



(51) International Patent Classification:

C03C 3/085 (2006.01) *C03C 10/14* (2006.01)
C03C 4/02 (2006.01) *C03C 4/10* (2006.01)

(21) International Application Number:

PCT/EP2013/074385

(22) International Filing Date:

21 November 2013 (21.11.2013)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1261122 22 November 2012 (22.11.2012) FR

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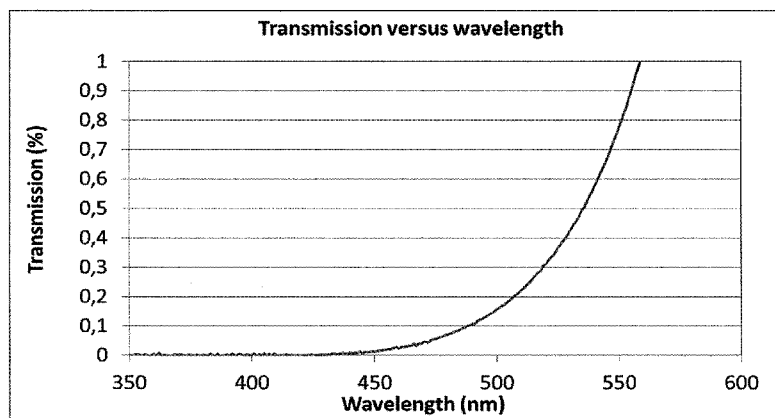
(81) **Designated States** (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) **Designated States** (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) **Title:** BETA-QUARTZ GLASS-CERAMICS WITH A CONTROLLED TRANSMISSION CURVE AND A HIGH IRON OXIDE CONTENT; ARTICLES COMPRISING SAID GLASS-CERAMICS, AND PRECURSOR GLASSES.

**FIG 1**

(57) **Abstract:** β -quartz lithium aluminosilicate (LAS) glass-ceramics contain neither arsenic oxide nor antimony oxide, are fired with tin oxide and include vanadium oxide, chromium oxide and a high iron oxide content (>950 ppm), and have a controlled transmission curve. Articles such as cook-tops can be made from such glass-ceramics.

**β -QUARTZ GLASS-CERAMICS WITH A CONTROLLED TRANSMISSION CURVE
AND A HIGH IRON OXIDE CONTENT; ARTICLES COMPRISING SAID GLASS-
CERAMICS, AND PRECURSOR GLASSES**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of priority under 35 U.S.C. § 119 of French Patent Application Serial No. 1261122 filed on November 22, 2012, the entire content of which is hereby incorporated by reference.

FIELD

[0002] The disclosure relates generally to lithium aluminosilicate (LAS) type glass-ceramics, and more particularly to darkened LAS glass-ceramics having a solid solution of β -quartz as the predominant crystalline phase. Also disclosed are articles formed from such glass-ceramics, precursor glasses of such glass-ceramics, and methods for obtaining such glass-ceramics and articles.

BACKGROUND

[0003] The disclosure relates to the field of β -quartz glass-ceramics. More particularly it relates to tin-fined, darkened glass-ceramics of the lithium aluminosilicate type, containing a solid solution of β -quartz as the main crystalline phase, essentially free of As_2O_3 and of Sb_2O_3 , articles comprising said glass-ceramics, and lithium aluminosilicate glasses as precursors of such glass-ceramics, as well as methods for forming said glass-ceramics and said articles.

[0004] With view to the toxicity of As_2O_3 and of increasingly strict regulations in effect, this toxic fining compound is desirably no longer used. For environmental considerations, it is also desired to no longer use Sb_2O_3 and not to use halogens, such as F and Br, which would have been able to replace at least partly said fining agents As_2O_3 and Sb_2O_3 .

[0005] SnO_2 has been proposed as a replacement fining agent. It is notably used when the precursor glass of the glass-ceramic (glass plate precursors of glass-ceramic plates, in fact) is obtained by floating. Indeed, applied with glasses containing As_2O_3 and/or Sb_2O_3 in their composition, such a floating method generates glass plates with a metal deposit at their surface (a metal deposit resulting from the reduction of As_2O_3 and/or Sb_2O_3).

[0006] The use of SnO_2 as a fining agent however has two major drawbacks. It is less efficient than As_2O_3 (and, in absolute terms, it should therefore be used in a relatively large amount, which is not without posing any problems, more particularly of devitrification) and, as a more powerful reducing agent than As_2O_3 and Sb_2O_3 , it is responsible for the appearance of an undesirable yellowish coloration during ceramming. This second drawback is of course a nuisance when it is sought to obtain transparent, essentially colorless glass-ceramics. This yellowish coloration results from Sn-Fe, Sn-Ti and Ti-Fe interactions, i.e., by way of charge transfer.

[0007] Patent application DE 10 2008 050 263 describes glass-ceramics, the composition of which is optimized with reference to transmission in the visible range (red, but also blue, green). The composition of said glass-ceramics contains SnO_2 as a fining agent, Fe_2O_3 and V_2O_5 as "main" coloring agents with a specific $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ proportion as well as optionally other coloring agents (chromium, manganese, cobalt, nickel, copper, selenium, rare earth and molybdenum compounds...). It is also indicated in this document that the presence of these other coloring agents is detrimental to optical transmission in the infrared. Thus, in the examples, no trace of chromium compounds as an additional coloring agent is found. It is also indicated in this document that the Fe_2O_3 content negatively affects transmission in the infrared. This is confirmed by the examples since when Fe_2O_3 is present in a content of 0.15% the characteristics at 1,600 nm are degraded and are less than 50%. The optical properties of the compositions described in this document fundamentally differ in terms of transmission in the visible compared to β -quartz glass-ceramic according to the present invention since the latter does not transmit blue light.

[0008] Patent application DE 10 2010 032 112 describes glass-ceramics, the composition of which is optimized with reference to transmission in the blue spectrum. In the examples, no trace of chromium compounds as an additional coloring agent is found. The optical properties of the compositions described in this document fundamentally differ in terms of transmission in the visible compared to the β -quartz glass-ceramic according to the present invention since the latter does not transmit blue light.

[0009] Patent application WO2011/089327 describes glass-ceramics, the composition of which is optimized with reference to the transmission at the wavelength between 400 and 500 nm (green or blue spectrum) which should be of between 0.2 and 4%. Indeed the glass

ceramics will be part of a display unit containing a light emitting device which has a transmission of non-zero intensity at said wavelength. In the examples the Cr_2O_3 content is very low and this document describes Cr_2O_3 as an impurity whose content should be kept low in order to obtain the desired properties. The optical properties of the compositions described in this document fundamentally differ in terms of transmission in the visible compared to the β -quartz glass-ceramic according to the present invention since the latter does not transmit blue light. This difference is visible in the optical transmission spectrum obtained (when comparing Figure 1 according to the present invention and figure 3 of this document).

[00010] Patent application WO2012/156444 teaches that to obtain the same optical properties as Kerablack[®] glass-ceramics by using SnO_2 as fining agent, it is necessary to use an SnO_2 content comprised between 0.3 and 0.6%, a V_2O_5 content comprised between 0.025 and 0.06%, a Cr_2O_3 content comprised between 0.01 and 0.04% and a Fe_2O_3 content comprised between 0.05 and 0.15%. The SnO_2 contents are even advantageously mentioned as before to be $> 0.3\%$ and a comparative example D with a SnO_2 content of 0.28% is indicated as not filling the optical transmission properties desired. Thus this document does not suggest that the optical properties desired can be preserved with a SnO_2 content below 0.3% and a high Fe_2O_3 content (greater than 0.095% and can go up to 0.32%).

[00011] In view of the foregoing, it would be advantageous to provide colored glass-ceramic compositions that are substantially free of As_2O_3 and Sb_2O_3 , and which possess desired optical properties particularly for their use in stove cook-tops.

BRIEF SUMMARY

[00012] A glass-ceramic of the lithium aluminosilicate (LAS) type contains a β -quartz solid solution as the predominant crystalline phase and, for a thickness of 4 mm, has an integrated optical transmission, T_v , in the visible range, of 0.8 to 2%, an optical transmission at 625 nm of more than 3.5%, an optical transmission at 950 nm between 40 and 70%, and an optical transmission at 1,600 nm between 50 and 75%.

[00013] The LAS composition, expressed as percentages by weight of oxides, comprises 0.2 to less than 0.3% SnO_2 , 0.025 to 0.2% V_2O_5 , 0.01 to 0.04% Cr_2O_3 , greater than 0.095 to 0.32% Fe_2O_3 , and less than 0.1% $\text{As}_2\text{O}_3 + \text{Sb}_2\text{O}_3$. A ratio $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ of the iron oxide and vanadium oxide content is from 1 to 4.

[00014] Additional features and advantages of the subject matter of the present disclosure will be set forth in the detailed description which follows, and in part will be readily apparent to those skilled in the art from that description or recognized by practicing the subject matter of the present disclosure as described herein, including the detailed description which follows as well as the claims.

[00015] It is to be understood that both the foregoing general description and the following detailed description present embodiments of the subject matter of the present disclosure, and are intended to provide an overview or framework for understanding the nature and character of the subject matter of the present disclosure as it is claimed. Additionally, the descriptions are meant to be merely illustrative, and are not intended to limit the scope of the claims in any manner.

DETAILED DESCRIPTION

[00016] Glass-ceramics colored with vanadium oxide (V_2O_5) can have a coefficient of thermal expansion close to zero in order to withstand thermal shock. For use as cooktops, they may possess a specific suite of optical transmission properties. In embodiments, the optical transmission curves for a 4 mm thick plate of the glass-ceramic include an integrated optical transmission T_v , in the visible range (i.e., between 380 and 780 nm) measured with the illuminant D65 with an angle of 2° to the observer of 0.8 to 2% (e.g., 1 to 1.7%). If the integrated optical transmission is greater than 2%, heating elements located under the plate will not be properly concealed when the cooktop is not in operation. If the integrated optical transmission is less than 0.8%, the heating elements will not be suitable visible during operation, which may pose a safety hazard.

[00017] In addition to the integrated transmission, the optical transmission at 625 nm (T_{625}) in embodiments is greater than 3.5% (e.g., greater than 4%). With this, it is possible to see red displays disposed under the plate. The optical transmission at 950 nm (near infrared), (T_{950}) can be between 40 and 70% (e.g., from 50 to 70%). A near-IR transmission greater than or equal to 50% makes it possible to use conventional electronic control buttons, emitting and receiving at these wavelengths. The infrared optical transmission at 1,600 nm (T_{1600}) can be between 50 and 75%. If the infrared optical transmission is less than 50%, the heating performances of the plates are not satisfactory, and if said infrared optical

transmission is greater than 75%, the heating performance may be excessive and, for example, induce dangerous heating of materials placed in proximity to the plate.

[00018] Boiling point measurement tests (of water) have shown that a transmission at 1,600 nm greater than or equal to 50% is sufficient to provide a satisfactory boiling time.

[00019] Boiling point tests were carried out by placing the glass-ceramic to be tested on a hotplate with a diameter of 145 mm. Two tests were carried out by calibrating the hotplate so that the maximum surface temperature of the glass-ceramic was 560°C or 620°C. In each case, the time required to raise the temperature of a liter of water from 20 to 98°C was measured. The water was placed in a pot covered with aluminum of the same diameter as the hotplate. Two comparative glass-ceramics were tested: Kerablack® glass-ceramic with a transmission of 67.9% at 1,600 nm and a glass-ceramic called "Glass-ceramic T" with a transmission of 54.9% at 1,600 nm. Results of the two materials are not significantly different (to be considered significantly different, the difference between two boiling times must exceed 30s).

[00020] Table 1. Boiling point data for comparative glass-ceramic plates

Glass-ceramic	"T"		Kerablack® Glass-Ceramic	
Transmission at 1,600 nm	54.9%		67.9%	
Maximum surface temperature	560°C	620°C	560°C	620°C
Boiling time				
Test 1	7' 14"	6' 27"	6' 40"	6' 29"
Test 2	9' 26"	7' 29"	9' 26"	7' 31"

[00021] While the boiling point data are satisfactory, each of the comparative compositions contains arsenic oxide as a fining agent. During the successive glass-ceramic formation steps of melting and fining of a vitrifiable load of raw materials, shaping, and crystallization (i.e., ceramming), the avoidance of arsenic oxide (and antimony oxide) as fining agents is desirable.

[00022] In various embodiments, glass-ceramics are disclosed having comparable optical transmission properties to Kerablack® glass-ceramic plates, but without the inclusion of arsenic oxide or antimony oxide in the composition.

[00023] Example glass-ceramic compositions include Fe₂O₃ and relatively low SnO₂ content. Relatively high Fe₂O₃ content enables the use of starting materials that are less pure

and thus less expensive, including a greater quantity of recycled materials (cullet). However, it is believed that the addition of iron oxide has an impact on the optical qualities of the product obtained, in terms of transmission in the visible as well as in the infrared.

[00024] Meanwhile, SnO_2 is an expensive raw material. Therefore, a relatively low content of tin oxide makes it possible to limit the raw material cost as well as minimize adverse effects associated with the condensation of tin metal within the furnace.

[00025] In such a context, disclosed are glass-ceramic compositions that are free of arsenic (and of antimony) or containing only traces thereof, including tin oxide and a high iron oxide content, and having an optimized optical transmission curve in the visible and infrared ranges. Such glass ceramics can be fired at conventional firing temperatures, generally between 1,600 and 1,700°C.

[00026] The disclosed compositions include relatively low proportions of SnO_2 (which provides a fining agent function and a reducing agent function, where the reducing agent participates in the final coloration of the product), high proportions of Fe_2O_3 , and one or more of V_2O_5 and Cr_2O_3 as coloring species.

[00027] In embodiments, the disclosed glass-ceramics are lithium aluminosilicate (LAS) type glass-ceramics containing Li_2O , Al_2O_3 and SiO_2 as essential constituents of the β -quartz solid solution, where a β -quartz solid solution is the predominant crystalline phase accounting for more than 80% by weight of the total crystalline phase of the crystallized fraction.

[00028] The disclosed glass-ceramics exhibit optical transmission characteristics, for a thickness of 4 mm of: $0.8\% \leq T_v \leq 2\%$, for example, $1\% \leq T_v \leq 1.7\%$, $T_{625} > 3.5\%$, for example, $T_{625} > 4\%$, $40\% \leq T_{950} \leq 70\%$, for example, $50\% \leq T_{950} \leq 70\%$, and $50\% \leq T_{1600} \leq 75\%$.

[00029] In further embodiments, the composition of the glass-ceramics, expressed as percentages by weight of oxides, includes SnO_2 : 0.2 to <0.3%, for example 0.23 to 0.29%, V_2O_5 : 0.025 to 0.2%, for example, 0.05 to 0.2%, Cr_2O_3 : 0.01 to 0.04%, Fe_2O_3 : >0.095 to 0.32%, $\text{As}_2\text{O}_3 + \text{Sb}_2\text{O}_3$: < 0.1%, and a ratio $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ of 1 to 4, for example 1 to 2. In contrast, Kerablack[®] glass-ceramics contain roughly 700 ppm of Fe_2O_3 .

[00030] The glass-ceramics have a dark color and are suitable for use, for example, as cooktops.

[00031] The glass-ceramics contain neither any As_2O_3 , nor any Sb_2O_3 or only contain traces of at least one of these compounds, SnO_2 being present instead of and in place of these

conventional fining agents. If traces of at least one of these compounds are present, this is as a contaminating product, which is likely due to the presence of recycled materials in the vitrifiable load of raw materials. In any case, only traces of these toxic compounds are likely to be present: $\text{As}_2\text{O}_3 + \text{Sb}_2\text{O}_3 < 1,000 \text{ ppm}$.

[00032] The compositions include tin oxide. The content of tin oxide can be controlled to achieve the desired fining while avoiding devitrification or adverse effects on the color package. Notably, SnO_2 is capable of reducing vanadium and the iron present during ceramming. In embodiments, the SnO_2 content ranges from 0.2 to $< 0.3 \text{ wt.}\%$, for example 0.23 to 0.29%, 0.24% to 0.29%, 0.25 to 0.28%, or 0.25 to 0.27%. The measure uncertainty of the SnO_2 content is of $\pm 50 \text{ ppm}$ ($\pm 0.005\%$).

[00033] Vanadium oxide is used as a coloring agent. Indeed, V_2O_5 in the presence of SnO_2 may significantly darken the glass during its ceramming. V_2O_5 is responsible for absorption mainly below 700 nm and it is possible in its presence to retain sufficiently high transmission in the infrared. An amount of V_2O_5 between 0.025 - 0.2% (i.e., between 250 and 2,000 ppm) may be used. In embodiments, the V_2O_5 content is between 0.03 and 0.2%, such as between 0.05 and 0.2%, between 0.06 and 0.2%, i.e., $> 0.06 - 0.2\%$, or between 0.07 and 0.2%.

[00034] It is challenging in a glass-ceramic comprising both SnO_2 and V_2O_5 to obtain the sought after integrated optical transmission (T_v) and the required optical transmission at 625 nm (T_{625}). Indeed, insofar that the absorption due to vanadium is relatively high at this wavelength (625 nm), when an acceptable value is reached for the integrated optical transmission, the value of the optical transmission at 625 nm may be too low and vice versa.

[00035] Applicants have solved the challenge by combining chromium oxide with vanadium oxide to create a coloring package (comprising V_2O_5 , Cr_2O_3 and Fe_2O_3) capable of providing the desired optical properties.

[00036] Chromium oxide (Cr_2O_3) can be used as a darkening agent in the visible range (400 – 600nm) while retaining high transmission in the wavelengths between 600 and 800 nm. The amount of Cr_2O_3 may range from 0.01 to 0.04% by weight. For instance, the Cr_2O_3 content may range from $>0.015 - 0.04\%$, e.g., $>0.015 - 0.035\%$ or $0.016 - 0.035\%$.

[00037] The glass-ceramics thus exhibit very low transmission in the blue range. For a thickness of 4 mm, the disclosed glass-ceramics generally have an optical transmission at 450

nm of less than 0.1% ($T_{450} < 0.1\%$), and/or an optical transmission at 465 nm of less than 0.1% ($T_{465} < 0.1\%$).

[00038] Iron oxide promotes absorption mainly in the infrared. In order to make efficient use of recycled products and low-cost starting materials, the Fe_2O_3 content may be greater than 950 ppm, e.g., at least 1,000 ppm. If the Fe_2O_3 content exceeds 3,200 ppm, however, absorption in the infrared may be too high. Such a high Fe_2O_3 content may also complicate the melting and fining processes. In example glass-ceramics, the iron oxide content is between 1,000 and 3,000 ppm, e.g., between 1,200 and 2,900 ppm, or between 1,500 and 2,900 ppm. It was surprisingly observed that a transmission at 1,600 nm greater than 50% could be obtained with iron oxide contents up to 3,200 ppm. Further, iron oxide content in the range of 950 to 3200 ppm promotes fining in combination with a relatively low amount of tin oxide. The combination of a relatively low SnO_2 content and high iron oxide content is thus particularly relevant both to decreasing costs and to maintaining proper fining capacities. The measure uncertainty of the Fe_2O_3 content is of ± 50 ppm ($\pm 0.005\%$).

[00039] In the visible range, iron is also involved in the coloration process. Its effect within the disclosed compositions may be compensated by that of the vanadium. It was observed that for an Fe_2O_3 content between 900 and 3,200 ppm, transmission in the visible range increased with increasing iron content. It is believed that over this range of iron content, tin oxide preferentially reduces Fe_2O_3 rather than V_2O_5 . Such lightening of the glass-ceramic may then be compensated by controlling the V_2O_5 content. Thus, in embodiments, the $\text{Fe}_2\text{O}_3/(\text{V}_2\text{O}_5)$ ratio ranges from 1 to 4, e.g., 1 to 2 or 1.3 to 1.8.

[00040] In addition to V_2O_5 , Cr_2O_3 and Fe_2O_3 , other coloring agent such as CoO , MnO_2 , NiO , CeO_2 may be included. In order to avoid significantly modifying the optical transmission curve, such additional colorants may be limited. CoO , for example, may be present in a very small amount insofar that it strongly absorbs in the infrared and at 625 nm. The disclosed glass-ceramics may include less than 200 ppm, e.g., less than 100 ppm of CoO .

[00041] According to further embodiments, the glass-ceramics do not contain any fining auxiliaries such as F and Br, except for inevitable traces. This is particularly advantageous considering the toxicity of these components.

[00042] In addition to SnO_2 , V_2O_5 , Cr_2O_3 and Fe_2O_3 in the weight percentages specified above (with $\text{As}_2\text{O}_3 + \text{Sb}_2\text{O}_3 < 1,000$ ppm), the glass-ceramic compositions may include:

SiO ₂	60 - 72
Al ₂ O ₃	18 - 23
Li ₂ O	2.5 - 4.5
MgO	0 - 3
ZnO	0 - 3
TiO ₂	1.5 - 4
ZrO ₂	0 - 2.5
BaO	0 - 5
SrO	0 - 5
BaO + SrO	0 - 5
CaO	0 - 2
Na ₂ O	0 - 1.5
K ₂ O	0 - 1.5
P ₂ O ₅	0 - 5
B ₂ O ₃	0 - 2.

[00043] According to embodiments, the glass-ceramics may have a composition consisting essentially of at least 98% by weight, e.g., at least 99% by weight, or even 100% by weight of SnO₂, V₂O₅, Cr₂O₃, Fe₂O₃, As₂O₃, Sb₂O₃, SiO₂, Al₂O₃, Li₂O, MgO, ZnO, TiO₂, ZrO₂, BaO, SrO, CaO, Na₂O, K₂O, P₂O₅ and B₂O₃. A corresponding base glass may be less viscous than competitive glasses such as glasses used to form Kerablack[®] glass-ceramic products. Indeed, the presently disclosed glass ceramics, which may exhibit less darkening during post-ceramics heat treatments, may be suitable alternatives to Kerablack[®] glass-ceramics.

[00044] The disclosed glass-ceramics may have a coefficient of thermal expansion lower than $10 \times 10^{-7} \text{ K}^{-1}$ over the range 25°C to 700°C, e.g., less than $3 \times 10^{-7} \text{ K}^{-1}$.

[00045] Further embodiments relate to articles comprising the disclosed glass-ceramic compositions. Such articles may consist essentially of or consist of the glass-ceramic. Example articles are cooktops, cooking utensils or microwave oven trays.

[00046] Still further embodiments relate to lithium aluminosilicate glasses that are precursors of the glass-ceramics. A precursor glass may have a composition equal to the corresponding glass-ceramic composition.

[00047] Methods for forming glass-ceramics and articles comprising the glass-ceramics are also disclosed. Such methods may include heat treating a vitrifiable load of raw materials under conditions which successively ensure melting, fining and then ceramming.

[00048] An example method for forming a glass-ceramic article successively comprises melting a load of vitrifiable raw materials, said load containing SnO_2 as a fining agent, fining of the obtained molten glass, cooling the fined molten glass and simultaneously shaping it to a desired shape for the article, and heat treating the shaped glass to transform the glass into a glass-ceramic.

[00049] FIG. 1 represents the optical transmission spectrum of a glass-ceramic plate according to example 1. In the graph, the percentage amount of light transmitted by the plate is plotted on the y-axis as a function of the wavelength, in nanometers, of the transmitted beam, given on the x-axis.

Examples

[00050] Raw materials were combined to form 1kg batches having the compositions summarized in Table 1. The mixtures were placed in platinum crucibles and melted at $1,650^\circ\text{C}$. After melting, the glasses were rolled to a thickness of 5 mm and annealed at 650°C for 1hr. Glass samples (in the form of plates of about 10 cm x 10 cm) undergo a crystallization treatment comprising a fast heating to 650°C , heating from 650°C to 820°C at a heating rate of $5^\circ\text{C}/\text{min}$, heating from 820°C to the maximum crystallization temperature, $T_{\text{max}} = 920^\circ\text{C}$ at a heating rate of $15^\circ\text{C}/\text{min}$, maintaining T_{max} for 8 minutes, then cooling at the cooling rate of the oven.

[00051] The optical properties of the obtained glass-ceramic plates are measured on polished samples with a thickness of 4 mm. The illuminant D65 (observer at 2°) was used. T_v is the integrated transmission in the visible range, and T_{450} , T_{465} , T_{625} , T_{950} and T_{1600} are the transmissions measured at 450, 465, 625, 950 and 1,600 nm respectively.

[00052] In Table 1b, the Examples A, B, C, D and E are comparative. Example A is a Kerablack[®] glass-ceramic, which contains arsenic. Example B has a $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ ratio of 4.64 and too high a visible transmission. Example C has a V_2O_5 content of 0.255 and too low a visible transmission. In Example D, the Fe_2O_3 content and the V_2O_5 content are each too high and the visible and infrared transmissions are too low. In Example E, the $\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$ ratio is too low and the visible transmission is too low.

[00053] Table 1a. Example Glass-Ceramics

Examples	1	2	3	4	5	6	7	8
SiO ₂	64.722	64.538	64.448	64.653	64.421	64.801	64.412	64.618
Al ₂ O ₃	21.05	21.12	21.23	20.96	21.15	20.71	21.02	21.1
Li ₂ O	3.8	3.8	3.8	3.8	3.8	3.8	3.8	3.8
MgO	0.33	0.34	0.34	0.33	0.34	0.34	0.34	0.34
ZnO	1.41	1.48	1.43	1.42	1.46	1.47	1.45	1.47
BaO	2.47	2.53	2.49	2.49	2.51	2.52	2.5	2.5
TiO ₂	3.06	3.07	3.05	3.05	3.04	3.07	3.07	3.03
ZrO ₂	1.45	1.38	1.37	1.5	1.37	1.4	1.44	1.39
SnO ₂	0.26	0.25	0.27	0.25	0.26	0.26	0.26	0.29
Na ₂ O	0.57	0.57	0.57	0.57	0.58	0.56	0.58	0.58
K ₂ O	0.24	0.24	0.24	0.24	0.24	0.25	0.24	0.24
CaO	0.41	0.41	0.42	0.41	0.42	0.43	0.42	0.42
V ₂ O ₅	0.083	0.091	0.126	0.111	0.153	0.128	0.158	0.073
Fe ₂ O ₃	0.123	0.158	0.192	0.192	0.232	0.226	0.283	0.125
Cr ₂ O ₃	0.0205	0.0220	0.0234	0.0228	0.0240	0.0333	0.0263	0.0228
CoO	0.0015	0.0010	0.0006	0.0012	0.0000	0.0017	0.0007	0.0012
Fe ₂ O ₃ /V ₂ O ₅	1.48	1.74	1.52	1.73	1.52	1.77	1.79	1.71
Tv (%)	1.57	1.98	2	1.87	1.86	1.56	1.45	1.38
T 450 (%)	0.01	0.01	0.01	0.01	0	0.00	0	0.01
T 625 (%)	5.14	6.35	6.52	6.17	6.24	5.35	5.13	4.63
T 950 (%)	61.42	58.01	54.4	53.98	50.4	50.05	44.5	60.9
T 1600 (%)	69.86	65.91	62	62.18	58.7	59.76	54.2	69.4

[00054] Table 1b. Comparative Glass-Ceramics

Examples	A	B	C	D	E
SiO ₂		64.918	64.710	64.709	64.880
Al ₂ O ₃		20.79	20.79	20.69	20.72
Li ₂ O		3.8	3.8	3.8	3.8
MgO		0.33	0.33	0.33	0.33
ZnO		1.4	1.4	1.51	1.53
BaO		2.48	2.48	2.5	2.51
TiO ₂		3.06	3.06	3.01	3.04
ZrO ₂		1.43	1.43	1.35	1.37
SnO ₂		0.25	0.25	0.27	0.26
Na ₂ O		0.56	0.56	0.56	0.57
K ₂ O		0.25	0.25	0.26	0.25
CaO		0.43	0.42	0.42	0.43
V ₂ O ₅		0.05	0.255	0.213	0.18
Fe ₂ O ₃		0.232	0.232	0.347	0.106
Cr ₂ O ₃		0.0192	0.0322	0.03	0.0223
CoO		0.0008	0.0008	0.001	0.0017
Fe ₂ O ₃ /V ₂ O ₅		4.64	0.91	1.63	0.59
Tv (%)	0.8-2.0	7.14	0.57	0.6	0.50
T 450 (%)		0.11	0.00	0.00	0.00
T 625 (%)	≥4.0	17.26	2.37	2.44	2.04
T 950 (%)	40-68	57.65	42.67	34.98	54.40
T 1600 (%)	50-75	59.55	57.17	48.10	70.30

[00055] Several additional characterizations were carried out on select glass-ceramics and results are presented in Table 2. The coefficient of thermal expansion between 25°C and 700°C (CTE_{25-700°C} (10⁻⁷ K⁻¹)) and an x-ray diffraction analysis were conducted on Examples 5 and 7. The x-ray data were used to calculate the percentage by weight of the beta-quartz phase and the average size of these crystals.

[00056] Table 2.

Example	5	7
CTE _{25-700°C} (10 ⁻⁷ K ⁻¹)		2.3
% β-quartz	96%	
Crystal size	39 nm	

[00057] A melting test was performed with precursor glasses corresponding to Example 9 and comparative Example F. Both glasses, the compositions of which are indicated in Table 3, were melted using an electric furnace pre-heated to 1,400°C. The melting cycle including

raising the temperature from 1,400°C to 1,600°C within 2hrs, and maintaining 1,600°C for 1hr.

[00058] The samples were taken out of the furnace and the molten glass was poured on a heated steel plate. The glass was rolled to a thickness of 5 mm and annealed for 1hr at 650°C. Because of the short hold time at 1,600°C, the fining is incomplete. The number of bubbles in the glass plates was counted by a camera coupled with an image analyzer. These results are given in Table 3, expressed as the number of bubbles per cm³. The data show that Example 9 is at least as well fined as the comparative glass F.

[00059] Table 3. Glass Fining Results

Examples	9	F
Composition		
SiO ₂	64.678	64.892
Al ₂ O ₃	20.8	20.8
Li ₂ O	3.8	3.8
MgO	0.35	0.35
ZnO	1.5	1.5
BaO	2.5	2.5
TiO ₂	3	3
ZrO ₂	1.4	1.4
SnO ₂	0.25	0.35
Na ₂ O	0.6	0.6
K ₂ O	0.25	0.25
CaO	0.4	0.4
V ₂ O ₅	0.154	0.05
Fe ₂ O ₃	0.3	0.09
Cr ₂ O ₃	0.0167	0.0167
CoO	0.0013	0.0013
Fe ₂ O ₃ /V ₂ O ₅	1.2	1.8
Number of bubbles per cm³	200	380

[00060] As used herein, the singular forms “a,” “an” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to a “vitrifiable raw material” includes examples having two or more such “vitrifiable raw materials” unless the context clearly indicates otherwise.

[00061] Ranges can be expressed herein as from “about” one particular value, and/or to “about” another particular value. When such a range is expressed, examples include from the one particular value and/or to the other particular value. Similarly, when values are

expressed as approximations, by use of the antecedent “about,” it will be understood that the particular value forms another aspect. It will be further understood that the endpoints of each of the ranges are significant both in relation to the other endpoint, and independently of the other endpoint.

[00062] Unless otherwise expressly stated, it is in no way intended that any method set forth herein be construed as requiring that its steps be performed in a specific order. Accordingly, where a method claim does not actually recite an order to be followed by its steps or it is not otherwise specifically stated in the claims or descriptions that the steps are to be limited to a specific order, it is no way intended that any particular order be inferred. Any recited single or multiple feature or aspect in any one claim can be combined or permuted with any other recited feature or aspect in any other claim or claims.

[00063] It is also noted that recitations herein refer to a component being “configured” or “adapted to” function in a particular way. In this respect, such a component is “configured” or “adapted to” embody a particular property, or function in a particular manner, where such recitations are structural recitations as opposed to recitations of intended use. More specifically, the references herein to the manner in which a component is “configured” or “adapted to” denotes an existing physical condition of the component and, as such, is to be taken as a definite recitation of the structural characteristics of the component.

[00064] While various features, elements or steps of particular embodiments may be disclosed using the transitional phrase “comprising,” it is to be understood that alternative embodiments, including those that may be described using the transitional phrases “consisting” or “consisting essentially of,” are implied. Thus, for example, implied alternative embodiments to a glass-ceramic that comprises a various oxides include embodiments where a glass-ceramic consists of such oxides and embodiments where a glass-ceramic consists essentially of a such oxides.

[00065] It will be apparent to those skilled in the art that various modifications and variations can be made to the present invention without departing from the spirit and scope of the invention. Since modifications, combinations, sub-combinations and variations of the disclosed embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the invention should be construed to include everything within the scope of the appended claims and their equivalents.

We claim:

1. A glass-ceramic of the lithium aluminosilicate type, containing a β -quartz solid solution as the predominant crystalline phase and having for a thickness of 4 mm:

an integrated optical transmission, T_v , in the visible range, of 0.8 to 2%,

an optical transmission at 625 nm of more than 3.5%,

an optical transmission at 950 nm between 40 and 70%, and

an optical transmission at 1,600 nm between 50 and 75%,

wherein its composition, expressed as percentages by weight of oxides, comprises:

SnO_2	0.2 – <0.3;
V_2O_5	0.025 – 0.2;
Cr_2O_3	0.01 – 0.04;
Fe_2O_3	>0.095 – 0.32;
$\text{As}_2\text{O}_3 + \text{Sb}_2\text{O}_3$	< 0.1; and
$\text{Fe}_2\text{O}_3/\text{V}_2\text{O}_5$	1 to 4.

2. The glass-ceramic according to claim 1, comprising

SnO_2 0.25 – 0.28.

3. The glass-ceramic according to claim 1 or 2, comprising

Fe_2O_3 0.12 – 0.29.

4. The glass-ceramic according to any of claims 1 to 3, comprising less than 200 ppm of CoO.

5. The glass-ceramic according to any of claims 1 to 4, the composition of which is free of F and of Br, except for inevitable traces.

6. The glass-ceramic according to any of claims 1 to 5, further comprising:

SiO ₂	60 - 72
Al ₂ O ₃	18 - 23
Li ₂ O	2.5 - 4.5
MgO	0 - 3
ZnO	0 - 3
TiO ₂	1.5 - 4
ZrO ₂	0 - 2.5
BaO	0 - 5
SrO	0 - 5
BaO + SrO	0 - 5
CaO	0 - 2
Na ₂ O	0 - 1.5
K ₂ O	0 - 1.5
P ₂ O ₅	0 - 5, and
B ₂ O ₃	0 - 2.

7. The glass-ceramic according to claim 6, the composition of which comprises at least 98% by weight of SnO₂, V₂O₅, Cr₂O₃, Fe₂O₃, SiO₂, Al₂O₃, Li₂O, MgO, ZnO, TiO₂, ZrO₂, BaO, SrO, CaO, Na₂O, K₂O, P₂O₅ and B₂O₃.

8. An article comprising the glass-ceramic according to any of claims 1 to 7.

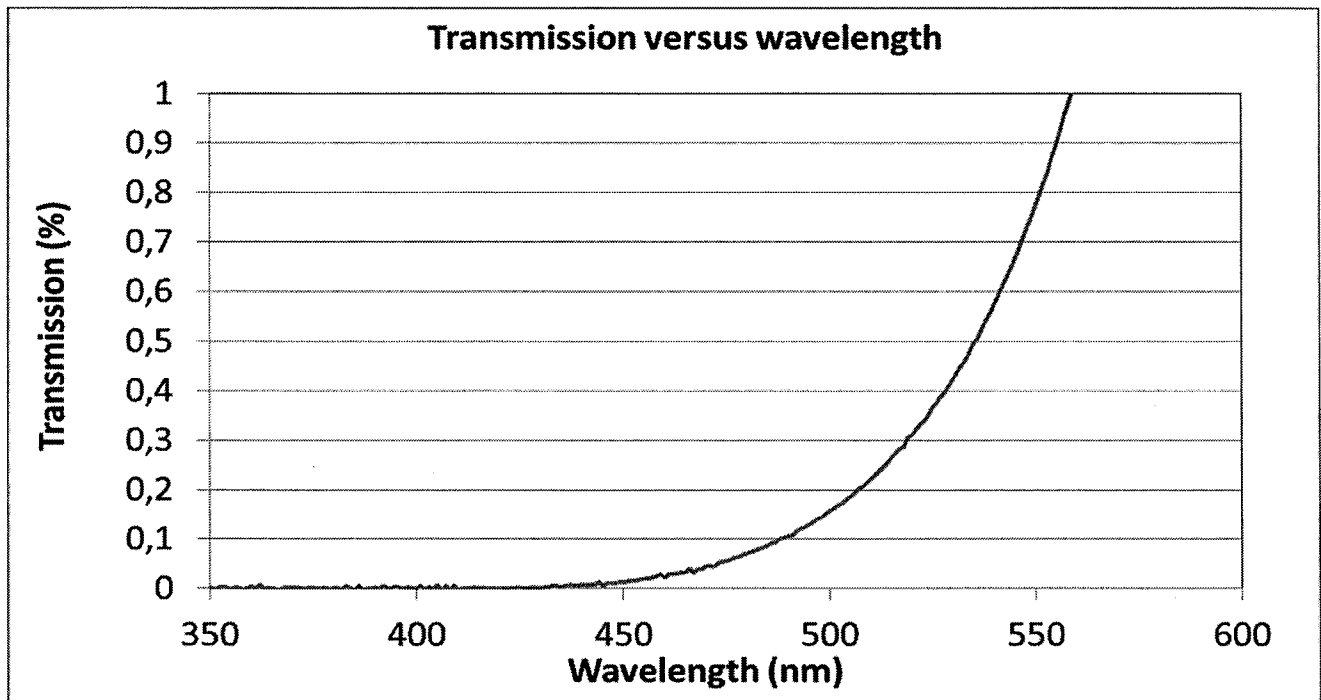
9. The article according to claim 8, selected from the group consisting of a cooktop, a cooking utensil and a microwave oven tray.

10. A lithium aluminosilicate glass, having a composition expressed as percentages by weight of oxides, comprising:

SnO ₂	0.2 - <0.3;
V ₂ O ₅	0.025 - 0.2;
Cr ₂ O ₃	0.01 - 0.04;
Fe ₂ O ₃	>0.095 - 0.32;
As ₂ O ₃ +Sb ₂ O ₃	< 0.1; and
Fe ₂ O ₃ /V ₂ O ₅	1 to 4.

11. A method for forming an article according to claim 8, successively comprising:
 - melting a load of vitrifiable raw materials, said load containing SnO_2 as a fining agent;
 - fining of the obtained molten glass;
 - cooling the fined molten glass and simultaneously shaping it to a desired shape for the article; and
 - heat treating the shaped glass to transform the glass into a glass-ceramic.

1/1

**FIG 1**

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/074385

A. CLASSIFICATION OF SUBJECT MATTER

INV. C03C3/085 C03C4/02 C03C10/14 C03C4/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EP0-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2011/089327 A1 (EUROKERA [FR]; MULET JEAN-PHILIPPE [FR]; CHARPENTIER BERTRAND [FR]; VI) 28 July 2011 (2011-07-28) page 3, line 11 - page 9, line 15; claims 1-18; figures 2,3; examples; table 1 -----	1-11
X,P	WO 2012/156444 A1 (EUROKERA [FR]; COMTE MARIE JACQUELINE MONIQUE [FR]; LISMONDE MICHEL [F] 22 November 2012 (2012-11-22) cited in the application claims 1-12; examples; tables 1-4 -----	1,2,4-11
A	DE 10 2010 032112 A1 (SCHOTT AG [DE]) 26 January 2012 (2012-01-26) claims 1-9; examples ----- -/--	1-11



Further documents are listed in the continuation of Box C.



See patent family annex.

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search

9 December 2013

Date of mailing of the international search report

18/12/2013

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2013/074385

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2013/074385

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