_2O_3) of lower than 1.21.

[0132] The laminate L31 suffered neither insufficient sintering nor gelation of the ceramic slurry, but had a Q value of lower than 1000, i.e., had a high dielectric loss. This low

Q value is presumably derived from the fact that the laminate L31 was formed from the glass G28 having a weight ratio of Al_2O_3 to ZnO (Al_2O_3/ZnO) of lower than 0.75.

[0133] The laminate L41 suffered neither insufficient sintering nor gelation of the ceramic slurry, but had a Q value of lower than 1000, i.e., had a high dielectric loss. This low Q value is presumably derived from the fact that the laminate L41 contained less than 45% by weight of the glass G36.

REFERENCE SIGNS LIST

[0134] **1**: laminate

[0135] **2**: electronic component

[0136] **3**: glass ceramic layer

[0137] **9**, **10**, **11**: conductive layer

[0138] **12**: via hole conductive layer

[0139] **13**, **14**: chip component

[0140] **21**: multilayer green sheet

[0141] **22**: green sheet

1. A glass comprising:

SiO_2 at a content of 15% by weight to 65% by weight;

B_2O_3 at a content of 11% by weight to 30% by weight;

Al_2O_3; and

ZnO, wherein

a weight ratio of the SiO_2 to the B_2O_3 (SiO_2/B_2O_3) is 1.21 or higher,

a weight ratio of the Al_2O_3 to the ZnO (Al_2O_3/ZnO) is 0.75 to 1.64, and

wherein an alkaline-earth metal is excluded as a material contained in the glass.

2. The glass according to claim **1**, wherein the content of the SiO_2 is 55% by weight to 65% by weight.

3. The glass according to claim **1**, wherein the content of the B_2O_3 is 18.8% by weight to 30% by weight.

4. The glass according to claim **1**, wherein Li is excluded as a sub-component.

5. The glass according to claim **1**, wherein the weight ratio of the SiO_2 to the B_2O_3 (SiO_2/B_2O_3) is 5.91 to 1.21.

6. The glass according to claim **1**, further comprising Li as a sub-component.

7. The glass according to claim **6**, wherein the glass has a Li_2O content of 0.05% by weight to 1% by weight.

8. The glass according to claim **7**, wherein a sum of an amount of the sub-component is 0.05% by weight to 5% by weight of the weight of a whole of the glass.

9. The glass according to claim **1**, further comprising at least one metal as a sub-component, the at least one metal being selected from the group consisting of an alkali metal and a different metal from that of a main component of the glass.

10. The glass according to claim **9**, wherein

the alkali metal comprises at least one selected from the group consisting of Na and K, and

the different metal comprises at least one selected from the group consisting of Ti, Zr, and Sn.

11. The glass according to claim **8**, wherein a sum of an amount of the sub-component is 0.05% by weight to 5% by weight of the weight of a whole of the glass.

12. A glass ceramic comprising 45% by weight to 100% by weight of the glass according to claim **1**.

13. The glass ceramic according to claim **12**, further comprising an aggregate.

14. The glass ceramic according to claim **13**, wherein the aggregate comprises at least one compound selected from the group consisting of SiO_2, TiO_2, ZnO_2, ZrO_2, Al_2O_3, and BaO.

15. A glass ceramic comprising 65% by weight to 100% by weight of the glass according to claim **1**.

16. A multilayer ceramic electronic component comprising multiple glass ceramic layers each of which is a sintered article of the glass ceramic according to claim **12**.

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