



166166

23 November 2004



G00002

1

Description

Glass ceramic mass and use thereof

5 The invention relates to a glass ceramic mass, comprising at least one oxide ceramic, containing barium, titanium and at least one rare earth metal Re_k and at least one glass material, containing at least one oxide with boron, at least one oxide with silicon and at least one oxide with at least one bivalent metal Me_{2+} . In addition to the glass ceramic mass, an application of the glass ceramic mass is described.

10 A glass ceramic mass of the aforementioned type is known from US 5 264 403. The oxide ceramic for the known glass ceramic mass is manufactured from barium oxide (BaO), titanium dioxide (TiO_2), a trioxide of a rare earth metal ($Re_k_2O_3$) and possibly bismuth trioxide (Bi_2O_3). The rare earth metal Re_k is for example neodymium. The glass material in the glass ceramic mass consists of boron trioxide (B_2O_3), silicon dioxide and zinc oxide (ZnO). A ceramic proportion of the oxide ceramic in the glass ceramic mass is for example 90% and a glass proportion of the glass material 10%.

15 A compression of the glass ceramic mass occurs at a sintering temperature of about $950^{\circ}C$. The glass ceramic mass is thus suitable for use in LTCC (low temperature cofired ceramics) technology. The LTCC technology is described for example in D. L. Wilcox et al, Proc. 1997 ISAM, Philadelphia, pp. 17 to 23. The LTCC technology is a ceramic multilayer method in which a passive electrical component can be integrated in the volume of a ceramic multilayer
20 body. The passive electrical component is for example an electrical conductor track, a coil, an induction or a capacitor. Integration is achieved, for example, by printing a metal structure corresponding to the component on one or more ceramic film blanks, stacking the printed

ceramic film blanks above one another to form a composite and sintering the composite. Since ceramic film blanks are used with a low sintering glass ceramic mass, electrically highly conductive elementary metal MeO with a low melting point such as silver or copper can be sintered in a composite with the ceramic film blank. In this situation, the functional integrity of the component integrated through the use of LTCC technology is crucially dependent on the dielectric material properties of the glass ceramic used. A material property of this type is for example the permittivity (ϵ_r), a quality factor (Q) and a temperature coefficient of frequency (Tf value).

With regard to the known glass ceramic mass, the glass proportion is relatively low, with the result that compression of the glass ceramic mass takes place as a result of reactive liquid phase sintering. During the sintering process, a liquid glass phase (glass melt) is formed from the glass material. At a higher temperature the oxide ceramic dissolves in the glass melt until a saturation concentration is reached and a separation of the oxide ceramic occurs once again. As a result of the oxide ceramic dissolving and separating out again, the composition of the oxide ceramic and thus also the composition of the glass phase or the glass material can change. During cooling, crystallization from the glass melt can additionally occur. For example, in this situation one constituent of the oxide ceramic remains in the glass phase after cooling of the glass ceramic mass. If the composition of the oxide ceramic and thus also the composition of the glass material changes as a result of compression, it is difficult to define the material properties of the compressed glass ceramic mass and thus to guarantee the functional integrity of the component integrated through the use of LTCC technology.

The object of the present invention is to specify a glass ceramic mass with an oxide

ceramic, whose composition remains essentially unchanged during a sintering process.

This object is achieved by specifying a glass ceramic mass comprising at least one oxide ceramic, containing barium, titanium and at least one rare earth metal Re_k and at least one glass material, containing at least one oxide with boron, at least one oxide with silicon and at least one oxide with at least one bivalent metal Me_{2+} . The glass ceramic mass is characterized by the fact that the glass material contains at least one oxide with bismuth.

The glass ceramic mass is a glass ceramic compound and is independent of its state. The glass ceramic mass can exist as a ceramic green body. With regard to a green body, a film blank for example, a powder of the oxide ceramic and a powder of the glass material can be combined with one another by means of an organic binding agent. It is also conceivable that the glass ceramic mass can exist as a powder mixture of the oxide ceramic and the glass material. Furthermore, the glass ceramic mass can exist as a sintered ceramic body. For example, a ceramic multilayer body produced in a sintering process consists of the glass ceramic mass. This ceramic multilayer body can be submitted to a further sintering process.

The oxide ceramic can be present as a single phase. However, it can also consist of a plurality of phases. It is conceivable, for example, for the oxide ceramic to consist of phases each having a differing composition. The oxide ceramic is thus a mixture of different oxide ceramics. It is also conceivable for one or more parent compounds of an oxide ceramic to be present which are then converted to form the actual oxide ceramic only during the sintering process.

The glass material can likewise be a single phase. For example, the phase is a glass melt consisting of boron trioxide, silicon dioxide, zinc oxide and bismuth trioxide. It is also conceivable for the glass material to consist of a plurality of phases. For example, the glass material consists of a powder mixture of the specified oxides. A joint glass melt is formed from the oxides during the sintering process. It is also conceivable for the glass material to be a crystallization product of the glass melt. This means that the glass material is present not only as a glass melt after the sintering process but can also be present in a crystalline form.

The fundamental concept of the present invention consists in using a bismuth oxide, in particular bismuth trioxide, in the glass material. One advantage in doing so consists in the fact that a softening temperature T_{soft} of the glass material can be lowered. The lower the glass transition point, the lower is the sintering temperature or a vitrification temperature for the corresponding glass ceramic mass. At the vitrification temperature, almost complete compression of the glass ceramic mass can be achieved in a short time.

In addition, bismuth trioxide influences the way in which the oxide ceramic dissolves and separates out again in the glass melt during the sintering process in a particularly advantageous manner (for example as a result of the lower vitrification temperature). Practically no elution of individual components of the oxide ceramic occurs. The composition of the oxide ceramic either does not change or changes only slightly and can therefore be very well predetermined.

It is known that bismuth which is present in the oxide ceramic reacts with elementary silver at an elevated temperature. With regard to the use of an oxide ceramic containing bismuth in LTCC technology in conjunction with the use of silver as

an electrically conducting material, this combination can result in an undesired reaction impairing the functional integrity of the component which is to be manufactured. If the glass material contains bismuth trioxide, the vitrification temperature is reduced. A sintering process can take place at lower temperatures. In this way, a reaction between bismuth, or bismuth trioxide, and elementary silver can be suppressed. Furthermore, if the glass proportion is relatively low, relatively little bismuth is also present, with the result that no noticeable reaction occurs between bismuth and silver.

In a special embodiment, the oxide ceramic has a formal composition $\text{BaRek}_2\text{Ti}_4\text{O}_{12}$. The oxide ceramic having the aforementioned composition is referred to as microwave ceramic since its material properties (permittivity, quality, Tf value) are very well suited for use in microwave technology.

In particular, the glass material contains at least one oxide with at least one rare earth metal Reg. The rare earth metal Reg is present for example as the trioxide Reg_2O_3 . By using the oxide of the rare earth metal Reg, it is possible match the permittivity of the glass material, which contributes to the permittivity of the overall glass ceramic mass, to the permittivity of the oxide ceramic. A glass ceramic mass exhibiting a permittivity of 20 to 80 or even higher is thus accessible.

In particular, the rare earth metal Rek and/or the rare earth metal Reg from the group comprising lanthanum and/or neodymium and/or samarium are selected. Other lanthanides or even actinides are also conceivable. The rare earth metals Rek and Reg can be identical, but can also be different rare earth metals.

In a special embodiment, the oxide ceramic contains the bivalent metal Me^{2+} . In particular, the

bivalent metal Me^{2+} is selected from the group comprising beryllium, magnesium, calcium, strontium, barium, copper and/or zinc. The bivalent metal Me^{2+} can be present as a separate oxidic phase. In particular, the bivalent metal Me^{2+} is a doping of the oxide ceramic. In the oxide ceramic, the bivalent metal Me^{2+} causes a significant reduction in the sintering temperature of the oxide ceramic. Furthermore, it is possible to control the dielectric material properties of the oxide ceramic. For example, the oxide ceramic having the composition $\text{BaRek}_2\text{Ti}_4\text{O}_{12}$ is doped with zinc. Like the oxide of bismuth, the bivalent metal Me^{2+} can bring about a suppression of the elution of individual components of the oxide ceramic during the sintering process. It has become apparent that it is particularly advantageous if the oxide ceramic is doped with the bivalent metal Me^{2+} which also occurs in the glass material. In particular, zinc is to be mentioned here as a bivalent metal Me^{2+} . Zinc has a particularly advantageous effect on reactive liquid phase sintering and on any process of dissolving and separating out again which occurs in this situation.

In a further embodiment, in addition to the oxide of silicon the glass material contains as a tetravalent metal at least one oxide of at least one further tetravalent metal Me^{4+} . In addition to the silicon dioxide, the glass material contains at least one further dioxide of a tetravalent metal. The further tetravalent metal Me^{4+} is selected in particular from the group comprising germanium and/or tin and/or titanium and/or zirconium. In addition to silicon dioxide, the oxides of the aforementioned tetravalent metals support a glassiness of the glass material. This means that these oxides are used, as incidentally are also the oxides of the aforementioned bivalent metals Me^{2+} , to control a viscosity temperature characteristic of the glass material. For example, the softening temperature T_{soft} of glass material can be set. Crystallization of the glass material can likewise be influenced.

- In a special embodiment, 100% by volume of the glass ceramic mass is composed of a ceramic proportion of the oxide ceramic which is selected from the range between 70% by volume inclusive to 95% by volume inclusive, and a glass proportion of the glass material which is selected from the range between 30% by volume inclusive to 5% by volume inclusive. If the glass ceramic mass is subjected to a sintering process, the aforementioned reactive liquid phase sintering takes place. In the case of particularly advantageous behavior with respect to any process of dissolving and separating out again, as is the situation in particular when the bivalent metal occurs in the oxide ceramic and in the glass material, it is also possible to keep the glass proportion below 5% by volume.
- 5
- 10 In particular, the oxide ceramic and/or the glass material contain a powder with a mean particle size (D_{50} value) which is selected from the range between $0.1\ \mu\text{m}$ inclusive and $1.5\ \mu\text{m}$ inclusive. The mean particle size is also referred to as half-value particle size. In order to maintain a very low glass proportion without restricting any process of dissolving and separating out again, powders having the specified particle sizes are particularly advantageous.
- 15 The powders have a large reactive surface which is necessary for the reactive liquid phase sintering process.

Normally, in order to reduce the sintering temperature and to increase the permittivity of the glass ceramic mass, lead oxide (PbO) is added to the glass material. With regard to the present invention, the lead oxide proportion and/or cadmium oxide proportion of the glass ceramic mass and/or of the oxide ceramic and/or of the glass material is a maximum 0.1 %, in particular a maximum of 1 ppm. By preference, with regard to environmental considerations, the proportion of lead oxide and cadmium oxide is almost zero. This is achieved by the present invention

20

without significant restriction of the material properties of the glass ceramic mass.

In a special embodiment, the ceramic mass exhibits a maximum vitrification temperature of 950°C, and in particular a maximum of 910°C or 890°C. In this situation, in particular, a glass ceramic mass is accessible with a permittivity which is selected from the range between 20 inclusive and 80 inclusive, a quality which is selected from the range between 800 inclusive and 5000 inclusive, and a Tf value which is selected from the range between - 20 ppm/K inclusive and + 20 ppm/K inclusive. With these material properties, the glass ceramic mass is very well suited for use in microwave technology.

According to a second aspect of the invention, a ceramic body using a previously described glass ceramic mass is specified. In particular, the ceramic body has at least one elementary metal MeO which is selected from the group comprising gold and/or silver and/or copper. By preference, the ceramic body is a ceramic multilayer body. The previously described glass ceramic mass is used to manufacture the ceramic body. As a result of using glass material containing bismuth, vitrification of the glass ceramic mass can already take place below 890°C.

With regard to a firing process in the presence of elementary silver, no disruptive interdiffusion occurs. In particular, a ceramic body in the form of a ceramic multilayer body can be manufactured in this manner. The glass ceramic mass is used in particular in ceramic film blanks in LTCC technology. In this way, glass ceramic masses are made available to the LTCC technology, having excellent material properties for the manufacture of microwave technology components.

To summarize, the following advantages result from the invention:

- The composition of the oxide ceramic remains essentially constant during sintering of the glass ceramic mass. The material properties of the glass ceramic mass can thus be pre-set in a defined manner.
- 5 • Almost complete compression (vitrification) of the glass ceramic mass is possible at a temperature of below 910°C, and even below 890°C.
- By means of suitable (oxidic) additions to the oxide ceramic and to the glass material, the sintering behavior of the glass ceramic mass and the material properties of the glass ceramic mass can be set specifically and almost as desired. It is thus possible, for example, to set
10 permittivity, quality and Tf value over a wide range in each case whilst retaining a low vitrification temperature.
- Compression is achieved without the use of lead oxide and/or cadmium oxide.

The invention will be described in the following with reference to an embodiment and the associated drawing. The drawing shows a schematic cross-section, not to scale, of a ceramic
15 body with the glass ceramic mass in a multilayer construction.

According to the embodiment, the glass ceramic mass 11 is a powder consisting of an oxide ceramic and a powder of a glass material. The oxide ceramic has the formal composition $\text{BaRe}_k\text{Ti}_4\text{O}_{12}$. The rare earth metal is neodymium. The oxide ceramic is doped with a bivalent metal Me^{2+} in the form of zinc. In order to manufacture the oxide ceramic, appropriate
20 quantities of barium oxide, titanium dioxide and neodymium trioxide are mixed together with

approximately one % by weight zinc oxide, calcinated or sintered, and subsequently ground to produce the corresponding powder.

The glass material contains boron, bismuth, silicon and zinc. The glass material is characterized by the following composition: 27.5 mol% boron trioxide, 34.8 mol% bismuth oxide, 32.5 mol% zinc oxide and 6 mol% silicon dioxide.

100% by volume of the glass ceramic mass is composed of 90% by volume of the ceramic material and 10% by volume of the glass material. Ceramic material and glass material have a D_{50} value of $0.8 \mu\text{m}$. The vitrification temperature of the glass ceramic mass is 900°C . The permittivity of the glass ceramic mass is 64, the quality is 820, and the Tf value is 4 ppm/K.

- 10 The glass ceramic mass 11 described is used in order to integrate a passive electrical component 6, 7 in the volume of a ceramic multilayer body 1 with the aid of LTCC technology. The ceramic multilayer body 1 produced in this manner has ceramic layers 3 and 4 which are produced from ceramic film blanks together with the glass ceramic mass 11. The ceramic layers 2 and 5 have a further glass ceramic mass 12 which is different from the glass ceramic mass 11.
- 15 The electrically conductive material comprising the electronic components is an elementary metal Me0 in the form of silver.

Claims

1. Glass ceramic mass
 - comprising at least one oxide ceramic, containing barium, titanium and at least one rare earth metal Re_k , and
 - 5 - at least one glass material, containing at least one oxide with boron, at least one oxide with silicon and at least one oxide with at least one bivalent metal Me_{2+} , and
 - at least one oxide with bismuth,
- characterized in that**
- 10 - a lead oxide proportion and/or a cadmium oxide proportion of the glass ceramic mass and/or of the oxide ceramic and/or of the glass material is a maximum 0.1 %.
2. Glass ceramic mass according to Claim 1, whereby the oxide ceramic has a formal composition $BaRe_kTi_4O_{12}$.
3. Glass ceramic mass according to Claim 1 or 2, whereby the glass material contains at least
- 15 one oxide with at least one rare earth metal Re_g .
4. Glass ceramic mass according to one of Claims 1 through 3, whereby the rare earth metal Re_k and/or the rare earth metal Re_g is selected from the group comprising lanthanum and/or neodymium and/or samarium.
5. Glass ceramic mass according to one of Claims 1 through 4, whereby the oxide ceramic
- 20 contains the bivalent metal Me_{2+} .
6. Glass ceramic mass according to one of Claims 1 through 5, whereby the bivalent metal Me_{2+} is selected from the group comprising beryllium, magnesium, calcium, strontium, barium, copper and/or zinc.

7. Glass ceramic mass according to one of Claims 1 through 6, whereby in addition to the oxide of silicon the glass material contains as a tetravalent metal at least one oxide with at least one further tetravalent metal Me₄⁺.
- 5 8. Glass ceramic mass according to Claim 7, whereby the further tetravalent metal Me₄⁺ is selected from the group comprising germanium and/or tin and/or titanium and/or zirconium.
9. Glass ceramic mass according to one of Claims 1 through 8, whereby 100% by volume of the glass ceramic mass is composed of a ceramic proportion of the oxide ceramic which is selected from the range between 70% by volume inclusive to 95% by volume inclusive, and a glass proportion of the glass material which is selected from the range between 30% by
10 volume inclusive to 5% by volume inclusive.
10. Glass ceramic mass according to one of Claims 1 through 9, whereby the oxide ceramic and/or the glass material contain a powder with a mean particle size which is selected from the range between 0.1 μ m inclusive and 1.5 μ m inclusive.
11. Glass ceramic mass according to one of Claims 1 through 10, whereby the lead oxide
15 proportion and/or the cadmium oxide proportion is a maximum of 1 ppm.
12. Glass ceramic mass according to one of Claims 1 through 11, with a maximum vitrification temperature of 950°C, in particular a maximum of 890°C.
13. Glass ceramic mass according to Claim 12, with
 - a permittivity which is selected from the range between 20 inclusive and 80 inclusive,
 - 20 - a quality which is selected from the range between 800 inclusive and 5000 inclusive, and
 - a Tf value which is selected from the range between - 20 ppm/K inclusive and + 20 ppm/K inclusive.
14. Ceramic body with a glass ceramic mass according to one of Claims 1 through 13.

15. Ceramic body according to Claim 14, with at least one elementary metal Me0 which is selected from the group comprising gold and/or silver and/or copper.
16. Ceramic body according to Claim 13 or 14, whereby the ceramic body is a ceramic multilayer body.