

## Description

The invention is directed to the production of sintered glass-ceramic bodies, and to the control of certain physical properties in such bodies.

Naturally occurring, crystalline cordierite is commonly identified as alpha-cordierite, and assigned the stoichiometric, molar oxide formula  $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ . However, up to eight moles of  $\text{SiO}_2$  may be accepted without altering the basic crystal structure. Further, other oxide constituents may be present in glasses from which glass-ceramics having an alpha-cordierite primary crystal phase are produced. Accordingly, the term "alpha-cordierite solid solutions" has been adopted to encompass any crystal phase having the characteristic alpha-cordierite structure. Likewise, "alpha-cordierite solid solution glass-ceramic" refers to a glass-ceramic having such a primary crystal phase, and "alpha-cordierite glass" refers to the precursor glass.

Considerable attention has heretofore been given to selecting materials for use in substrates and packaging for integrated circuits. Organics have been widely used, but have limited temperature capabilities and may lack adequate hermeticity. Consequently, alumina has become the standard material where temperature is involved. However, its coefficient of thermal expansion ( $65 \times 10^{-7}/^\circ\text{C}$ ) is not a match for silicon chips, and its dielectric constant is relatively high.

Therefore, largely because of their relatively low coefficients of thermal expansion, alpha-cordierite solid solution glass-ceramics have been the object of recent studies. Some of the history is reviewed in US-A-4,897,509, issued 30 January, 1990.

US-A-4,897,509 discloses modified alpha-cordierite solid solution compositions that can be sintered below  $1000^\circ\text{C}$ . This low temperature firing permits co-sintering of substrate and metallizing, that is, firing metal paste circuitry and its substrate in one operation. It also permits using better conductors, such as gold and copper. The compositions, expressed in weight percent on an oxide basis, consist essentially of 2-18% MgO, 0-21% ZnO, the total MgO + ZnO being 10-25%, 20-38%  $\text{Al}_2\text{O}_3$ , 40-52%  $\text{SiO}_2$ , and 2-15% total of at least one oxide selected from up to 8%  $\text{K}_2\text{O}$  and/or  $\text{Rb}_2\text{O}$  and/or  $\text{Cs}_2\text{O}$ , up to 10% CaO and/or SrO and/or BaO and/or PbO and up to 5%  $\text{B}_2\text{O}_3$ .

US-A-4,906,514, issued 6 March 1990 describes the use of alpha-cordierite solid solution glass-ceramic as a substrate in electrical components. More particularly, that application is directed to metallizing pastes adapted to use in forming circuitry on such substrates.

Customarily, glass-ceramic bodies are formed in the glassy state. The glass body is then subjected to a crystallizing heat treatment referred to as "ceramming". However, United States Patent No. 3,940,255 (Harrington et al.), teaches that a substantial amount of glassy phase may result.

Accordingly, particularly in the electrical components field, it has become the practice to quench a stream of molten glass and pulverise the resulting fragments of glass to a powder. The powdered glass may then be formed to the desired shape and fired. This forms a dense, sintered body that may then be crystallized to a glass-ceramic state.

The Harrington et al. patent teaches that a small amount of nucleating agent, combined with finely ground glass, enhances the degree of crystallization that occurs at a crystallizing temperature. Thereby, the amount of glassy phase is reduced. The patent further teaches that the amount of nucleating agent added to the glass may, and should, be much smaller than normally used. It is suggested that the nucleating agent may be added to the powdered glass after melting. However, a clear preference is shown for the standard practice of incorporating the nucleating agent in the glass batch prior to melting.

In the course of developing a commercial process for sintered, alpha-cordierite solid solution glass-ceramic substrates to be used with integrated circuits, it was discovered that physical properties, particularly coefficient of thermal expansion, could vary significantly with no apparent change in the parent glass.

A basic purpose, then, is to provide sintered, alpha-cordierite solid solution glass-ceramic bodies having controlled and stabilized properties.

Another purpose is to provide means for controlling and stabilizing certain properties during the production of such sintered bodies.

A further purpose is to provide a method of producing such bodies having enhanced mechanical strength.

A still further purpose is to provide greater flexibility in material preparation for sintered, alpha-cordierite solid solution glass-ceramic bodies.

An article in accordance with our invention is composed of a sintered, alpha-cordierite solid solution glass-ceramic having a primary crystal phase with an alpha-cordierite structure and a secondary crystal phase with a gahnite structure, the relative amounts of the alpha-cordierite and gahnite crystal phases, as shown by x-ray diffraction (XRD) peaks, being in the range of 4:1 to 6:1, preferably about 5:1, the glass-

ceramic having a coefficient of thermal expansion (CTE) in the range of  $25.6\text{--}30 \times 10^{-7}/^{\circ}\text{C}$  and a modulus of rupture (MOR) of at least 172.5 MPa (25 Kpsi). The coefficient of thermal expansion is preferably within the range of  $26\text{--}30 \times 10^{-7}/^{\circ}\text{C}$ .

- Another aspect of our invention is a method of producing a sintered, alpha-cordierite solid solution, glass-ceramic body which comprises,
- a. providing a glass that is capable of being nucleated and crystallized to form a glass-ceramic material having a primary crystal phase of alpha cordierite solid solution, and that is essentially free from devitrification,
  - b. pulverizing the glass to a powder,
  - c. adding two dopants to the glass powder to control properties in the sintered body, one dopant being at least 0.001% by weight of finely divided, pre-crystallized alpha-cordierite solid solution, and the second being up to about 5% by weight of a nucleating agent which is  $\text{TiO}_2$ ,
  - d. shaping the doped powder to desired form, and
  - e. firing the shaped body at low temperatures to burn out the organics, and
  - f. heating it to above  $900^{\circ}\text{C}$  to create a primary crystal phase with an alpha-cordierite structure and a secondary crystal phase with a gahnite structure.

The second dopant is preferably used in an amount of 1 to 3%, in particular about 2.0% and preferably has a particle size below  $3.5\text{ }\mu\text{m}$  (microns). The second dopant is  $\text{TiO}_2$  or fumed  $\text{TiO}_2$ . As indicated, the glass is preferably pulverized to an average particle size of less than about 2 (microns) and preferably sintered at a temperature of up to  $900^{\circ}\text{C}$  and crystallized to a glass-ceramic at a higher temperature. The coefficient of thermal expansion, after ceramming is preferably maintained in the range of  $26\text{--}30 \times 10^{-7}/^{\circ}\text{C}$  and modulus of rupture is at least 172.5 MPa (25 Kpsi).

A further aspect of the invention is a method of controlling the physical properties of a sintered alpha-cordierite solid solution glass-ceramic body which comprises mixing a powdered glass frit, capable of crystallization to a glass-ceramic having alpha-cordierite solid solution as a primary crystal phase, with, as a first additive, at least 0.001% finely divided, pre-crystallized alpha-cordierite and, as a second additive, up to 5% of a nucleating agent which is  $\text{TiO}_2$ , forming a body from the mixture, and firing the body to sinter and crystallize the glass, the additives increasing the MOR of the body and stabilizing the CTE, preferably in the range of  $26\text{--}30 \times 10^{-7}/^{\circ}\text{C}$ .

In addition to the applications and patent already noted, the following patents may be of interest.

United States Patent No. 4,015,048 (Martin) discloses sinterable powdered glasses having the basic alpha-cordierite oxide components and modified by at least one modifying oxide selected from the group consisting of BaO, PbO, SrO and CaO. The modifiers are incorporated in the glass composition, not as dopants to the powdered glass.

United States Patent No. 3,778,242 (Francel et al.) discloses lead-zinc-borate sealing glasses mixed with a refractory oxide, such as beta-eucryptite, and a minute amount of a pre-crystallized lead-zinc-borate glass. The resulting sealing glass compositions are said to have an increased compressive stress, and to be useful in joining alumina ceramic components in microelectronic circuitry. The materials disclosed are distinctly different from those employed in the present invention.

There are numerous disclosures of alpha-cordierite glasses in the literature, including the Harrington et al. patent and the U.S.A Patents 4,897,509 and 4,906,514 previously noted. These are incorporated herein by reference.

The present invention is based on discoveries made in the course of developing a process for producing a sintered, alpha-cordierite solid solution glass-ceramic body.

Initially, glasses used in developing such glass-ceramic bodies were quenched from the melt and ball milled. The resulting powdered glass was mixed with organics to form a casting slurry. This slurry was tape cast, dried and fired. This removed the organics, and subsequently sintered and crystallized the glass to the glass-ceramic state.

The glass being used was a ZnO-modified glass as disclosed in the U.S.A Patent No. 4,897,509. The fully sintered and crystallized body was targeted to have a CTE of  $26\text{--}30 \times 10^{-7}/^{\circ}\text{C}$  and a MOR of at least 172.5 MPa (25 Kpsi). In the course of scaling up the material preparation procedure, a number of changes were made. One such change, from use of a ballmill to use of a vibratory mill, was found to have a profound effect. When this change was made, control of CTE, which had been marginal before, was completely lost.

X-ray diffraction (XRD) studies of the two differently milled materials were made at various stages in their sintering and crystallizing firing cycle. These revealed major variations occurring, both in the rate and degree of crystal phase development. Such studies showed that a metastable, mu-cordierite phase, having a beta-quartz crystal structure, developed initially in each material. This subsequently was replaced by an

alpha-cordierite type structure in each case. However, both the initial crystal development and the change initiated about 50 °C earlier in the ballmilled material. Thus, the mu-cordierite phase appeared at about 850 °C in the ballmilled material, but not until about 900 °C in the vibratory milled material.

Of more significance was the development of a secondary crystal phase, generally termed a gahnite phase and having a spinel structure. In the ballmilled material, this phase developed later than the change to alpha-cordierite. It tended to be in a small, but relatively consistent, ratio to the alpha-cordierite solid solution phase. In contrast, the spinel phase appeared coincident with the cordierite phase change in the vibratory milled material. It developed more erratically, but usually to a greater extent than in the ballmilled material. "Gahnite" is a generally accepted, mineral name for the zinc analog of spinel ( $\text{MgAl}_2\text{O}_4$ ). Gahnite and spinel form a continuous solid solution between the end members. XRD data indicate a very limited presence of Mg in the gahnite phase of the present materials. However, to the extent that solid solutions do occur and have the characteristic spinel-type crystal structure, they are encompassed within the term "gahnite crystal phase" as used herein.

The XRD studies, confirmed by chemical studies, revealed substantial contamination of the ballmilled material, but much less contamination in the vibratory milled material. These studies suggested a possible seeding effect, or other variable effect, by the contaminants on crystallization.

Accordingly, numerous additives, or dopants, were investigated to determine what, if any, seeding action might be exerted on the crystal phases involved. It was found that powdered, pre-crystallized, alpha-cordierite solid solution glass-ceramic had a remarkable effect as an additive. As little as 0.001% by weight tended to stabilize both the CTE and MOR of a fully sintered and crystallized glass-ceramic having a primary alpha-cordierite solid solution crystal phase.

The effect of the pre-crystallized additive appeared similar to that of the unintended contaminants from the ballmill. However, it appeared to be even more selective with respect to mu-cordierite, and consequent alpha-cordierite solid solution development. As an apparent result of the selective action, the MOR was within a normal range of 137.6 to 158.7 MPa (20 to 23 Kpsi), but the CTE was reduced to about  $21 \times 10^{-7}/^\circ\text{C}$ . That value was considerably below a desired range of 26-30 units, and approached the value of pure alpha-cordierite.

Accordingly, it became necessary to seek a further dopant to increase the CTE value without adverse effect on the MOR. Among the numerous dopants tried, titania was found to be most effective. Also, a new initial crystal phase, identifiable as a magnesium aluminum silicate phase having a petalite crystal structure, appeared along with the mu-cordierite. Both subsequently disappeared and were replaced by an alpha-cordierite solid solution phase.

At least a half percent of the titania is generally necessary for a significant effect. While up to 5% may be employed, over about 3% tends to interfere with densification. The optimum control appears to be obtained with titania.

The dopants of our invention are considered to be effective in stabilizing properties in any sintered alpha-cordierite solid solution glass-ceramic material. However, a preferred use is sintered alpha-cordierite glass-ceramic articles wherein the precursor glass is selected from the composition family set forth in the U.S.A. Patent No. 4,897,509. These glasses consist essentially, in calculated percent by weight on the oxide basis, of 2-18% MgO, up to 21% ZnO, the total MgO + ZnO being 10-25%, 20-38%  $\text{Al}_2\text{O}_3$ , 40-52%  $\text{SiO}_2$ , and 2-15% total of at least one oxide selected from up to 8%  $\text{K}_2\text{O}$  and/or  $\text{Rb}_2\text{O}$  and/or  $\text{Cs}_2\text{O}$ , up to 10% CaO and/or SrO and/or BaO and/or PbO, and up to 5%  $\text{B}_2\text{O}_3$ . The ZnO content should be sufficient to provide a secondary gahnite crystal phase in the glass-ceramic in an amount such that the ratio of alpha-cordierite to gahnite phase is within the range of 4:1 to 6:1, as shown by XRD peaks. The crystallized glass-ceramic will further have a CTE of  $25.6\text{-}30 \times 10^{-7}/^\circ\text{C}$ , and an MOR greater than 172.5 MPa (25 Kpsi).

In exploring the ramifications of the invention, the glass employed had the following composition, in calculated weight percent: 51.0%  $\text{SiO}_2$ , 24.8%  $\text{Al}_2\text{O}_3$ , 13.1% MgO, 3.1% BaO, 1.4%  $\text{B}_2\text{O}_3$  and 6.6% ZnO. The glass was drawn as thin ribbon, quenched and milled in a vibratory mill unless otherwise indicated. The dopants were separately milled for control purposes.

Numerous casting slips were prepared by blending glass and dopants with organics, including a binder, solvent, dispersant and plasticizer. The slips were then tape cast, with the aid of a 15 cm (6-inch) doctor blade, as sheets having green thicknesses of 0.25-0.75 mm (10-30 mils). The sheets, or tapes, thus formed, were dried, and stacked and laminated as necessary to provide a desired ultimate thickness.

The laminated bodies were fired at 300 to 550 °C to burn out organic. They were then heated to 950 °C to form sintered, alpha-cordierite solid solution glass-ceramic bodies. The glass frit softened at 600-750 °C, underwent viscous sintering at 750-900 °C, and crystallized at higher temperatures, e.g. at 950 °C.

The effect of pre-crystallized alpha-cordierite alone as a dopant may be seen from the data in TABLE 1. Therein, the CTE, MOR and relative X-ray peaks for alpha-cordierite: gahnite are shown for four levels of

dopant in both ball milled and vibratory milled glasses. Dopant level is in weight percent; CTE is in units of  $10^{-7}/^{\circ}\text{C}$ ; MOR is in MPa (Kpsi); X-ray peaks are measured by X-ray diffraction, and shown as C/G peaks.

TABLE 1

| Ball mill      |             |             |             |             |
|----------------|-------------|-------------|-------------|-------------|
| Doping level   | 0.00        | 0.05        | 0.1         | 0.2         |
| CTE            | 21.9        | 21.8        | 21.4        | 21.8        |
| MOR            | 188.4(27.3) | 186.3(27.0) | 202.9(29.4) | 185.6(26.9) |
| C/G peaks      | 100:18      | 100:17      | 100:19      | 100:18      |
| Vibratory mill |             |             |             |             |
| Doping level   | 0.00        | 0.05        | 0.1         | 0.2         |
| CTE            | 50.0        | 21.7        | 21.4        | 20.9        |
| MOR            | (86.9)12.6  | 192.5(27.9) | 211.1(30.6) | 199.4(28.9) |
| C/G peaks      | 100:62      | 100:19      | 100:18      | 100:17      |

TABLE 2 sets forth similar data, arranged in the same manner, for different doping levels of fumed  $\text{TiO}_2$ . The dopants were added to vibratory milled frit containing 0.05% pre-crystallized alpha-cordierite.

TABLE 2

| $\text{TiO}_2$ |             |             |             |             |
|----------------|-------------|-------------|-------------|-------------|
| Doping level   | 1.0         | 2.0         | 3.0         | 5.0         |
| CTE            | 25.6        | 28.3        | 30.5        | 32.2        |
| MOR            | 209.1(30.3) | 225.6(32.7) | 217.4(31.5) | 202.9(29.4) |
| C/G peaks      | 100:19      | 100:20      | 100:20      | 100:20      |

Further experiments were conducted to determine the effect of varying material particle size on properties. These tests were made using a dopant combination considered optimum, that is, 0.05% pre-crystallized cordierite and 2.0%  $\text{TiO}_2$ . The latter was used in its customary particle size of two  $\mu\text{m}$  (microns), and also in a sub  $\mu\text{m}$  size provided by fumed  $\text{TiO}_2$ . Also, the glass frit was used in two average particle sizes, 3.5  $\mu\text{m}$  (microns) and 2.1  $\mu\text{m}$  (microns).

No significant effects were noted on CTE values which remained about  $29 \times 10^{-7}/^{\circ}\text{C}$ . However, MOR values were substantially enhanced by reduction in particle size. Thus, double doping with normal particle materials increased the MOR value from about 151.8 MPa (22 Kpsi) to about 172.5 MPa (25 Kpsi). However use of the sub  $\mu\text{m}$   $\text{TiO}_2$  for doping raised the MOR to about 220.8 MPa (32 Kpsi). When the frit particle size was also decreased to 2.1  $\mu\text{m}$  (microns), an MOR of about 262.2 MPa (38 Kpsi) was observed. Thus, the invention provides means for attaining a sintered, glass-ceramic body having an alpha-cordierite solid solution primary crystal phase of stable CTE value in the  $26\text{-}30 \times 10^{-7}/^{\circ}\text{C}$  range and surprisingly high MOR values.

#### Claims

1. A sintered, alpha-cordierite solid solution, glass-ceramic body having a primary crystal phase with an alpha-cordierite structure and a secondary crystal phase with a gahnite structure, the relative amounts of the alpha-cordierite and gahnite crystal phases, as shown by XRD peaks, being in the range of about 4:1 to 6:1, the glass-ceramic body having a coefficient of thermal expansion in the range of  $25.6\text{-}30 \times 10^{-7}/^{\circ}\text{C}$  and a modulus of rupture of at least 172.5 MPa (25 Kpsi).
2. A sintered, alpha-cordierite solid solution glass-ceramic body in accordance with claim 1 wherein the chemical composition of the precursor glass, calculated in percent by weight on the oxide basis, consists essentially of 2-18%  $\text{MgO}$ , up to 21%  $\text{ZnO}$ , the  $\text{ZnO}$  content being sufficient to form a secondary gahnite crystal phase when the glass is crystallized, the total  $\text{MgO} + \text{ZnO}$  being 10-25%, 20-38%  $\text{Al}_2\text{O}_3$ , 40-52%  $\text{SiO}_2$  and 2-15% of at least one oxide selected from up to 8%  $\text{K}_2\text{O}$  and/or  $\text{Rb}_2\text{O}$



dopant in both ball milled and vibratory milled glasses. Dopant level is in weight percent; CTE is in units of  $10^{-7}/^{\circ}\text{C}$ ; MOR is in MPa (Kpsi); X-ray peaks are measured by X-ray diffraction, and shown as C/G peaks.

TABLE 1

| Ball mill      |             |             |             |             |
|----------------|-------------|-------------|-------------|-------------|
| Doping level   | 0.00        | 0.05        | 0.1         | 0.2         |
| CTE            | 21.9        | 21.8        | 21.4        | 21.8        |
| MOR            | 188.4(27.3) | 186.3(27.0) | 202.9(29.4) | 185.6(26.9) |
| C/G peaks      | 100:18      | 100:17      | 100:19      | 100:18      |
| Vibratory mill |             |             |             |             |
| Doping level   | 0.00        | 0.05        | 0.1         | 0.2         |
| CTE            | 50.0        | 21.7        | 21.4        | 20.9        |
| MOR            | (86.9)12.6  | 192.5(27.9) | 211.1(30.6) | 199.4(28.9) |
| C/G peaks      | 100:62      | 100:19      | 100:18      | 100:17      |

TABLE 2 sets forth similar data, arranged in the same manner, for different doping levels of fumed  $\text{TiO}_2$ . The dopants were added to vibratory milled frit containing 0.05% pre-crystallized alpha-cordierite.

TABLE 2

| $\text{TiO}_2$ |             |             |             |             |
|----------------|-------------|-------------|-------------|-------------|
| Doping level   | 1.0         | 2.0         | 3.0         | 5.0         |
| CTE            | 25.6        | 28.3        | 30.5        | 32.2        |
| MOR            | 209.1(30.3) | 225.6(32.7) | 217.4(31.5) | 202.9(29.4) |
| C/G peaks      | 100:19      | 100:20      | 100:20      | 100:20      |

Further experiments were conducted to determine the effect of varying material particle size on properties. These tests were made using a dopant combination considered optimum, that is, 0.05% pre-crystallized cordierite and 2.0%  $\text{TiO}_2$ . The latter was used in its customary particle size of two  $\mu\text{m}$  (microns), and also in a sub  $\mu\text{m}$  size provided by fumed  $\text{TiO}_2$ . Also, the glass frit was used in two average particle sizes, 3.5  $\mu\text{m}$  (microns) and 2.1  $\mu\text{m}$  (microns).

No significant effects were noted on CTE values which remained about  $29 \times 10^{-7}/^{\circ}\text{C}$ . However, MOR values were substantially enhanced by reduction in particle size. Thus, double doping with normal particle materials increased the MOR value from about 151.8 MPa (22 Kpsi) to about 172.5 MPa (25 Kpsi). However use of the sub  $\mu\text{m}$   $\text{TiO}_2$  for doping raised the MOR to about 220.8 MPa (32 Kpsi). When the frit particle size was also decreased to 2.1  $\mu\text{m}$  (microns), an MOR of about 262.2 MPa (38 Kpsi) was observed. Thus, the invention provides means for attaining a sintered, glass-ceramic body having an alpha-cordierite solid solution primary crystal phase of stable CTE value in the  $26\text{-}30 \times 10^{-7}/^{\circ}\text{C}$  range and surprisingly high MOR values.

#### Claims

1. A sintered, alpha-cordierite solid solution, glass-ceramic body having a primary crystal phase with an alpha-cordierite structure and a secondary crystal phase with a gahnite structure, the relative amounts of the alpha-cordierite and gahnite crystal phases, as shown by XRD peaks, being in the range of about 4:1 to 6:1, the glass-ceramic body having a coefficient of thermal expansion in the range of  $25.6\text{-}30 \times 10^{-7}/^{\circ}\text{C}$  and a modulus of rupture of at least 172.5 MPa (25 Kpsi).
2. A sintered, alpha-cordierite solid solution glass-ceramic body in accordance with claim 1 wherein the chemical composition of the precursor glass, calculated in percent by weight on the oxide basis, consists essentially of 2-18% MgO, up to 21% ZnO, the ZnO content being sufficient to form a secondary gahnite crystal phase when the glass is crystallized, the total MgO + ZnO being 10-25%, 20-38%  $\text{Al}_2\text{O}_3$ , 40-52%  $\text{SiO}_2$  and 2-15% of at least one oxide selected from up to 8%  $\text{K}_2\text{O}$  and/or  $\text{Rb}_2\text{O}$



and/or  $\text{Cs}_2\text{O}$ , up to 10%  $\text{CaO}$  and/or  $\text{SrO}$  and/or  $\text{BaO}$  and/or  $\text{PbO}$ , and up to 5%  $\text{B}_2\text{O}_3$ .

3. A sintered, alpha-cordierite solid solution glass-ceramic body in accordance with claim 2 wherein the precursor glass consists of 51%  $\text{SiO}_2$ , 24.8%  $\text{Al}_2\text{O}_3$ , 13.1%  $\text{MgO}$ , 3.1%  $\text{BaO}$ , 1.4%  $\text{B}_2\text{O}_3$  and 6.6%  $\text{ZnO}$ .
4. A sintered, alpha-cordierite solid solution glass-ceramic body in accordance with any of claims 1-4 containing 0.5-5%  $\text{TiO}_2$  as an additive.
5. A method of producing a sintered, alpha-cordierite solid solution glass-ceramic body which comprises,
  - a. providing a glass free from devitrification and being capable of being nucleated and crystallized to form a glass-ceramic material having a primary crystal phase of alpha-cordierite solid solution,
  - b. pulverizing the glass to a powder,
  - c. adding a combination of two dopants to the glass powder to control properties in the sintered body, one dopant being at least about 0.001% by weight of finely divided, pre-crystallized alpha-cordierite solid solution, and the second being up to about 5% by weight of a nucleating agent which is  $\text{TiO}_2$ ,
  - d. shaping the doped powder to desired form, and
  - e. firing the shaped body at low temperatures to burnt out organics, and
  - f. heating it to above  $900^\circ\text{C}$  to create a primary crystal phase with an alpha-cordierite structure and a secondary crystal phase with a gahnite structure.
6. A method in accordance with claim 5 wherein the second dopant is 1 to 3% and/or has a particle size below  $3.5\text{ }\mu\text{m}$  (microns).
7. A method in accordance with claim 6 wherein the  $\text{TiO}_2$  is fumed  $\text{TiO}_2$ .
8. A method in accordance with claim 7 wherein the content of  $\text{TiO}_2$  or fumed  $\text{TiO}_2$  is about 2%.
9. A method in accordance with claim 5, 6, 7 or 8 wherein the glass is pulverized to an average particle size less than about  $5\text{ }\mu\text{m}$  (microns), and/or sintered at a temperature up to about  $900^\circ\text{C}$  and crystallized to the glass-ceramic state at a higher temperature.
10. A method in accordance with any one of claims 5-9, wherein the glass is quenched from the melt.

#### Patentansprüche

1. Gesinterter Glaskeramikkörper mit einem Alpha-Cordierit-Mischkristall mit einer primären Kristallphase mit einer Alpha-Cordierit-Struktur und einer sekundären-Kristallphase mit einer Gahnit-Struktur, wobei die relativen Mengen der Alpha-Cordierit- und Gahnitkristallphasen, angegeben durch XRD-Peaks, im Bereich von etwa 4:1 bis 6:1 liegen und der Glaskeramikkörper einen Wärmeausdehnungskoeffizienten im Bereich von  $25,6$  bis  $30 \times 10^{-7}/^\circ\text{C}$  und ein Bruchmodul von wenigstens  $172,5\text{ MPa}$  ( $25\text{ Kpsi}$ ) aufweist.
2. Gesinterter Glaskeramikkörper mit einem Alpha-Cordierit-Mischkristall nach Anspruch 1, worin die chemische Zusammensetzung des Vorläuferglases, berechnet in Gew.-%en auf Oxidbasis, im wesentlichen besteht aus 2-18%  $\text{MgO}$ , bis 21%  $\text{ZnO}$ , wobei der  $\text{ZnO}$ -Gehalt ausreicht, um eine sekundäre Gahnit-Kristallphase zu bilden, wenn das Glas kristallisiert wird, wobei der Gesamtgehalt  $\text{MgO} + \text{ZnO}$  bei 10-25% liegt, 20-38%  $\text{Al}_2\text{O}_3$ , 40-52%  $\text{SiO}_2$  und 2-15% wenigstens eines Oxids, ausgewählt aus bis zu 8%  $\text{K}_2\text{O}$  und/oder  $\text{Rb}_2\text{O}$  und/oder  $\text{Cs}_2\text{O}$ , bis zu 10%  $\text{CaO}$  und/oder  $\text{SrO}$  und/oder  $\text{BaO}$  und/oder  $\text{PbO}$ , und bis zu 5%  $\text{B}_2\text{O}_3$ .
3. Gesinterter Glaskeramikkörper mit einem Alpha-Cordierit-Mischkristall nach Anspruch 2, worin das Vorläuferglas aus 51%  $\text{SiO}_2$ , 24,8%  $\text{Al}_2\text{O}_3$ , 13,1%  $\text{MgO}$ , 3,1%  $\text{BaO}$ , 1,4%  $\text{B}_2\text{O}_3$  und 6,6%  $\text{ZnO}$  besteht.
4. Gesinterter Glaskeramikkörper mit einem Alpha-Cordierit-Mischkristall nach irgendeinem der Ansprüche 1-4, der 0,5-5%  $\text{TiO}_2$  als ein Additiv enthält.



5. Verfahren zur Herstellung eines gesinterten Glaskeramikkörpers mit einem Alpha-Cordierit-Mischkristall, wobei das Verfahren die folgenden Schritte aufweist:
  - a. Bereitstellen eines entglasungsfreien Glases, das einer Kristallkeimbildung und einer Kristallisation unterzogen werden kann, um ein Glaskeramikmaterial mit einer primären Kristallphase eines Alpha-Cordierit-Mischkristalls zu bilden,
  - b. Pulverisieren des Glases zu einem Pulver,
  - c. Zugabe einer Kombination aus zwei Dotierungsmitteln zum Glaspulver, um die Eigenschaften im gesinterten Körper zu regulieren, wobei ein Dotierungsmittel aus wenigstens etwa 0,001 Gew.-% eines fein zerteilten, vorkristallisierten Alpha-Cordierit-Mischkristalls und das zweite Dotierungsmittel aus bis zu etwa 5 Gew.-% eines Keimbildungsmittels, das  $\text{TiO}_2$  ist, besteht,
  - d. Formen des dotierten Pulvers zur gewünschten Form, und
  - e. Brennen des geformten Körpers bei niedrigen Temperaturen, um die organischen Stoffe auszubrennen, und
  - f. Erhitzen des Körpers auf über  $900^\circ\text{C}$ , um eine primäre Kristallphase mit einer Alpha-Cordierit-Struktur und einer sekundären Kristallphase mit einer Gahnitstruktur zu erzeugen.
6. Verfahren nach Anspruch 5, worin das zweite Dotierungsmittel 1-3% und/oder eine Teilchengröße von unter  $3,5\text{ }\mu\text{m}$  (Micron) aufweist.
7. Verfahren nach Anspruch 6, worin das  $\text{TiO}_2$  verdampftes  $\text{TiO}_2$  ist.
8. Verfahren nach Anspruch 7, worin der Gehalt an  $\text{TiO}_2$  oder verdampftem  $\text{TiO}_2$  etwa 2% beträgt.
9. Verfahren nach Anspruch 5, 6, 7 oder 8, worin das Glas zu einer mittleren Teilchengröße von unter etwa  $5\text{ }\mu\text{m}$  (Micron) pulverisiert und/oder bei einer Temperatur von bis zu etwa  $900^\circ\text{C}$  gesintert und zum Glaskeramikzustand bei einer höheren Temperatur kristallisiert wird.
10. Verfahren nach irgendeinem der Ansprüche 5-9, worin das Glas aus der Schmelze schockgeköhlt wird.

### 30 Revendications

1. Une pièce frittée en vitrocéramique à solution solide de cordiérite alpha, comportant une phase cristalline principale à structure de cordiérite alpha et une phase cristalline secondaire à structure de gahnite, les proportions relatives des phases cristallines de cordiérite alpha et de gahnite, telles qu'indiquées par les extrema de diffraction de rayons X, se situant dans l'intervalle d'environ 4:1 à 6:1, la pièce de vitrocéramique présentant un coefficient de dilatation thermique se situant dans l'intervalle de  $25,6 \times 10^{-7}/^\circ\text{C}$  à  $30 \times 10^{-7}/^\circ\text{C}$  et un module de rupture d'au moins 172,5 MPa.
2. Une pièce frittée en vitrocéramique à solution solide de cordiérite alpha selon la revendication 1 dans laquelle la composition chimique du verre précurseur, calculée en pourcentages pondéraux sur la base des oxydes, est essentiellement constituée de 2 à 18 % de  $\text{MgO}$ , jusqu'à 21 % de  $\text{ZnO}$ , la teneur en  $\text{ZnO}$  étant suffisante pour former une phase cristalline secondaire de gahnite lors de la cristallisation du verre, la teneur totale en  $\text{MgO} + \text{ZnO}$  étant de 10 à 25 %, 20 à 38 % d' $\text{Al}_2\text{O}_3$ , 40 à 52 % de  $\text{SiO}_2$  et 2 à 15 % d'au moins un oxyde choisi parmi jusqu'à 8 % de  $\text{K}_2\text{O}$  et/ou de  $\text{Rb}_2\text{O}$  et/ou  $\text{Cs}_2\text{O}$ , jusqu'à 10 % de  $\text{CaO}$  et/ou de  $\text{SrO}$  et/ou de  $\text{BaO}$  et/ou de  $\text{PbO}$ , et jusqu'à 5 % de  $\text{B}_2\text{O}_3$ .
3. Une pièce frittée en vitrocéramique à solution solide de cordiérite alpha selon la revendication 2 dans lequel le verre précurseur est constitué de 51 % de  $\text{SiO}_2$ , 24,8 % d' $\text{Al}_2\text{O}_3$ , 13,1 % de  $\text{MgO}$ , 3,1 % de  $\text{BaO}$ , 1,4 % de  $\text{B}_2\text{O}_3$  et 6,6 % de  $\text{ZnO}$ .
4. Une pièce frittée en vitrocéramique à solution solide de cordiérite alpha selon l'une quelconque des revendications 1 à 4, renfermant 0,5 à 5 % de  $\text{TiO}_2$  en tant qu'additif.
5. Un procédé de production d'une pièce frittée en vitrocéramique à solution solide de cordiérite alpha qui comprend les opérations consistant :
  - a. à prendre un verre exempt de dévitrification et apte à être nucléé et cristallisé pour former une matière vitrocéramique comportant une phase cristalline principale de cordiérite alpha en solution solide,



- b. à réduire le verre en une poudre,  
c. à ajouter à la poudre de verre une combinaison de deux agents dopants visant à agir sur les propriétés de la pièce frittée, l'un des agent dopants étant au moins environ 0,001 % en poids de solution solide de cordiérite alpha précristallisée, et le second étant jusqu'à environ 5 % en poids d'un agent de nucléation qui est  $\text{TiO}_2$ ,  
d. à façonner la poudre dopée à la forme désirée,  
e. à cuire la pièce façonnée à de basses températures pour pyrolyser les matières organiques, et  
f. à la chauffer au-dessus de 900 °C pour donner naissance à une phase cristalline principale à structure de cordiérite alpha et à une phase cristalline secondaire à structure de gahnite.

6. Un procédé selon la revendication 5 dans lequel le second agent dopant est présent en proportion de 1 à 3 % et/ou a une granulométrie inférieure à 3,5  $\mu\text{m}$ .  
7. Un procédé selon la revendication 6 dans lequel le  $\text{TiO}_2$  est du  $\text{TiO}_2$  de fumée.  
8. Un procédé selon la revendication 7 dans lequel la teneur en  $\text{TiO}_2$  ou en  $\text{TiO}_2$  de fumée est d'environ 2 %.  
9. Un procédé selon la revendication 5, 6, 7 ou 8 dans lequel le verre est réduit en une poudre de granulométrie moyenne inférieure à environ 5  $\mu\text{m}$ , et/ou est fritté à une température pouvant aller jusqu'à environ 900 °C et cristallisé en une matière vitrocéramique à une température plus élevée.  
10. Un procédé selon l'une quelconque des revendications 5 à 9, dans lequel le verre est séparé de la masse fondue par trempe thermique.