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(54) Title: ALBITE AND/OR ANORTHITE GLASS CERAMIC MATERIAL EXHIBING THERMAL WARMTH

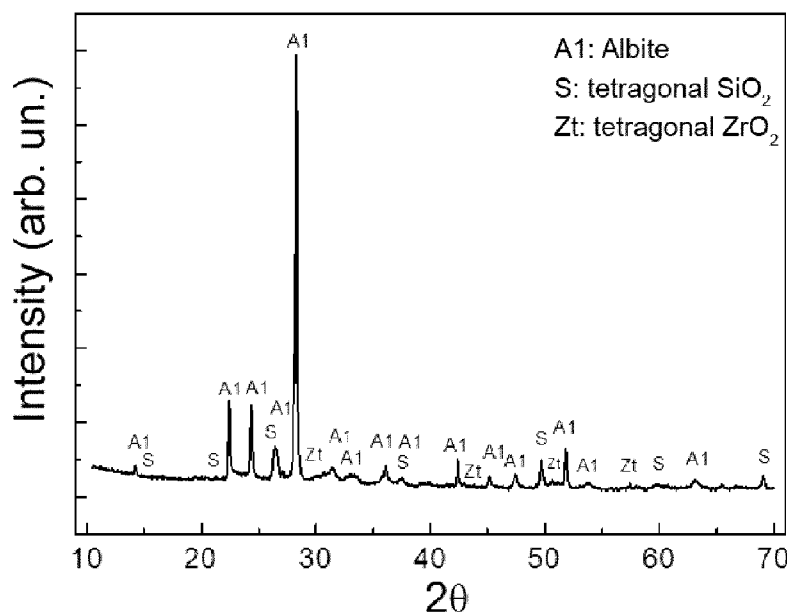


FIG. 1

(57) Abstract: The present invention relates to an albite and/or anorthite glass ceramic material, which exhibits a sensation of thermal warmth and its production process. Furthermore, the present invention relates to the use of this glass-ceramic material for the manufacturing of industrial, structural and ornamental ceramic products.



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ALBITE AND/OR ANORTHITE GLASS CERAMIC MATERIAL EXHIBING THERMAL WARMTH

DESCRIPTION

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The present invention relates to an albite and/or anorthite glass ceramic material, which exhibits a sensation of thermal warmth and its production process. Furthermore, the present invention relates to the use of this glass-ceramic material for the manufacturing of industrial, structural and ornamental ceramic products.

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Therefore, the invention could be included in the field of the ceramics industry.

15 **STATE OF THE ART**

A glazed ceramic product consists of a ceramic product with a coating in the form of vitrified layer or glaze. In the scope of the technology, the glaze is the result of the melting of the layer of coating in the form of powder with a ceramic or metal substrate through a firing process. The powder is melted and when hardened forms a greatly hardened smooth and glassy coverage which provides many functional applications.

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In the preparation of glazes, the components are individually dosed and they are generally homogenized by a grinding process with water in ball mills, obtaining aqueous suspensions of said components. The resulting suspension is called barbotine. They can also be dry ground and used in a water suspension and/or dry for special applications. Currently, the digital decoration processes by "inkjet" technology have required suspensions in non-aqueous media and submicron particle sizes. There are various types of glaze depending on the physical function and packaging form. They are largely composed of frits, non-fritted raw materials, additives and ceramic colours. The additives are substances that are added so that the glaze, once ground, has the stability and

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properties suitable for the intended application.

An glazed ceramic product, such as, for example, a ceramic tile, acquires an water-tight, protective and decorative layer with the glaze, which provides the product with aesthetic qualities and specific technical characteristics, such as water-tightness, hardness and resistance to scratching, acids and abrasion and detergents, they may preserve shiny colours for a long time and it is not combustible.

Among its disadvantages, we can highlight two aspects related to:

- Its tendency to break when subjected to deformations, stresses or an impact, and
- Its ease of easily absorbing heat giving a cold sensation when touched.

The sensation of cold or heat perceived on touching a body is the consequence of heat transmission between both bodies on coming into contact. In the case of solids in direct contact, this heat transfer occurs by thermal conduction. The distribution of temperatures reached in equilibrium depends on the properties of both bodies such as their thermal conductivity, density and specific heat. These properties are determined by the composition of the material and its microstructure.

In insulated ceramic materials, heat conduction occurs via phonons, oscillations of the atoms of the crystalline network that are propagated through the material. In general, the thermal conductivity of the ceramic products ranges between values of 2 to 50 $\text{Wm}^{-1}\text{K}^{-1}$. Glass and amorphous ceramics have lower thermal conductivity values, since the dispersion of phonons is much more effective when the crystalline structure is highly disorganized and irregular.

The presence of vitreous phase is typical in glazed ceramic products. This is the case of porcelain-type ceramic products, which by definition have

more than 8 % vitreous phase, being very typical that the vitreous phase percentage of a porcelain reaches values of up to 60 %. In a ceramic glaze, the proportion of vitreous phase may even exceed those values and be close to 100 %. However, the thermal conductivity values of the glass and porcelain materials range between $1.7 \text{ Wm}^{-1}\text{K}^{-1}$ for borosilicate glass to $0.8 \text{ Wm}^{-1}\text{K}^{-1}$ for glazed ceramic floor tiles. These values are less than those corresponding to other materials used as flooring and cladding in constructions such as granite and marble with thermal conductivity values of 3 and $4.5 \text{ Wm}^{-1}\text{K}^{-1}$ respectively and which are considered as cold materials from the standpoint of thermal warmth.

The porosity of the ceramic materials may have a drastic influence on the thermal conductivity. The pores contain air the thermal conductivity of which is very low, $0.02 \text{ Wm}^{-1}\text{K}^{-1}$, and provides the porous structure with a decrease in thermal conductivity with respect to the material of greater density. The increase in the pore volume fraction generally leads to reduction in thermal conductivity. Characteristic examples of materials with high porosity are woods, which with density values between $0.55 - 0.85 \text{ kgm}^{-3}$ have thermal conductivity values as low as $0.10 - 0.35 \text{ Wm}^{-1}\text{K}^{-1}$. The thermal conductivity values of polymers are, in general, also very low, in the order of $0.3 \text{ Wm}^{-1}\text{K}^{-1}$, if they are compared with the ceramic products. In these materials, the heat transfer occurs by vibration, translation and rotation of the molecules. The use of wooden materials or polymeric materials as flooring is widespread in construction and it is considered a benchmark in thermal warmth flooring despite its durability problems, poor resistance to chemical attack and fire.

With the aim of providing a thermal warmth sensation on touching a ceramic product, one of the solutions of the state of the art is to incorporate porosity therein. The addition of hollow particles is used in order to decrease thermal conductivity: when they are incorporated in the surface of glazes (JP2005041741); or when they are incorporated both inside the layer of glaze and in the layer of support (JP2005133337); or by the incorporation of an

intermediate layer with porous structure (JP2005139797); or by the incorporation of an intermediate layer with sponge structure (JP2005139796). In these solutions, the improvement in the sensation of thermal warmth is performed without decreasing the stain resistance properties of glazed ceramic surfaces. However, the incorporation of porosity represents a clear worsening in the mechanical response of the glazed ceramic materials, in addition to introducing a greater complexity and cost in the material processing.

Other solutions proposed to provide a sensation of thermal warmth on touching a ceramic product are based on the incorporation of a coating of organic nature (WO2013095308), or in the generation of an inorganic-organic composite product (WO2008122677). As a whole, the composite materials combining organic materials and inorganic materials move away from the state of the art as regards glazed ceramic products since they represent a worsening of the durability and resistance properties of the glazed ceramic products.

The thermal conductivity of the human body is approximately $0.6 \text{ Wm}^{-1}\text{K}^{-1}$, however, the average conductivity of human skin is $0.34 \text{ Wm}^{-1}\text{K}^{-1}$. Therefore, a limitation in the state of the art consists of the lack of glazed ceramic products with thermal conductivities close to the values of human skin, but preserving the other characteristic functional properties of glazed ceramic products.

A way of reducing the thermal conductivity of ceramic products requires hindering phonon propagation. The reduction in grain size means a decrease in thermal conductivity since more grain boundaries appear which involve a barrier for heat transmission. In the state of the art, in BaTiO_3 ceramic materials, a reduction has been disclosed in thermal conductivity values from $100 \text{ Wm}^{-1}\text{K}^{-1}$ to $1.2 \text{ Wm}^{-1}\text{K}^{-1}$ on reducing grain size to sizes of 30 nm (A. Jeżowski et al, Influence of crystallite size on the thermal conductivity in BaTiO_3 nanoceramics, Appl. Phys. Lett. 90 (2007) 114104). It has also been disclosed that ceramic products with different phases also show an effective reduction in thermal conductivity, since the phonon dispersion ratios are characteristic of each

material and, on going from one material to another, they must change their properties (W Pabst, E Gregorová, The sigmoidal average – a powerful tool for predicting the thermal conductivity of composite ceramics, J. Phys. Conf. Ser. 395 (2012) 012021).

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Although it is possible to modulate the thermal properties of a ceramic material by the design of its microstructure, ceramic products with thermal conductivity values comparable to the thermal conductivity values of human skin are not disclosed in the state of the art.

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A ceramic glaze is characterized in that it has a microstructure which combines a glass matrix wherein different crystalline phases are located. The most common crystalline phases found in a ceramic glaze are quartz, cristobalite, mullite, alumina, zircon, zirconia, celsian, leucite, wollastonite, cordierite, diopside, albite, anorthite or ganhite. The presence of vitreous phase is also common in a ceramic glaze due to its composition. Crystalline glazes are generally multiphase and to develop a single crystalline phase on a majority basis requires complex processes which are far removed from industrial processes.

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A strategy to obtain ceramic glazes with multiple interfaces corresponds to glass-ceramic interfaces. A glass-ceramic is a polycrystalline solid that contains a residual vitreous phase and is obtained by melting and solidification of inorganic vitreous compositions susceptible to controlled crystallization. The controlled crystallization process is the separation of a crystalline phase from the precursor glass in the form of crystals of reduced size, where the number of crystals, growth rate and final size are a consequence of the thermal cycle performed. To obtain a glass-ceramic material, a high number of crystalline nuclei are required distributed homogeneously throughout the volume and which reach grain sizes between 0.1 and 1 μm with the temperature increase until the crystalline phase represents > 50 % of the original volume of the glass. The glass-ceramics which give rise to the best properties are those which

achieve a crystallization greater than 90 % of the vitreous mass with crystal sizes between 0.5 and 1 μm . The separation of phases to achieve the production of glass-ceramic materials from silicate glass occurs when nucleants in the form of cations whose coordination number varies with temperature such as Ti and Zr or cations with a charge different to that of silicon such as Fe^{2+} and P^{5+} and/or anions with charge different to that of oxygen such as F^- or cations with high field intensity such as Cr^{3+} , Li^+ or Mg^{2+} . The nucleants used in the state of the art produce translucent and largely coloured glass-ceramics since the majority of the nucleating agents also act as chromophore agents.

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The production of glass-ceramics with β -spodumene crystalline structure in the $\text{Li}_2\text{O}.\text{Al}_2\text{O}_3.n\text{SiO}_2$ system is defined in the state of the art (US3445252). The formation of the crystals requires later thermal treatments of the melted and solidified product using two-steps processes at temperatures between 800 °C and 900 °C and suitable residence times to favour the nucleation and crystallization processes, respectively. The crystals are gradually and constantly developed with heating rates not greater than 5 °Cmin⁻¹. Both the nucleation and growth temperatures and the heating rates are very limiting. The translucent glass-ceramics with β -quartz or β -eucryptite crystalline structure (US5017519) also have good mechanical resistance. The coefficients of thermal expansion of glass-ceramics with β -spodumene, β -quartz or β -eucryptite crystalline structure with values close to 0 °C⁻¹ are too low to be applied as glazes on most ceramic products. Another limitation of these materials to be used as glazes to provide thermal warmth is that their thermal conductivity values are in the range of 0.9 – 1.7 Wm⁻¹K⁻¹.

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The translucent glass-ceramics suitable to be used as ceramic glazes in ceramic products have been developed based on compositions which give rise to crystallizations with crystalline structure of feldspars such as anorthite and albite. In general, glass-ceramics with feldspar structure are of great interest since said crystallizations have a positive effect on the improvement in the mechanical properties of glazes.

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The production of glazes with anorthite crystallizations is known (A.Tunali et al. Production and characterisation of granulated frit to achieve anorthite based glass-ceramic glaze. J. Eur. Ceram. Soc. 35,1089–1095,2015) where using suitable treatments and adjustments of composition it modifies the size of the anorthite crystals with the aim of obtaining glass-ceramics with transparent matt appearance where the transparency is provided by the vitreous phase wherein the crystallizations of anorthite are found.

The production of glazes with crystallizations of albite is known in the state of the art (ES2444740) and the glazes developed are characterized by their transparency and that they are based on vitreous phase contents > 70 %, being in practice glass glazes with a limited percentage of crystallizations. The crystallization of albite is extremely difficult to achieve and albite compositions are avoided in the production of glass-ceramics. To obtain glass-ceramics with majority albite phase complex sol-gel chemical processes are used which must require the addition of seeds in the form of anorthite crystals (C. Liu et al. Crystallization of Anorthite-Seeded Albite Glass by Solid-State Epitaxy, J. Am. Ceram Soc. 75, 10. 26675-80.1992).

To date, the sensation of thermal warmth of ceramics has been exclusively treated from the standpoint of effective thermal conductivity. The most common approach has been to generate porous materials and the properties of the interfaces have scarcely been explored. The dynamic aspect of heat transmission has been taken into account when tackling the problem of thermal warmth. In general, the state of equilibrium fundamentally depends on effective thermal conductivity. However, the sensation of cold or heat does not only depend on the temperature reached in the equilibrium between two bodies, but also on the rate said equilibrium reaches. A limitation of the state of the art is the lack of definition of a factor which allows quantifying the sensation of thermal warmth.

Therefore, the development is necessary of new ceramic materials that display thermal warmth, particularly to be able to use this type of materials in cold climates.

5 **DESCRIPTION OF THE INVENTION**

The present invention has the following advantages with respect to the glass-ceramic products found in the state of the art:

- the glass-ceramic material has a vitreous phase in a proportion
10 less than 18 % with respect to the total weight of the glass-ceramic material;
- the values of thermal conductivity of the glass-ceramic materials are less than $0.50 \text{ Wm}^{-1}\text{K}^{-1}$, between 0.25 and $0.5 \text{ Wm}^{-1}\text{K}^{-1}$;
- the compositions used are based on minerals highly abundant in nature;
- 15 • it has a high whiteness with L-coordinate values greater than 86, reaching whiteness values of up to 96.5 which allows four-colour decoration process applications using digital decoration;
- the glass-ceramic material developed is compatible with the ceramic products based on silicates and their industrial production processes;
- 20 • the glass-ceramic material of the invention has achieved a mechanical resistance to bending greater than 110 MPa;
- the glass-ceramic material of the invention has a negative thermal warmth factor TWF;
- The sintering process of this glass-ceramic material is carried out
25 by rapid sintering in treatments lasting less than 120 minutes at temperatures between 980°C and 1280°C

The term “glass-ceramic” is understood in the present invention as a polycrystalline ceramic material generally formed through the controlled
30 devitrification of a precursor in vitreous phase. It is a hard material, vitrified throughout its mass and very compact, which has the essential characteristic of low and closed porosity, mechanical properties such as resistance to breaking

and resistance to wear, resistant to chemical attack and practically impermeable. In this invention, the term glass-ceramic glaze relates to a glaze that is of glass-ceramic nature.

5 The term “thermal warmth” is understood in the present invention as the absence of sensation of cold that a person experiences when touching a foreign body. Although the sensation of cold is subjective, it is regulated by heat receptors that are a set of ion channels that are activated by different physiological temperatures.

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 In the present invention, a parameter called Thermal Warmth Factor (TWF), as an adimensional parameter that defines the degree of heat transfer from one hot body area to a body of lower temperature in the initial contact time.

15 For the determination of the TWF, the dynamic variation has been established of the temperature the hot body experiences on coming into contact with a body with a temperature lower than 30 °C, the temperature of the hot body being 40 °C since it is a temperature slightly higher than that corresponding to the human body, but similar. The body at a lower temperature
20 is kept at 10 °C. The TWF value is determined in a material with respect to the temperature gradient that the two reference materials experience after a certain time. The reference materials have been selected from materials used as standard materials in thermal conductivity calibration equipment using the heat flow method.

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 The materials used as reference are a Vespel polymer with a thermal conductivity value of $0.37 \text{ Wm}^{-1}\text{K}^{-1}$, and steel material with a high thermal conductivity value of $14.2 \text{ Wm}^{-1}\text{K}^{-1}$. The TWF value is obtained for different temperatures, such as, for example, example 2 s, 30 s, 50 s or 300 s, although
30 not limited to these examples.

 The TWF value is normalized with respect to a corresponding scale the

TWF value = 2 with the TWF value of the Vespel polymer, and the TWF value = 12 with the TWF value of the steel.

Therefore, the TWF value is determined using the following formula:

$$FCT = \frac{\Delta T - \Delta T_{vespel}}{\Delta T_{steel} - \Delta T_{vespel}} \cdot 10 + C$$

With ΔT being the temperature differential of the sample to measure for a time t with respect to the initial temperature, in this case 40 °C, and ΔT_{vespel} and ΔT_{steel} the temperature differentials for the reference samples for a time t with respect to the initial temperature, in this case 40 °C. C is an experimental constant which has a value approximate to 2.

In this way, if the TWF of the material to study approximates 2, it will have a similar behaviour to that of the polymer, and there we will have a “comfort” material or “which exhibits thermal warmth”. And if it approximates 12 we will have a highly heat conductor material, comparable with steel. A TWF value less than 2 implies a material with features of thermal comfort or thermal warmth greater than those of the Vespel polymer.

In a first aspect, the present invention relates to a glass-ceramic material (called “glass-ceramic material of the invention”) which exhibits a sensation of thermal warmth, characterized in that it has a thermal conductivity between 0.25 and 0.5 Wm⁻¹K⁻¹ and in that it comprises

albite NaAlSi₃O₈ microcrystals and nanocrystals,
optionally, anorthite CaAl₂Si₂O₈ microcrystals and nanocrystals
and vitreous phase,

wherein the microcrystals are separated by a region formed by the nanocrystals and the vitreous phase, and wherein said vitreous phase is in a proportion less than 18 % with respect to the total weight of the glass-ceramic material.

In the present invention, the microcrystals that form the glass-ceramic

material of the invention are isolated from one another, in the exceptional cases that they are connected, their degree of percolation is very low. The region that separates the microcrystals formed by nanocrystals and vitreous phase is continuous. The vitreous phase is minority and its degree of percolation is also
5 low, i.e. it does not in itself form a single continuous phase in the glass-ceramic material of the invention.

The glass-ceramic material of the invention is obtained by devitrification of the mixture formed by the frit obtained and the kaolin. The frit has a largely
10 amorphous structure resulting from the sudden cooling process from its melted state and it may contain a proportion by weight of crystalline phases of remains of raw materials < 10 % resulting as infused during the fritting process. The frit particles have a radial devitrification process from the surface. However, this devitrification is not complete. During the production process of the glass-
15 ceramic material of the invention the surface size of the particles is increased by grinding so that it produces a decrease in crystal size. The devitrification is more effective when laminar kaolin particles are found on the surface of the frit particles. The kaolin used is characterized in that it has a content expressed in terms of equivalent oxide of Al_2O_3 greater than 30 wt% and a joint content of
20 divalent and monovalent cations expressed in terms of equivalent oxides XO , wherein $\text{X} = \text{Mg}, \text{Sr}, \text{Ba}, \text{Ca}, \text{Pb}$ or Zn , and $\text{X}'_2\text{O}$, wherein $\text{X}' = \text{Na}, \text{K}$ or Li , less than 5 wt%. The kaolin particles sequester glass network forming cations and this process reduces the vitreous phase percentage in the microstructure of the glass-ceramic glaze. The proportion of frit and kaolin produces a high degree of
25 devitrification when the ratio is between 24 parts of frit per 1 part of kaolin and 4 parts of frit per 1 part of kaolin. Thus, the glass-ceramic materials of the present invention have an advantage compared with those in the state of the art since preferential heat transmission paths are not established using phonons through the microcrystal network. The manner in which the phonons are dispersed
30 through the material of the invention reduces thermal conductivity and favours the sensation of thermal warmth.

The glass-ceramic material of the invention comprises a α ratio defined as

$$\alpha = \frac{\%Al_2O_3}{\Sigma \%XO + \Sigma \%X'_2O}$$

5 which corresponds to the ratio in percentage of the equivalent oxide of Al_2O_3 compared with the sum in percentage expressed in terms of the equivalent oxides of glass network forming cations, fundamentally divalent and monovalent cations of oxides XO, wherein X = Mg, Sr, Ba, Ca, Pb or Zn, and X'_2O , wherein X' = Na, K or Li. The α ratio determines the solubility of the
10 alumina in the vitreous phase. If the value of α is greater than 1.2 it causes the devitrification of crystalline phases of high thermal conductivity in the material.

The glass-ceramic material of the present invention is characterized in that it has values of α less than 1.1, even less than 0.9. In this way, the
15 compositions of glass-ceramic material of the present invention are advantageous as it shows an absence of crystalline phases of high thermal conductivity in its microstructure.

The glass-ceramic material of the present invention is characterized in
20 that it largely has a feldspar-type structure with general formula AB_4O_8 wherein cation A is a cation of large size and low charge such as Mg, Sr, Ba, Ca, Pb Zn, Na, K or Li and B is a cation comprising Si and Al. The anorthite phase of general formula $CaAl_2Si_2O_8$ and the albite phase of general formula $NaAlSi_3O_8$ belong to the group of minerals of feldspar structure. Each B cation is
25 tetrahedrally surrounded by 4 oxygens. The presence of cations with different charge in B positions implies that to maintain the electroneutrality of the crystalline cell it also produces the presence of cations A with divalent and monovalent nature. Among the cations A, the presence of Sr is an advantage since its ionic radius is sufficiently large to prevent the collapse of the structure
30 of tetrahedrons, but sufficiently small to favour highly disordered structures in the

crystalline phases of the glass-ceramic materials that are suitable to prevent the transmission of the network phonons.

In the present invention, the microcrystals are called “purely albite” when
5 the proportion of albite is greater than 90 % and the proportion of anorthite is less than 10 %.

In the present invention, the microcrystals are called “purely anorthite”
when the proportion of anorthite is greater than 90 % and wherein the
10 proportion of albite is less than 10 %.

With the term “albite and anorthite microcrystals” the present invention
also includes mixture of other proportions different to those of purely albite or
purely anorthite, provided that the sum of the percentages is of 100 %, any
15 proportion would be considered in the definition of mixture. In the present
invention, the term “albite and anorthite microcrystals” refers not only to
crystalline phases but also to their solid solutions.

The coefficient of thermal expansion in the range of temperatures between
20 50 °C and 300 °C is less than $55 \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ for purely albite microcrystals and is
less than $66 \cdot 10^{-7} \text{ }^{\circ}\text{C}^{-1}$ for purely anorthite microcrystals.

In a preferred embodiment, the glass-ceramic material of the invention
comprises anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals. The glass-
25 ceramic material of the invention gives a sensation of thermal warmth and is
characterized in that it has a thermal conductivity between 0.25 and $0.5 \text{ Wm}^{-1}\text{K}^{-1}$
and it is characterized in that it comprises albite $\text{NaAlSi}_3\text{O}_8$ microcrystals and
nanocrystals and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals, wherein
the microcrystals are separated by a region formed by the nanocrystals and the
30 vitreous phase, wherein said the vitreous phase is in a proportion less than 18
% with respect to the total weight of the glass-ceramic material.

In another preferred embodiment, the albite microcrystals that form the glass-ceramic material of the invention have elongated morphologies with smaller diameter between 0.3 μm and 1.5 μm and larger diameter between 1.5 μm and 8 μm .

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In another preferred embodiment, the anorthite microcrystals that form the glass-ceramic material of the invention have elongated morphologies with smaller diameter of between 0.2 μm and 0.5 μm and larger diameter of between 5 μm and 30 μm .

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In a preferred embodiment, the glass-ceramic material of the invention contains at least a weight percent with respect to the end material expressed in terms of the following equivalent oxides:

- between 45 % and 68 % of SiO_2 ,
- 15 • between 15 % and 27 % of Al_2O_3 ,
- between 4.5 % and 13 % of CaO ,
- between 0 % and 9 % of SrO ,
- between 1 % and 5.5 % of Na_2O ,
- between 1 % and 5 % of K_2O ,
- 20 • between 0 % and 2 % of B_2O_3 ,
- between 0 % and 14 % of ZrO_2 ,
- and between 0 % and 5 % of MgO , BaO and ZnO .

Preferably, the weight percent with respect to the SiO_2 end material is
25 between 45 % and 68 %. More preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of SiO_2 is between 49 % and 60 %.

Preferably, the weight percent with respect to the Al_2O_3 end material is
30 between 17 % and 25 %. More preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of Al_2O_3 is between 19 % and 23 %.

Preferably, the weight percent with respect to the CaO end material is between 6 % and 12 %. More preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of CaO is between 7.5 %
5 and 11 %.

Preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of SrO is between 0 % and 9 %.

10 Preferably, the weight percent with respect to the end material in equivalent oxides of Na₂O is between 1.5 % and 4 %. More preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of Na₂O is between 2 % and 3.5 %.

15 Preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of K₂O is between 1.5 % and 4 %. More preferably, the weight percent with respect to the end material expressed in terms of equivalent oxides of K₂O is between 2 % and 3 %.

20 In another preferred embodiment, the glass-ceramic material of the invention further comprises zirconia crystals ZrO₂ or zirconium silicate crystals ZrSiO₄, wherein said crystals are distributed throughout the region of nanocrystals and vitreous phase that separate the microcrystals of the glass-ceramic material, and is characterized in that the material displays a thermal
25 conductivity between 0.31 and 0.45 Wm⁻¹K⁻¹.

The addition of zirconia crystals ZrO₂ or zirconium silicate crystals ZrSiO₄ increases the percentage of crystalline phase of the glass-ceramic material of the invention and also provides whiteness and hardness. Whiteness
30 is a highly desired property in the sector for decoration applications, for example, to enhance the yield of four-colour process by digital decoration.

In a preferred embodiment, the zirconia crystals ZrO_2 may be in the form of cubic, tetragonal or monoclinic crystalline phase.

In another preferred embodiment, the zirconia crystals ZrO_2 have an
5 average size of between 50 and 200 nm.

In another preferred embodiment, the zirconium silicate crystals ZrSiO_4 have an average size of between 200 nm and 500 nm.

10 Preferably, the weight percent in equivalent oxides of the zirconia crystals ZrO_2 or of the zirconium silicate crystals ZrSiO_4 with respect to the total weight of the glass-ceramic material is between 2 % and 14 %. More preferably, between 2 % and 8 %.

15 The glass-ceramic material of the invention may further comprise crystals of quartz, cristobalite, alumina, diopside, wollastonite, spinel, garnet, cordierite, willemite or rutile. The inclusion of these crystals as part of the glass-ceramic material of the invention has the purpose of providing transparency, colour, melting capacity or coefficient of expansion thereto.

20

A second aspect of the invention relates to the production process of the glass-ceramic material of the invention comprising the following steps:

- 25 a) melting at least one compound selected from the list comprising sassolite H_3BO_3 , quartz SiO_2 , dolomite $\text{CaMg}(\text{CO}_3)_2$, calcium carbonate CaCO_3 , zincite ZnO , kaolin $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, strontianite SrCO_3 , alumina Al_2O_3 , calcium phosphate $\text{Ca}_3(\text{PO}_4)_2$, a zirconium compound selected from among zirconia ZrO_2 or zirconium silicate ZrSiO_4 and an alkali feldspar selected from among albite $\text{NaAlSi}_3\text{O}_8$ and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, or any combination thereof, a temperature of between 1400 °C and 1550 °C and fritting;
- 30 b) grinding the frit obtained in step a) with kaolin;
- c) forming the product obtained in b);
- d) sintering the product formed in c) at temperatures of between 980 °C

and 1280 °C.

The final composition of the material expressed in terms of equivalent oxides is the following:

- between 45 % and 68 % of SiO_2 ,
- 5 • between 15 % and 27 % of Al_2O_3 ,
- between 4.5 % and 13 % of CaO ,
- between 0 % and 9 % of SrO ,
- between 1 % and 5.5 % of Na_2O ,
- between 1 % and 5 % of K_2O ,
- 10 • between 0 % and 2 % of B_2O_3 ,
- between 0 % and 14 % of ZrO_2 ,
- and between 0% and 5 % of MgO , BaO and ZnO .

15 In a preferred embodiment, the percentage of the frit obtained in step a) is between 70 % and 96 wt% in step b).

In another preferred embodiment, the percentage of kaolin is between 4 % and 15 wt% in step b).

20 The product obtained in step b) can be dried by atomization or combining press filter and dryer processes.

Step c) of forming of the product obtained in step b) can be carried out by uniaxial pressing, isostatic pressing or extrusion of ceramic bodies.

25

Preferably, step c) of forming of the product obtained in b) is carried out to obtain the glass-ceramic material of the invention in the form of floor tile or in the form of glaze.

30 When one wants to form the product obtained in step b) in the form of glaze coating a ceramic product, the glass-ceramic material of the invention can be directly deposited on a ceramic product such as porcelain stoneware or

porcelain stoneware coated by slip.

Any person skilled in the art would serve to deposit the glaze formed by the glass-ceramic material of the invention, preferably using standard
5 techniques of spraying or bell-shaped glaze application.

Step d) of sintering of the product formed in step c) can be carried out in a continuous or discontinuous oven, preferably it is carried out in a rapid single-channel roller kiln.
10

Preferably, step d) of sintering of the product formed in step c) is carried out at temperatures of between 1100 °C and 1220 °C.

Step d) of sintering can be carried out by rapid sintering cycles at heating
15 or cooling rates of between 30 and 55 °C/min providing a significant energy saving. The rapid sintering cycles represent an advantage over the conventional sintering cycles of glass-ceramic materials with heating rates less than 5 °C/min and isothermal periods at intermediate temperatures to favour crystallization, such as, for example, maintaining at 900 °C 4 hours during the heating ramp.

20 In a preferred embodiment, the process of the invention is characterized in that it comprises an additional step e), after the step of sintering (d), this step e) including rectifying and polishing with abrasives. Preferably, the abrasives are selected from the list comprising diamond, silicon carbide or magnesite. By
25 this step e), surfaces of the glass-ceramic material of the invention are obtained with specular reflection of interest for decoration.

Another aspect of the invention relates to the use of the glass-ceramic materials of the invention for the manufacturing of industrial, structural or
30 ornamental ceramic products.

In the present invention, the term "industrial, structural or ornamental

ceramic products” is understood as a ceramic piece which makes it possible to form or coat a surface, whether horizontal or vertical, internal or external, straight or curved which is used as an element which forms part of a structure or which is used as decorative motif and industrial means are used in its
5 production.

In a preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of floor tiles or glazes of floor tiles with applications in floors, walls and facades.
10

The glass-ceramic materials formed in the form of floor tiles have a density of between 2.4 and 2.8 kgm⁻³ and closed porosity.

In the present invention, “closed porosity” is understood as the porosity which is impermeable to boiling water. It is a porosity which is in the interior of a ceramic body.
15

The decrease in percentage of porosity of the glass-ceramic material of the present invention is achieved by the addition of a flux in the form of feldspar or of a frit of a greater flux in percentages of up to 30 wt%. The decrease in porosity gives improved resistance to stains that occur on the surface of the glass-ceramic material of the invention coming to behave as a glass-ceramic material with glazed surface.
20

The glass-ceramic glaze is formed on a ceramic “substrate or support” which may optionally be previously coated with a layer of slip. The thicknesses of the glass-ceramic glazes are between 50 and 1000 µm.
25

In another preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of tiles for flooring and cladding and roof tiles.
30

In another preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of ceramic pieces of electrical appliances.

5 In another preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of ceramic pieces for costume jewellery and jewellery.

10 In another preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of sanitary ware and furniture.

In another preferred embodiment, it relates to the use of the glass-ceramic material of the invention for the manufacturing of crockery.

15 The last aspect of the invention relates to the use of the glass-ceramic material of the invention as thermal insulator.

In a preferred embodiment, the invention relates to the use of the glass-ceramic material of the invention, as an energy saving material, this is, as a component of a cool roof, cool room or cool façade. For example, a cool roof can be desirable to a building owner since it reduce energy bills by decreasing air conditioning needs, improve indoor thermal comfort for spaces that are not air conditioned, and decrease roof operating temperature, which may extend roof service life. Cool roofs can also benefit the environment, can reduce local air temperatures, which improves air quality and slows smog formation; reduce peak electric power demand, which can help prevent power outages; reduce power plant emissions, including carbon dioxide, sulfur dioxide, nitrous oxides, and mercury, by reducing cooling energy use in buildings; and reduce heat trapped in the atmosphere by reflecting more sunlight back into space, which can slow climate change.

Throughout the description and the claims the word “comprises” and its

variants are not intended to exclude other technical characteristics, additives, components or steps. For persons skilled in the art, other objects, advantages and characteristics of the invention will be inferred in part from the description and in part from the practice of the invention. The following figures and
5 examples are provided by way of illustration, and are not intended to limit the present invention.

BRIEF DESCRIPTION OF THE FIGURES

10 FIG.1. Powder X-ray diffractogram of the sample of example 1 sintered at 1100 °C. A1: Albite; S: Tetragonal silica, Zt: Tetragonal zirconia.

FIG. 2. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the sample of example 1
15 sintered at 1100 °C, showing the microcrystallizations of albite (1) and a region with nanoparticles (2).

FIG. 3. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the sample of example 1
20 sintered at 1220 °C, showing the microcrystallizations of albite (1) and a region with nanoparticles (2).

FIG. 4. Diagrammatic figure of the crystallizations present in the micrographs of the sample of example 1 sintered at 1100 °C differentiating the
25 albite microcrystals (1) and the region with nanoparticles which separates them (2).

FIG. 5. Powder X-ray diffractogram of the samples of example 2. A1: Albite; Zc: Zirconia (cubic); Zo: Zirconia (orthorhombic); Zm: Zirconia
30 (monoclinic); ZSt: Tetragonal zircon; S: Tetragonal silica.

FIG. 6. Scanning electron microscope micrographs of the polished

surface and surface chemically attacked with HF of the sample of example 1 sintered at 1220 °C with 4 % (figure 6a) and 10 % Zircon (figure 6b), showing the microcrystallizations of albite (1) and the region with nanoparticles (2), of zirconia (3) and of zircon (4).

5

FIG. 7: Diagrammatic figures of the crystallizations observed in the micrographs of example 2 sintered at 1220 °C with 4 % Zr and 10 % Zr (figure 7a and 7b respectively). Figure 7a shows the albite microcrystals (1), the region with nanoparticles that separates the crystals (2) and zircon (4) and zirconia (3) crystals. Figure 7b shows area 4, which corresponds to areas 1 and 2 of Figure 7a, the zircon (4) and/or zirconia (3) crystals and the pores (5).

10

FIG. 8. Powder X-ray diffractogram of the sample of example 3. A1: Albite; A2: Anorthite; Zt: Zirconia (tetragonal); Zm: Zirconia (monoclinic); ZSt: Tetragonal zircon;

15

FIG. 9. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the sample of example 3, showing the crystallizations of anorthite (7) and the region with nanoparticles (8), crystallizations of zirconia (3) and zircon (4).

20

FIG. 10: Diagrammatic figure of the crystallizations present in the micrographs of the sample of example 3 differentiating the anorthite microcrystals (7), the region with nanoparticles (8) and the crystallizations of zircon (4) and zirconia (3).

25

FIG. 11: X-ray diffractogram of the samples of example 4. A1: Albite; A2: Anorthite; S: Tetragonal silica; Zt: Tetragonal zirconia; Zm: Monocyclic Zirconia.

30

FIG. 12. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the sintered mixtures of example 4 with a 90 % - 10 % (mixture 1, figure 12a), a 50 % - 50 % (mixture 2,

figure 12b) and 10 % - 90 % (mixture 3, figure 12c) of the frits obtained in example 1 and 3, respectively. Likewise, the diagrammatic figures are also observe showing each type of crystallization present in the microstructure of the sintered mixtures of example 4 for mixture 1 (figure 12d), mixture 2 (figure 12e) and mixture 3 (figure 12f), where the numbers represent: (6) phase 1 and 2 of example 1; (9) phase 7 and 8 of example 3; (4) zircon; (5) pore; (10) quartz.

FIG. 13: X-ray diffractogram of the samples of example 5. M: Mullite; A1: Albite; S: Tetragonal silica; A3: Alumina.

10

FIG. 14. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the samples of example 5, showing the crystallizations of mullite (11) and nanocrystallizations (12), crystallizations of albite (1) and of zirconia (3) and of zircon (4), and vitreous phase (13).

15

Fig.15: X-ray diffractogram of the conventional matt glaze comparative of example 7. A1: Albite; A2: Anorthite; Q: Quartz; ZSt: Tetragonal zircon.

FIG. 16. Scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF of the samples of the comparative conventional matt glaze on the support of example 7, showing the crystallizations of anorthite (7) and vitreous phase (13), crystallizations of zirconia (3) and of zircon (4), of quartz (10) and pores (5).

20

25

FIG. 17: Photographs taken with with the thermographic camera (real image (a and b) and infrared camera (c, d and e) which show the blind test experiment performed with the conventional floor tiles (14) and anorthite tiles (15). Points 16 and 17 show the initial temperature of each floor tile which is 12 °C in both cases. Points 18 and 19 show the temperature of each foot at the time of stepping on the floor tiles, which is 28.3 °C in both feet. Points 21 and 22 show the temperatures of the prints left by the feet on conventional floor tiles

30

(14) and anorthite tiles (15) after stepping on them for 5 seconds and which are 15.8 °C and 13.8 °C respectively.

FIG. 18: Photographs taken with the thermographic camera (real image
5 (a and b) and infrared (c, d and e) which show the blind test experiment performed with conventional floor tiles (14) and albite tiles (22). Points 23 and 24 show the initial temperature of each floor tile, which is 11 ° C, and 12 °C respectively. Points 25 and 26 show the temperature of each foot at the time of stepping on the floor tiles, which is 31.7 °C in both feet. Points 27 and 28 show
10 the temperatures of the prints left by the feet on the conventional floor tiles (14) and anorthite tiles (15) after stepping on them for 5 seconds, and which are 14.6 °C and 13.1 °C, respectively.

FIG. 19: Total reflectance of decorated and non-decorated example 6
15 and example 7 enamels.

FIG. 20. Temperature curves registered by the thermocouples inside the fabricated boxes with enamels of the example 6 and conventional ones (example 7 enamel), and the difference between them.
20

FIG. 21. Temperature curves registered by the thermocouples inside the fabricated boxes with enamels of the example 6 and the example 7 (conventional), and the difference between them, along several day-night cycles.

25

FIG. 22. Temperature curves registered by the thermocouples inside and in the outside surfaces of the boxes when wenge decorated example 6 enamel and wenge decorated example 7 enamel are used.

FIG. 23. Experimental setup of the energy saving test in the inside of a lined-tile box with white materials of example 6.

FIG. 24. Total reflectance curves of the material of the example in comparison with commercial a) ATH and b) TiO_2 .

FIG. 25. X-ray diffractograms of the enamel obtained according to EP 2759 524 A1 and the enamel of example 6.

FIG. 26: SEM micrograph of a glaze obtained according to EP 2759 524 A1.

FIG. 27. Total Reflectance of a glaze obtained according to EP 2759 524 A1 and an enamel prepared according to Example 6.

EXAMPLES

The invention will be illustrated below by tests performed by the inventors.

Example 1. Glass-ceramic material with principal crystallizations of albite phase.

The following formulation was used expressed in weight percent of equivalent oxides with respect to the total to obtain the glass-ceramic material with principal crystallizations of albite phase set down in Table 1.

Table 1: Weight percents expressed in terms of equivalent oxides of the composition of glass-ceramic material with principal crystallizations of albite phase.

Equivalent oxides	wt%
SiO_2	54.67

Al ₂ O ₃	22.63
CaO	7.73
SrO	7.20
Na ₂ O	2.14
K ₂ O	1.44
ZrO ₂	1.24
Others*	2.96

*Others: B₂O₃, TiO₂, P₂O₅, Fe₂O₃, MgO, BaO, ZnO with the weight percent of each one of them being less than 1%.

- 5 In a first step, the homogenized raw materials were melted with the following composition described in wt% in Table 2 and in wt% expressed in term of equivalent oxides in table 3.

10 Table 2: Raw materials in wt% used to obtain a frit in step a) for a glass-ceramic material with principal crystallizations of albite phase.

Raw materials	wt%
Potassium feldspar	6.96
Quartz	19.12
Dolomite	3.63
Calcium carbonate	10.98
Kaolin	6.86
Sodium feldspar	28.04
Calcined alumina	9.32
Strontium carbonate	10.69
Zircon flour	1.96
Others**	2.45

**Others: Boric acid, ZnO, Bicalcium phosphate, with the weight percent of each one of them being less than 1%.

Table 3: Weight percent expressed in terms of equivalent oxides of the frit obtained in step a) for a glass-ceramic material with principal crystallizations of albite phase.

5

Equivalent oxides	wt%
SiO ₂	54.54
ZrO ₂	1.43
SrO	8.31
Al ₂ O ₃	19.56
CaO	8.90
Na ₂ O	2.47
K ₂ O	1.46
Others***	3.32

***Others: B₂O₃, TiO₂, P₂O₅, Fe₂O₃, MgO, BaO, ZnO with the weight percent of each one of them being less than 1%.

10 The melting is carried out in an industrial melting oven at temperatures between 1450 °C and 1500 °C. Once the melting has been performed, the melted glass is cooled using water via a sudden cooling process to obtain the frit.

15 The term "frit" is understood to be a vitreous material obtained from the melting at high temperatures, generally of over 1400 °C, and a rapid cooling generally on water, or with air.

20 Then, the frit in aqueous suspension is ground together with a kaolin clay in step b). The kaolin used has the composition expressed in Table 4. The ground mixture had a ratio of 90 wt% of the frit and 10 wt% of kaolin. The aqueous suspension was formed by 63 wt% of the mixture obtained with 37 wt% of water. Two additives, carboxymethyl cellulose and tripolyphosphate,

were added to the aqueous suspension in an excess with respect to the solid content of 0.2 wt% each one. The grinding took place in a rapid alumina ball mill during 20 minutes until obtaining a barbotine characterized in that it has a rejection less than 6 % in a 63 μm mesh, obtaining the end material in the form of aqueous barbotine.

Table 4: Composition expressed in terms of equivalent oxides of the kaolin clay used in step b) to prepare a glass-ceramic material with principal crystallizations of albite phase.

Equivalent oxides	wt%
SiO_2	48.60
TiO_2	0.06
Al_2O_3	37.02
K_2O	1.06
Ignition weight losses	8.0
Others****	4.42

****Others: B_2O_3 , TiO_2 , P_2O_5 , Fe_2O_3 , CaO , MgO , BaO , ZnO with the weight percent of each one of them being less than 1%.

The material resulting from the grinding was dried in an oven at 60 °C during 8 hours until obtaining a powder suitable to undergo a forming process by pressing in the form of disks with dimensions of 6 cm in diameter and 12 mm thickness. The pressing pressure used in the forming step was of 400 $\text{kg}\cdot\text{cm}^{-2}$.

The disks obtained in the forming step underwent firing in a single-channel roller kiln in a 90-minute cycle and maintaining the maximum temperature of 1100 °C during 6 min.

In FIG. 1, the powder X-ray diffractograms are shown of the glass-ceramic material sintered at 1100 °C described in this example where the peaks

corresponding the following crystallizations were identified: A1: Albite; S: Tetragonal silica. From this spectrum, the vitreous phase percentage of the glass-ceramic material was obtained. The α ratio for this composition is 0.886 being very favourable to obtaining a high crystallization of albite phase and
5 being free from crystalline phases of greater conductivity.

FIG. 2 shows the micrographs obtained via scanning electron micrograph of the polished surface and surface chemically attacked with HF at 5 % by volume of the material described in this example 1 sintered at 1100 °C
10 with a heating rate of 30 °C/min and a time of remaining at the maximum temperature of 6 minutes.

In these micrographs, micrometric albite crystals (1) are observed with elongated morphologies and sizes between 300 nm and 1500 nm for the
15 smaller diameter and between 3 and 8 μ m for the larger diameter. These microcrystals are separated from one another by regions with nanocrystals (2) of diameters comprised between 40 and 80 nm and vitreous phase indicated as the cavities that remain between the nanocrystals.

FIG. 3 shows the micrographs obtained via scanning electron micrograph of the polished surface and surface chemically attacked with HF at 5 % vol of the material described in example 1 sintered at 1220°C with a heating rate of 30 °C/min and a time of remaining at the maximum temperature of 6 minutes. The same microstructure is observed, where the albite crystals (1)
20 have slightly reduced their size of larger diameter with respect to the glass-ceramic material sintered at 1100 °C, due to the increase in temperature, and they are also separated by a region with nanocrystals of size between 40 and 80 nm (2) and remains of vitreous phase. This microstructure maintains the values of thermal conductivity and increases the values of mechanical
25 resistance module.
30

In FIG. 4, a diagram is shown of the different structures observed in the

micrographs of FIG 2, distinguishing the albite microcrystals (1) and the region with nanocrystals that separates them (2).

As a result of the sintering step, a glass-ceramic material was obtained with the following properties set down in Table 5. The glass-ceramic material has a thermal conductivity comparable to that of human skin and in the range of materials such as wood. These properties represent an advantage for the production of ceramic products with thermal warmth factor values similar to those of human skin.

Table 5: Main properties for the glass-ceramic material formed as a coating sintered at different temperatures.

Maximum sintering temperature (°C)	1100	1220
Density (g cm ⁻³)	2.63	2.64
Coefficient of thermal expansion (°C ⁻¹)	53.32	53.32
Modulus of rupture (MPas)	52	71
Whiteness coefficient (L*)	87.7	91.1
Thermal conductivity (Wm ⁻¹ K ⁻¹)	0.31	0.29
Thermal warmth factor (TWF)	0.45	0.47
Vitreous phase percentage (%)	7.2	6.8

The density of the material is calculated using Archimedes' principle.

The coefficient of thermal expansion was measured in the temperature range from 30 to 500 °C using a DIL 801L dilatometer from Bahr.

The modulus of rupture (MOR) was obtained using the configuration of three bending points using an Instron 4411 Testing machine apparatus (Series IX, Boston, MA), equipped with 2 kN.

The whiteness coefficient (L*) was measured with a Coloreye XTH

colorimeter.

The thermal conductivity was measured using a DTC-25 device from TA Instrument using the controlled heat flow method.

5

The Thermal Warmth Factor was calculated from the abovementioned formula taking the value obtained in the cooling curve at 50 s, and the values of the calibration materials (Vespel and Steel STM) at the same seconds.

10

The vitreous phase percentage is obtained from the X-ray diffraction spectrum, by subtracting the crystalline phase from the total spectrum, in the range of $2\theta = 10 - 70$ from the calculation of areas.

15 The glass-ceramic material obtained has a thermal conductivity value similar (even less) than the average of human skin.

The material obtained has a high whiteness value for a percentage of zircon in the final composition of just 1.46 wt% which corresponds to 2 wt% of zircon added in the frit.

20

The glass-ceramic material has a high modulus of rupture, above the value of porcelain stoneware material used as a ceramic floor tile (modulus of rupture greater than 25 MPas).

25 **Example 2: Glass-ceramic material with principal crystallizations of albite phase and crystals with different percentages of ZrSiO_4 in the frit.**

30 The formulation described in Table 6 expressed in weight percent expressed in terms of equivalent oxides with respect to the total of the glass-ceramic material was used to obtain the glass-ceramic material with principal crystallizations of albite phase and different weight percents of ZrSiO_4 added in

the frit.

Table 6: Compositions in wt% expressed in terms of equivalent oxides with respect to the total of the glass-ceramic material with principal crystallizations of albite phase and different wt% of ZrSiO_4 added in the frit.

% of ZrSiO_4 added in the frit	0	2	4	6	8	10
% Equivalent oxides						
SiO_2	54.90	54.62	54.15	53.78	53.40	53.05
ZrO_2	0	1.30	2.55	3.75	4.90	6.01
Al_2O_3	20.10	21.59	21.35	20.98	20.63	20.29
CaO	9.10	8.13	7.94	7.77	7.62	7.46
SrO	8.50	7.57	7.40	7.25	7.10	6.95
Na_2O	2.50	2,25	2.18	2,13	2.09	2.04
K_2O	1.50	1.45	1.41	1.38	1.36	1.34
Others*	3.33	3.08	3.01	2.98	2.91	2.86

Others*: B_2O_3 , TiO_2 , P_2O_5 , Fe_2O_3 , MgO , BaO , ZnO with the weight percent of each one of them being less than 1%.

10

Similarly to example 1, the raw materials were melted, this time in a crucible oven.

In accordance with the wt% of ZrSiO_4 added in the frit and for samples sintered at 1220 °C, values of whiteness coefficient, thermal conductivity and proportion of vitreous phase are obtained, set down in Table 7.

Table 7: Values of whiteness coefficient, thermal conductivity and proportion of vitreous phase in the glass-ceramic materials with phase principal of albite with different wt% of ZrSiO_4 added in the frit.

20

% ZrSiO ₄ added in the frit	Whiteness coefficient (L*)	Thermal conductivity (Wm ⁻¹ K ⁻¹)	Vitreous phase (%)
0	86.3	0.55	84.90
2	87.9	0.31	93.15
4	90.1	0.44	82.90
6	91.4	0.45	82.48
8	91.5	0.33	83.07
10	92.3	0.35	88.04

In FIG. 5, the powder X-ray diffractograms are observed of glass-ceramic materials described in this example that have been identified with the following crystalline phases. A1: Albite; Zc: Zirconia (cubic); Zo: Zirconia (orthorhombic); Zm: Zirconia (monoclinic); ZSt: Tetragonal zircon; S: Tetragonal silica. It is observed that as the proportion of Zirconium increased in the formulation of the frit, the crystalline phases of Tetragonal zircon (ZSt) increased with all certainty due to saturation of the Zr⁴⁺ cation in the vitreous phase which causes its devitrification.

FIG. 6 shows the scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF (5 % vol.) of the glass-ceramic materials described in this example with 4% (FIG. 6a)) and 10% (FIG. 6b)) Zirconium content. As can be observed, for low concentrations of zirconium the crystallizations are of smaller size (3) and they are homogeneously distributed throughout the micro-nanostructure (2), preferably in the crystal interfaces. However, for higher Zircon concentrations, crystallizations in Zircon (4) form were produced, which had sizes of 200 – 500 nm, forming agglomerations in some regions.

FIG. 7 shows the diagrammatic images of the crystallizations observed in the micrographs with addition of ZrSiO₄ in the frit of 4 wt% (FIG. 7a)) and 10 wt% (FIG. 7b)). Figure 7a) shows the albite microcrystals (1), separated from

one another by a region of nanoparticles (2) and the ZrO_2 (3) and Zircon (4) crystals. Figure 7b) shows an area (6) which corresponds to a microstructure diagrammatically shown in Figure 7a) considered as an assembly to be able to define the zircon (4) and of zirconia (3) crystals and the pores formed (5).

5

Therefore, the addition of a percentage of ZrSiO_4 in the frit of 2 wt% is advantageous as it favours the crystallization processes of the albite-type feldspar crystalline phases, which leads to a reduction in thermal activity. As more zircon is added to the composition, the amount of zircon crystals increase, which in high quantities also decreases the thermal conductivity of the glass-ceramic materials.

10

Example 3: Glass-ceramic material with principal crystallizations of anorthite phase.

15

The following formulation was used to obtain the glass-ceramic material with principal crystallizations of anorthite phase, described in Table 8 expressed in weight percent of equivalent oxides with respect to the total of the glass-ceramic material:

20

Table 8: Weight percent expressed in terms of equivalent oxides of the composition of glass-ceramic material with principal crystallizations of anorthite phase.

Equivalent oxides	wt%
SiO_2	47.99
ZrO_2	7.31
SrO	0
Al_2O_3	21.42
CaO	11.82
Na_2O	4.58
K_2O	1.65

ZnO	4.30
Others*	0.94

*Others: TiO₂, P₂O₅, Fe₂O₃, MgO, PbO with the weight percent of each one of them being less than 1%.

- 5 The process described in example 1 was followed to develop the glass-ceramic materials sintered at 1220 °C with the properties set down in Table 9:
Table 9: Main parameters determined for the glass-ceramic material with principal crystallizations of anorthite phase.

Density (g.cm ⁻³)	2.63
Coefficient of thermal expansion (°C ⁻¹)	65.3
Modulus of rupture (MPas)	84
Whiteness coefficient (L*)	91.7
Thermal conductivity (Wm ⁻¹ K ⁻¹)	0.35
Thermal warmth factor (TWF)	-4.8
Vitreous phase percentage (%)	9.1

10

- In FIG. 8, the powder X-ray diffractogram of the sample described in this example is observed, identifying the peaks corresponding to the following crystallizations: A1: Albite; A2: Anorthite; Zt: Tetragonal zirconia; Zm: Monocyclic Zirconia; ZSt: Tetragonal zircon. From this diffractogram, the
15 crystallization percentage of the sample was extracted, which as is observed in Table 9 is very high. The α ratio for this composition of 0.946 being very favourable to obtain a high crystallization of anorthite phase and be free from crystalline phases of greater conductivity.

- 20 FIG. 9 shows the scanning electron microscope micrographs of the polished surface and surface chemically attacked with HF. In these micrographs, the anorthite crystals (7) are observed, in addition to a region with nanocrystals (8) which separates the larger crystals. The anorthite microcrystals

that form the glass-ceramic material of the invention have elongated morphologies with smaller diameter of between 200 nm and 500 nm and larger diameter of between 5 μ m and 30 μ m. Likewise, crystallizations of zirconia (3) less than 100 nm and of zircon (4) of size between 200 and 500 nm are also
5 observed, especially placed on the crystal edges. The vitreous phase has been eliminated with the chemical attack, and as observed is minority, although greater than the vitreous phase corresponding to example 1, being only found in the interfaces between crystallizations.

10 In FIG. 10, a diagram is shown of the crystallizations present in the micrographs of the material differentiating the anorthite microcrystals (7), the region with nanocrystals (8) and the crystallizations of zircon (4) or zirconia (3).

The glass-ceramic material obtained has a very high whiteness. It also has very high modulus of rupture values.

15

Example 4: Glass-ceramic materials obtained by mixing of frits.

To obtain glass-ceramic materials with a mixture of anorthite and albite phases, the frits of examples 1 and 3 were mixed. Table 10 represents the
20 weight percents of the frits of examples 1 and 3 used to prepare mixtures 1 to 3. Table 11 sets down the properties of the materials sintered at 1100 °C.

Table 10: Compositions in wt% for the glass-ceramic material with mixtures of anorthite and albite phases

25

Material mixture	Mixture 1	Mixture 2	Mixture 3
wt% frit example 1	90	50	10
wt% frit example 3	10	50	90

Table 11: Main properties determined for the glass-ceramic material with mixtures of anorthite and albite phases.

	Mixture 1	Mixture 2	Mixture 3
Coefficient of thermal expansion ($^{\circ}\text{C}^{-1}$)	53.95	57.71	61.96
Whiteness coefficient (L^*)	87.0	88.6	91.2
Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	0.31	0.30	0.46
Vitreous phase percentage (%)	9.0	4.7	12.1
Modulus of rupture (MPas)	52	110	84

In FIG. 11, the X-ray diffractogram of the materials is observed identifying the following crystalline phases: A1: Albite; A2: Anorthite; S: Tetragonal silica; Zt: Tetragonal zirconia; Zm: Monoclinic zirconia. It was observed that, in the material of mixture 1, the majority spectrum is of albite crystals with a small contribution of the anorthite phase. It also observed the presence of tetragonal silica and tetragonal zirconia. As the concentration of the frit of example 3 increased, a greater contribution of the anorthite phase appeared, with the disappearance of the tetragonal zirconia and the monoclinic phase appearing. This is more pronounced in mixture 3. As regards the vitreous phase, it was observed that it increased when the crystallization of anorthite increases, in accordance with the conductivity values which also increase for the case of mixture 3.

In FIG. 12, the micrographs obtained by scanning electron microscope are observed showing the different mixtures: mixture 3 (FIG. 12 a)), mixture 2 (FIG. 12 b)) and mixture 1 (FIG. 12c)). Likewise, diagrammatic figures are observed of the different types of structures shown in the micrographs in Figures 12 d), 12 e) and 12 f), respectively. In FIG. 12 a) a crystalline phase of albite (1) was observed surrounded by a region of nanoparticles (2) in majority form, which is defined as area 6, and in some isolated areas, regions appear with crystals of anorthite crystalline phase (7) with their region with nanoparticles (8) which is defined as area 9, and it is attributed to the fact that no reaction occurs in the mixtures between the different frit particles during the sintering.

The distribution of the microstructures of mixture 3 can be clearly seen in the diagram of FIG 12 d). The ratio between the anorthite and albite phases was of 10 and 90 % respectively in area. Likewise, zircon (4) and zirconia (3) crystals, quartz crystals (10) and pores of sizes between 1 – 20 μm (5) were observed.

FIG. 12 e) shows the diagram of the distribution of microstructures corresponding to a ratio between the anorthite and albite phases of 45 and 55 % respectively in area.

FIG. 12 f) shows the diagram of the distribution of microstructures corresponding to a ratio between the anorthite and albite phases of 80 and 20 % respectively in area.

The preparation of mixtures allows the control of the desired final properties, mixtures can be prepared with intermediate properties in some parameters such as the coefficients of thermal expansion and whiteness, whilst in other mixtures improvements occur in the values of thermal conductivity and percentages of crystallization. From a production standpoint, obtaining glass-ceramic materials with thermal warmth via the preparation of mixtures makes it possible to compensate for deviations in the composition during their production and adjusting parameters in accordance with its application.

Example 5: Comparative example of conventional glass-ceramic material with mullite phase.

As a comparative example, the properties were analysed of a comparative glass-ceramic material with mullite phase whose composition is set down in Table 12.

Table 12: Weight percent expressed in terms of equivalent oxides of the composition of conventional glass-ceramic material with mullite.

Equivalent oxides	wt%
SiO ₂	43.70
B ₂ O	3.50
P ₂ O ₅	2.88
Al ₂ O ₃	32.20
CaO	2.98
MgO	2.63
BaO	3.12
SrO	3.28
ZnO	2.14
Na ₂ O	1.50
K ₂ O	1.59
Others*	0.21

*Others: ZrO₂, TiO₂, Fe₂O₃ with the weight percent of each one of them being less than 1%.

5

The raw materials used to obtain the frit of this material with mullite phase, expressed in weight percents, are those set down in table 13. The properties of the sintered material are included in table 14.

- 10 Table 13: Weight percent of raw materials used for the composition of the frit used is of production of conventional glass-ceramic material with mullite phase.

Raw materials	wt%
Borax pentahydrate	6.0
Boric acid	1.3
Quartz	39.3
Potassium nitrate	2.8
Zinc oxide	1.8

Dicalcium phosphate	5.3
Alumina	30.0
Barium carbonate	3.5
Strontium carbonate	4.6
Magnesite	5.4

Table 14: Main properties determined for the conventional glass-ceramic material with mullite phase.

Density (g/cm^3)	2,70
Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	0.77
Coefficient of thermal expansion ($^{\circ}\text{C}^{-1}$)	41.58
Thermal warmth factor (TWF)	4,9
Vitreous phase percentage (%)	35,0

5

In FIG. 13, the powder X-ray diffractogram of the sample described in example 5 is observed, identifying the peaks corresponding to the following crystallizations: M: Mullite; A1: Albite; S: Tetragonal silica; A3: Alumina. From this diffractogram, the percentage of crystallization of the material with mullite phase was determined. This percentage is clearly less than that observed in examples 1, 2, 3 and 4. The α ratio is for this composition 1.870 being highly favourable to obtaining a crystallization of mullite phase. The thermal conductivity of the mullite phase is $6 \text{ Wm}^{-1} \text{ K}^{-1}$ and, therefore, not desirable.

FIG. 14 shows the micrographs obtained by scanning electron microscope of the material with mullite phase distinguishing different crystallizations of microcrystals: mullite (11) and albite (1) and an important proportion of interconnected vitreous phase (13) which is surrounding the crystallizations and isolated regions of nanocrystals (12). The presence of a region with nanocrystals as boundary between the microcrystals was not observed.

Therefore, the material with mullite phase shown in this example does not display thermal warmth and its properties moves away from the product of the invention.

5 **Example 6: Glass-ceramic material formed as coating in the form of glaze of porcelain stoneware.**

The glass-ceramic material obtained in example 1 is processed in the form of ceramic glaze on porcelain stoneware by bell-shaped glaze application
 10 in an glazing line on a compacted porcelain stoneware support with a layer of slip previously deposited using the same bell-shaped glaze application method. Then, a palette of digital printing inks was applied on the green glaze surface with colour configuration CMBYPK with the aid of a Kerajet machine. Next, it underwent standard firing in an industrial oven at 1200 °C with a cold-to-cold
 15 cycle of 60 minutes.

Coatings were prepared in the form of glazes with different thicknesses, varying the passage rate of the slipped support by the flow of the bell-shaped glaze application. In the tile industry, glazes are usually identified by grammage
 20 expressed as grams of glaze per m² of support. In the following Table 15, the thermal conductivity, TWF and roughness of the glazes on porcelain stoneware with grammages of 750 gm⁻² and 2500 g.m⁻² are shown.

Table 15: Values of thermal conductivity, Thermal warmth factor and roughness
 25 for the glass-ceramic material formed as coating in the form of glaze of porcelain stoneware with different grammages.

Grammage (g.m ⁻²)	750	2500
Thermal conductivity (Wm ⁻¹ K ⁻¹)	0.46	0.44
Thermal warmth factor (TWF)	0.62	0.34
Roughness (µm)	8.9	8.4

As is observed, on applying the glass-ceramic material on the porcelain

stoneware in the form of glaze coating, the thermal conductivity increases from a value obtained in example 1 of $0.31 \text{ Wm}^{-1}\text{K}^{-1}$ to values of $0.44 - 0.46 \text{ Wm}^{-1}\text{K}^{-1}$. The thermal conductivity of the porcelain stoneware support without the glaze was determined as $0.7 \text{ Wm}^{-1}\text{K}^{-1}$, so that on adding a coating in the form of glaze
 5 formed by the glass-ceramic material of example 1 a significant reduction is obtained of the thermal conductivity of the ceramic floor tile, which is advantageous for its uses as cladding tiles with thermal warmth.

Likewise, the glass-ceramic material applied on porcelain stoneware was
 10 subjected to different sintering temperatures. In table 16, the thermal conductivity and thermal warmth factor TWF data are observed of the glazes on porcelain stoneware sintered at different temperatures in a laboratory muffle furnace.

15 Table 16: Values of thermal conductivity and of Thermal warmth factor for the glass-ceramic material formed as coating in the form of glaze of porcelain stoneware at different sintering temperatures.

Sintering temperature (°C)	Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	Thermal warmth factor (TWF)
1200	0.46	-0.9
1210	0.48	0.95
1220	0.46	0.45
1240	0.40	0.51
1250	0.38	0.66

20 **Example 7: Comparative example of a conventional matt glaze applied on porcelain stoneware.**

A conventional matt ceramic glaze has crystallizations of anorthite in a much greater proportion than in the glass-ceramic glaze of the present invention
 25 since it has a vitreous phase higher than 20%. A conventional matt glaze is obtained from a frit which partially crystallizes in anorthite and which has been

mixed in a step with different minerals such as kaolin, clay, nepheline, dolomite, zircon, quartz and α -alumina.

The properties of this conventional glaze as comparative example
5 sintered in a rapid single channel roller industrial kiln at 1200 °C with 60-minute cold-to-cold cycle are set down in table 17.

Table 17: Values of thermal conductivity and vitreous phase percentage of a conventional matt glaze applied on porcelain stoneware.

10

Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)	0.77
Vitreous phase percentage (%)	26.3

In FIG. 15, the X-ray diffractogram of the conventional matt ceramic glaze is shown, distinguishing the following crystallizations: A1: Albite; A2: Anorthite; Q: Quartz; ZSt: Tetragonal zircon. Unlike the glass-ceramic material
15 of the invention, the conventional matt ceramic glaze also has a quartz crystalline phase. The vitreous phase percentage of 26.3% was taken from the diffractogram, observing that the vitreous phase increases with respect to the glass-ceramic material obtained in examples of glass-ceramic material of the present invention, example 1, 2, 3, and 4.

20

FIG. 16 shows the micrographs obtained by scanning electron microscope of the polished surface and surface chemically attacked with HF of the conventional matt glaze, observing that its microstructure is characterized by a percolation of the vitreous phase (13) which forms a continuum. The
25 crystallizations of anorthite (7) separated by the vitreous phase (13), and quartz crystals (10), zircon crystals (4) and pores (5) are also observed. No regions with nanoparticles are observed. The vitreous phase is considerably greater than 18 % and it is also percolated, in this way being responsible for the increase in thermal conductivity, for which reason it is not a material suitable for
30 the application of thermal warmth.

Example 8: Blind experiment.

A blind experiment was performed evaluating the sensation of heat experienced by 10 middle-aged people chosen at random (5 women and 5 men). 3 pieces of floor tiles were placed with the same final product finish in a room at ambient temperature (values between 21.5 and 23 °C). The room's floor was wooden. The pieces of floor tile were cooled to 10 °C and they were placed on the wooden floor. The temperature was determined by thermographic means.

The three pieces of the floor tiles are described below:

1. Conventional (14): This floor tile was prepared with the comparative conventional matt glaze described in example 7. The support used was a 1cm-thick porcelain tile.
2. Floor tile with principal crystalline phase of anorthite (15): This floor tile was prepared as coating in the form of glaze using the glass-ceramic material of example 3. The support used was a 1cm-thick porcelain tile.
3. Floor tile with principal crystalline phase of albite (22): This floor tile was prepared as coating in the form of glaze using the material described in example 1. The support used was a 1cm-thick porcelain tile.

The experiment consisted of making each individual separately take off their shoes and step on the wooden floor during 15 seconds, then they had to step on floor tile 14 (conventional) which was at 10 °C during 5 seconds and again step on the wood for another 15 seconds. This process was repeated with each one of the floor tiles (15 and 22) using the same foot. Finally, the individual had to establish which of the 3 floor tiles gave him or her the greatest sensation of warmth in contact with the foot.

In 100 % of the cases, the individuals replied that the floor tile which gave them the greatest sensation of cold was 14 (conventional). 80 % of the individuals determined that the floor tile which gave them greatest sensation of

thermal warmth was floor tile 22 (albite), and the remaining 20 % determined that it was 15 (anorthite).

Photographs were also taken with an infrared camera or thermographic
5 camera, which takes real images and their equivalent with thermographics or infrared, during the process, simultaneously stepping on both floor tiles, with one foot on floor tile 14 and the other on floor tile 15 in first place, and then the same was done with floor tiles 14 and 22 changed in order to avoid conditioning. In this way, the difference in sensation of thermal warmth between
10 floor tiles was compared with thermal data.

In FIG. 17 and FIG. 18, the real images a) and b) and the photographs taken with the thermographic camera c), d) and e) of the blind experiments performed on one of the individuals was observed in representative form.

15

FIG. 17 shows the differences between floor tile 14 and floor tile 15, which are initially at 11.8 and 12.4 °C (16 and 17) respectively. Both feet are at the same temperature, 28.2 and 28.4 °C (18 and 19). After 5 seconds of stepping on the two floor tiles with the two feet, the real and infrared
20 photographs were taken observing that the conventional floor tile (14) has a footprint with a larger temperature gradient (20), 15.8 °C, than in the case of floor tile 15 (anorthite), 13.8 °C (21). This means that floor tile 14 has absorbed more heat from the foot, because its thermal conductivity is greater, and therefore there is more heat transmission, which translates into a greater
25 sensation of cold in the foot.

However, in floor tile 15, the temperature gradient has been less (2 °C less) (21), so that the heat transmission from the foot to the floor tile has been less in those 5 seconds, the reason for which the sensation of warmth is greater
30 in this floor tile.

When floor tile 14 and floor tile 22 (FIG. 18) are compared, the same

occurs. In this case, floor tile 22 is at an initial temperature of 11 °C (23), and floor tile 14 of 12 °C (24). The feet are at a temperature of 31.6 and 31.8 °C (25 and 26) and the temperature gradient on stepping on the conventional floor tile 1 is 14.6 °C (27), 1.5 °C greater than on stepping on floor tile 22, 13.1°C (28),
5 so that it also gives a sensation of greater warmth on stepping on floor tile 22 than floor tile 14.

As a result, and using the blind experiment, it statistically demonstrates that the materials designed with low thermal conductivity provide a greater
10 subjective sensation of thermal warmth for the materials of the present invention.

Example 9: Reflectance and solar reflectivity properties of glass ceramic materials.

15

Total reflectance measurements of glass ceramic coatings of porcelain stoneware have been carried out by means of a spectrophotometer with integrated sphere. Coatings of grammage 2500 g.m⁻² were prepared according to example 6 and 7 (conventional glass ceramic glaze) for comparison.
20 Furthermore, the same enamels described in this example but decorated by inkjet in wenge color, has been prepared and measured in order to check the total reflectance of these materials when the whiteness is lost. Herein, these samples are denoted as decorated example 6 and decorated example 7. The reflectance curves of the decorated enamels compared to the non-decorated
25 enamel (White) are shown in Figure 19.

The reflectance spectrum of wenge enamels varies, especially in the visible range, and presents lower reflectance than the white enamels. In Figure 19 it is also observed that the total reflectance of the wenge example 6 enamel is higher than the wenge example 7 (conventional wenge decorated example
30 7). Table 19 shows the average reflectance values in the range of 300-2500 nm.

The solar reflectivity has been calculated through the reflectance of each material and the solar spectrum according to the standard ASTM G173-03, by means of the following equation in the whole solar spectrum (320-2500nm):

$$SR = \frac{\int_{320}^{2500} R \cdot IS \cdot d\lambda}{\int_{320}^{2500} IS \cdot d\lambda}$$

5 Where SR is the solar reflectivity and IS is the solar spectrum irradiance.

The integrals are the mathematical representation of the area below the curve of each spectrum: the solar spectrum and the resultant of multiplying the material reflectance and the solar spectrum. Hence, solar reflectivity is defined as the proportion of the solar spectrum that the material is able to reflect and its values are between 0 to 1 where 0 is the minimum reflectivity this is when the material absorbs the whole solar spectrum; and 1 is the maximum when the material reflects the whole solar spectrum. According to this definition, solar reflectivities of the enamels have been obtained. The solar reflectivity values are shown in Table 19 in the range 300-2500 nm. As expected, the solar reflectivity increases with the enamel thickness. The example 6 enamel presents larger solar reflectivity than example 7 enamel (conventional). When the wenge is applied to the enamels, the SR decreases, especially in the visible range, although the example 6 enamel is also superior to the conventional (example 7).

20

Sample	weight (g)	Average reflectance (%)	Solar Reflectivity (SR)
Example 6	80	75.8	0.74
	120	81.9	0.80
	300	90.3	0.86

Conventional (Example 7)	80	74.6	0.70
	300	89.2	0.84
Wenge sample (decorated Example 6)	300	62.7	0.42
Conventional wenge sample (decorated example 7)	300	55.7	0.36

Table 19: Reflectance and solar reflectivity values.

The solar reflectivity values observed for the example 6 enamels are high, with similar or higher results as applying several reflective paints (reference: Special Infrared Reflective Pigments Make a dark roof reflect almost like a white roof. Performance of Exterior Envelopes of Whole Buildings IX International Conference, ASHRAE, December, 2004).

Table 20 shows the specific heat, conductivity and solar reflectivity values for the conventional (example 7) and example 6 enamels with grammage 2500 g.m⁻².

Sample	Specific heat (J/kg°C)	Conductivity (W/mK)	Solar reflectivity
Example 6	765.1	0.44	0.86
Conventional (example 7)	741.8	0.77	0.84

Table 20: Specific heat, conductivity and solar reflectivity values for the example 6 and example 7 (conventional) with grammage 2500 g.m⁻².

The thermal diffusivity (α) expresses the rate of change of temperature and flow in a material until it reaches thermal equilibrium; as higher is the diffusivity as faster is the equilibrium temperature reached and therefore, higher is the heat flux. To obtain lower diffusivities and to slow down the heat flux, low thermal conductivities and large specific heats are needed.

$$\alpha = \frac{\kappa}{\rho C_p}$$

wherein κ is the thermal conductivity, ρ is the material density and C_p is the specific heat.

As seen in Table 20, the specific heat and thermal conductivity values of the example 6 material fulfill the necessary conditions to obtain lower thermal diffusivity than the conventional enamel (example 7 enamel), constituting a material with higher thermal comfort. These characteristics in addition to a larger solar reflectance which avoids the heat absorption from the outside, provide an adequate material to achieve a greater energy saving.

Energy saving estimation:

According to these results, energy efficiency test have been carried out using coatings made of example 6 and conventional (example 7) materials, calculating the difference in temperature. Two boxes of 15cmx15cm have been fabricated with white materials of example 6 and example 7 (conventional), and they were situated as a roof of a building during 21h (from 18:00 to 15:21 of the next day). Temperature measurements have been registered inside each box through two thermocouples. During the night it was observed that the temperature difference between both boxes are minimum ($\sim 0.5^\circ\text{C}$), as the solar reflection was not produced. However, during the central hours of the day, the highest temperature difference are registered, achieving up to 3°C of difference, where the box fabricated with the example 6 material heated less than the conventional (example 7), due to a larger solar reflection. Figure 20

shows the temperature curves registered by the thermocouples in both boxes and the temperature difference.

A similar test was carried out by repeating several day-night cycles obtaining the curves shown in Figure 21. These curves shows that in the central hours of the day, it was achieved temperature differences up to 2 °C, which confirms that the material of example 6 has larger solar reflection and heated less.

A calculation of the energy savings that would produce the substitution of the conventional tiles by tiles made of example 6 materials was performed. Knowing that the temperature difference between the two materials was ranged between 1.5 and 3 °C in the central hours of the day, when acclimatization systems were required, and considering same mass for both materials, it is possible to calculate the necessary energy to bring both materials to a comfort temperature of 25 °C in summer, by means of the following equation:

$$Q = m \cdot C_p \cdot (T_i - T_f)$$

Therefore, considering a building with tiles of Example 3 that are set at a temperature of 30 °C, and another one with conventional tiles that are set at a temperature of 31.5 °C; the energy required for cooling each material to the comfort temperature of 25 °C is the following::

$$\text{Example 6: } Q/m = 765.1 \text{ J/kg}^\circ\text{C} \cdot (30-25)^\circ\text{C} = 3825.5 \text{ J/kg}$$

$$\text{Example 7 (Conventional): } Q/m = 741.8 \text{ J/kg}^\circ\text{C} \cdot (31.5-25)^\circ\text{C} = 4821.7 \text{ J/kg}$$

Consequently, less energy is required to achieve the comfort temperature for tile made of example 6 material than for tiles made of example 7 material (conventional). An energy saving of almost 21 % is obtained.

$$\text{Energy saving} = \frac{4821.7 - 3825.5}{4821.7} \cdot 100 = 20.7\%$$

If the same calculations are done for a temperature difference of 3 °C between both enamels, an energy saving of 35.5% obtained:

$$\text{Example 6: } Q/m = 765.1 \text{ J/kg}^\circ\text{C} \cdot (30-25)^\circ\text{C} = 3825.5 \text{ J/kg}$$

$$\text{Conventional: } Q/m = 741.8 \text{ J/kg}^\circ\text{C} \cdot (33-25)^\circ\text{C} = 5934.4 \text{ J/kg}$$

$$5 \quad \text{Energy saving} = \frac{5934.4 - 3825.5}{5934.4} \cdot 100 = 35.5\%$$

Therefore, along the central hours of the day, it is possible to obtain an energy saving in a range of **20.7-35.5%** if conventional tiles are substituted by the material of example 6 in the buildings facades.

10 The same test was performed for wenge decorated enamels in order to check the absorption of the solar radiation by the enamels with a dark color. In this case, in addition of the thermocouples situated inside the boxes, two more thermocouples were used, situated in contact with the outside surface of the boxes, to check the heating of each one.

15 The results are depicted in Figure 22. It is found that, for the inner temperature, the enamel of wenge decorated example 6, transmits less heat than the conventional wenge decorated enamel as it reflects more of the solar spectrum, in spite of both enamels absorb more in the visible range. The temperature differences between the enamels achieve 1.6 °C in the central hours of the day. In the case of outside temperature, the differences between
20 both enamels are minimal, achieving only 0.5 °C in some cases. This fact is due to the dark color that absorbs more of the solar radiation, matching the surface temperatures. However, the different favorable characteristics of the enamel of the example 6, as low thermal conductivity and larger specific heat, allow that heat is not transferred into the box.

25 Finally, to study the energy saving when white example 6 tiles are situated inside a room, ceramic boxes were fabricated with dimensions of 35cmx35cm of surface, one with the white example 6 and another with white example 7 material (conventional). The glazed faces were disposed into the

boxes, to simulate a tile-lined room. The inner of the boxes was heated by means a heat external source, a radiator, and the achieved temperatures in one of the faces were measured related to the exposition time, with a thermographic camera. The experimental setup is shown in Figure 23.

- 5 Four measurements were performed, registering the achieved temperature in the enamel after 600s. In all the measurements, the white enamel of example 6 achieves lower temperature gradients, up to 1.4 °C lower, after the same time, than the white conventional one. The gradient values are shown in Table 21. Therefore, the white material of example 6 is heated less
- 10 than white conventional enamel, with the same heat source (same energy), so less energy is transmitted to the outside, which produces an energy saving. This energy saving can be calculated with the above equation, which allows a saving of ~20%.

Sample	Temperature gradient (ΔT) (°C) after 600 s			
	Measure 1	Measure 2	Measure 3	Measure 4
Example 6	8.2	7.7	5.9	11.9
Example 7 (Conventional)	9.6	8.2	7.5	12.9

- 15 Table 21: Temperature gradient obtained for example 6 and example 7 (conventional) materials in the inner of the box.

- According to the data obtained in this example, materials of the invention, provide significant energy savings when they are used as lining. These linings can be used in outside facades and roofs, as they reflect more solar radiation
- 20 than the current methods. In addition, the reflecting paints used currently required several coatings to achieve the same solar reflectivity values than the enamel of invention. Moreover, they undergo high degradation along short time,

and need constant arrangements unlike ceramic tiles, that have high coefficients of resistance and durability.

Likewise, these ceramic linings can be used in the inside of buildings providing a great heating savings, as they have high reflectance in the infrared, which produces that the heat is not absorbed by the walls, remaining inside the room.

Example 10: Comparison of TiO₂ powder and milled glass- ceramic material of example 6.

The glass-ceramic of example 6 has been milled with alumina balls mill to reduce its size below 10 μm . This process consist in milling procedure using 0.05 %wt. of de sodium tripolyphosphate, 0.05 %wt. of sodium chloride and 37 %wt. of water. 40 kg of the material were milled in the first step during 24 h. After milling the material rejection thorough a 63 μm sieve was less than 1%. Thereafter the same composition was milling with continuous microballs Netzsch milling system. The time of this milling was 20 min (1 KW/h) achieving a d_{90} below 10 μm and a d_{50} between 3-7 μm .

Likewise, two commercial materials commonly used to the reflective pigment preparation for their opacifiers and whitening properties, were chosen, TiO₂ and Al(OH) (ATH). Table 22 shows the particle sizes and whiteness of these 3 materials. The average size of the enamel of this example is similar to the commercial materials; however, the d_{90} is one magnitude order higher. The whiteness-opacity values are very high in all cases, and are very similar in the case of the enamel and TiO₂. The whiteness of ATH is slightly lower.

	TiO ₂	ATH	Example 10
Particle size (d_{50}) (μm)	0.4	2.14	3.39
Particle size (d_{90}) (μm)	0.8	4.70	23.04
Whiteness	98.4	99.0	98.2

Table 22: Particle size and whiteness values of the material of this example and the commercial products, TiO₂ y ATH.

Total reflectance and solar reflectivity of these three materials were measured. The reflectance of powder material from example 10 (Figure 24), measured in a range of 319-2500nm, with integrating sphere, was 101.7%. That is, the average reflectance of the material was higher than the reference target used for the measurement. In the case of ATH shows that in some wavelengths was more reflective than the example 10 powder (mainly in the visible), however, its reflectance was lower in the near-infrared (NIR). The average reflectance of ATH is 86.1%. The TiO₂ was more reflecting than the enamel of the example in the visible range, but it was less reflective in the near infrared. TiO₂ has an average reflectance of 90.7%. Therefore, the material of example 10 has a greater reflectance than the two commercial products used in reflective paints, especially in the range of NIR. The reflectance values in whole spectrum and NIR are seen in Table 23.

Solar reflectivity measurements were similar in the three materials, with differences in the NIR. Table 23 shows the solar reflectivity values of the whole spectrum and in the specific case of NIR. The material of example 10 has the largest solar reflectivity in the whole spectrum and especially in the NIR, which will be more efficient in energy saving applications such as facades, roofs and interiors.

Sample	Average Reflectance (%)	Average Reflectance (%) NIR (700-2500nm)	Solar Reflectivity (SR)	Solar Reflectivity (SR) in the NIR (700-2500nm)
Example 10	101.7	103.2	0.971	0.985
TiO ₂	90.7	92.4	0.950	0.979
ATH	86.1	83.3	0.971	0.958

Table 23: Solar reflectance and reflectance values in the whole spectrum and in the near infrared (NIR), of material from Example 10, the TiO₂ and ATH.

Moreover, this type of milled glass ceramic material, thanks to its optical
5 properties, can be used in many applications such as paints, whiteners-opacifier in paper industry, painting or polymers.

Example 11: Comparative example of a glaze according to patent EP 2759 52 A1 with an enamel of example 6.

As a comparative example, the properties of a comparative glass-
10 ceramic material (as described in EP 2759524 A1) which includes the crystal phases albite and anorthite as well as glassy phase.

A pressed disk from a material according to EP 2759 524 A1 was prepared and sintered at 1220 °C. After the thermal treatment it was observed that the sample melted and it was not possible to obtain a disk of this material. It
15 was only possible to obtain a glaze coating which was applied over a porcelain stoneware as described in the patent EP 2759 524 A1.

Figure 25 shows the X-ray diffractograms of the glaze obtained according to EP 2759 524 A1 and the glaze of example 6 sintered at 1220 °C, wherein the X Ray diffraction peaks corresponding to the following crystallizations were
20 identified: A1 Albite ; Anorthite A2. The proportion of glassy phase was determined in the same way as described in Example 1. The glaze obtained according to EP 2759 524 A1 has a glass phase ratio of **33.5%** and the one of example 6 of **13.8%**. Therefore, under the same preparation conditions, both enamels differ widely in their percentage of vitreous phase.

25 Figure 26 shows a Scanning electron microscopy micrograph corresponding to the glaze of EP 2759 524 A1 wherein micrometer albite and anorthite crystals dispersed in a vitreous phase are observed.

Figure 27 shows the total reflectance obtained by means of a spectrophotometer with integrating sphere, of a glaze obtained according to EP

2759 524 A1 and an enamel obtained according to Example 6. These curves show that the enamel of Example 6 has a reflection 30% higher than a glaze obtained according to EP 2759 524 A1 in the whole spectrum.

Table 24 shows the main properties of a glaze obtained according to EP 2759 524 A1 and an enamel prepared according to Example 6.

	Example 6	EP 2759 524 A1
Whiteness coefficient (L*)	95,4	76,6
Thermal Conductivity (Wm ⁻¹ K ⁻¹)	0,56	-
Vitreous phase percentage (%)	13,8	33,5

Table 24: Main properties of a glaze obtained according to EP 2759 524 A1 and an enamel prepared according to Example 6. The solar reflectivity is obtained following the method described in the example 9. For the enamel of Example 6 the solar reflectivity is 0.89 and for the enamel obtained according to EP 2759 524 A1 is 0.57, which is ~30% lower.

CLAIMS

1. Glass-ceramic material which exhibits a sensation of thermal warmth, characterized in that it has a thermal conductivity between 0.25 to $0.5 \text{ Wm}^{-1}\text{K}^{-1}$
5 and comprising
- albite $\text{NaAlSi}_3\text{O}_8$ microcrystals and nanocrystals ,
 - optionally, anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals
 - and vitreous phase,
- wherein the microcrystals are separated by a region formed by the nanocrystals
10 and the vitreous phase,
and wherein said the vitreous phase is in a proportion less than 18 % with respect to the total weight of the glass-ceramic material.
2. Glass-ceramic material according to the preceding claim, comprising
15 anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals.
3. Glass-ceramic material according to any of claims 1 or 2, wherein the albite microcrystals have elongated morphologies with smaller diameter of between $0.3 \mu\text{m}$ and $1.5 \mu\text{m}$ and larger diameter of between $1.5 \mu\text{m}$ and $8 \mu\text{m}$.
20
4. Glass-ceramic material, according to any of claims 1 to 3, wherein the anorthite microcrystals have elongated morphologies with smaller diameter of between $0.2 \mu\text{m}$ and $0.5 \mu\text{m}$ and larger diameter of between $5 \mu\text{m}$ and $30 \mu\text{m}$.
- 25 5. Glass-ceramic material, according to any of claims 1 to 4, wherein said material contains at least a weight percent with respect to the end material expressed in terms of the following equivalent oxides:
- between 45 % and 68 % of SiO_2 ,
 - between 15 % and 27 % of Al_2O_3 ,
 - 30 • between 4.5 % and 13 % of CaO ,
 - between 0 % and 9 % of SrO ,
 - between 1 % and 5.5 % of Na_2O ,

- between 1 % and 5 % of K_2O ,
- between 0 % and 2% of B_2O_3 ,
- between 0 % and 14 % of ZrO_2 ,
- and between 0% and 5 % of MgO , BaO and ZnO .

5

6. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of SiO_2 is between 49 % and 60 %.

10 7. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Al_2O_3 is between 17 % and 25 %.

15 8. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Al_2O_3 is between 19 % and 23 %.

20 9. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of CaO is between 6 % and 12 %.

10. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of CaO is between 7.5 % and 11 %.

25

11. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Na_2O is between 1.5 % and 4 %.

30 12. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Na_2O is between 2 % and 3.5 %.

13. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of K_2O is between 1.5 % and 4 %.

5

14. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of K_2O is between 2 % and 3 %.

10 15. Glass-ceramic material according to any of claims 1 to 14, wherein

- it further comprises zirconia crystals ZrO_2 or zirconium silicate crystals $ZrSiO_4$, where said crystals are distributed throughout the region of nanocrystals and vitreous phase which separate the microcrystals of the glass-ceramic material,

15 and wherein the material displays a thermal conductivity between 0.31 and 0.45 $Wm^{-1}K^{-1}$.

16. Glass-ceramic material according to the preceding claim, wherein the zirconia crystals ZrO_2 may be in the form cubic, tetragonal or monoclinic.

20

17 Glass-ceramic material according to any of claims 15 or 16, wherein the zirconia crystals ZrO_2 have an average size of between 50 and 200 nm.

18. Glass-ceramic material according to claim 15, wherein the zirconium
25 silicate crystals $ZrSiO_4$ have an average size of between 200 nm and 500 nm.

19. Glass-ceramic material according to any of claims 15 to 18, wherein the weight percent of the zirconia crystals ZrO_2 or of the zirconium silicate crystals $ZrSiO_4$ expressed in terms in equivalent oxide with respect to the total weight of
30 the glass-ceramic material is between 2 % and 14 %.

20. Glass-ceramic material according to the preceding claim, wherein the

weight percent of the zirconia crystals ZrO_2 or of the zirconium silicate crystals ZrSiO_4 expressed in terms in equivalent oxide with respect to the total weight of the glass-ceramic material is between 2 % and 8 %.

5 21. Production process of the glass-ceramic material according to any of claims 1 to 20, comprising the following steps:

a) melting at least one compound selected from the list comprising sassolite H_3BO_3 , quartz SiO_2 , dolomite $\text{CaMg}(\text{CO}_3)_2$, calcium carbonate CaCO_3 , zincite ZnO , kaolin $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, strontianite SrCO_3 , alumina Al_2O_3 , calcium
10 phosphate $\text{Ca}_3(\text{PO}_4)_2$, a zirconium compound selected from among zirconia ZrO_2 or zirconium silicate ZrSiO_4 and an alkali feldspar selected from among albite $\text{NaAlSi}_3\text{O}_8$ and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, or any combination thereof, at a temperature of between 1400 °C and 1550 °C, and fritting;

b) grinding the frit obtained in step a) with kaolin;

15 c) forming the product obtained in b);

d) sintering the product formed in c) at temperatures of between 980 °C and 1280 °C.

22. Process according to the preceding claim, wherein the percentage of the
20 frit used in the grinding mixture of step b) is between 70 % and 96 wt%.

23. Process according to any of claims 21 or 22, wherein the percentage of kaolin is between 4 % and 15 wt% in step b).

25 24. Process according to any of claims 21 to 23, wherein step d) of sintering is carried out at temperatures of between 1100 °C and 1220 °C.

25. Process according to any of claims 21 to 24, comprising an additional step e), after the step of sintering (d), of rectifying and polishing with abrasives.

30

26. Use of the glass-ceramic material according to any of claims 1 to 20, for the manufacturing of industrial, structural or ornamental ceramic products.

27. Use according to the preceding claim, for the manufacturing of floor tiles or glazes of floor tiles.

5 28. Use of the glass-ceramic material according to any of claims 1 to 20, as thermal insulator.

29. Use of the glass-ceramic material according to claim 28, as a component of a cool roof, cool room or cool façade.

AMENDED CLAIMS

received by the International Bureau on 24th May 2016 (24.05.2016)

CLAIMS

1. Glass-ceramic material which exhibits a sensation of thermal warmth,
characterized in that it has a thermal conductivity between 0.25 to $0.5 \text{ Wm}^{-1}\text{K}^{-1}$
5 and comprising
- albite $\text{NaAlSi}_3\text{O}_8$ microcrystals and nanocrystals ,
 - optionally, anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals
 - and vitreous phase,
- wherein the microcrystals are separated by a region formed by the nanocrystals
10 and the vitreous phase,
and wherein said the vitreous phase is in a proportion less than 18 % with
respect to the total weight of the glass-ceramic material.
2. Glass-ceramic material according to the preceding claim, comprising
15 anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$ microcrystals and nanocrystals.
3. Glass-ceramic material according to any of claims 1 or 2, wherein the
albite microcrystals have elongated morphologies with smaller diameter of
between $0.3 \mu\text{m}$ and $1.5 \mu\text{m}$ and larger diameter of between $1.5 \mu\text{m}$ and $8 \mu\text{m}$.
20
4. Glass-ceramic material, according to any of claims 1 to 3, wherein the
anorthite microcrystals have elongated morphologies with smaller diameter of
between $0.2 \mu\text{m}$ and $0.5 \mu\text{m}$ and larger diameter of between $5 \mu\text{m}$ and $30 \mu\text{m}$.
- 25 5. Glass-ceramic material, according to any of claims 1 to 4, wherein said
material contains at least a weight percent with respect to the end material
expressed in terms of the following equivalent oxides:
- between 45 % and 68 % of SiO_2 ,
 - between 15 % and 27 % of Al_2O_3 ,
 - 30 • between 4.5 % and 13 % of CaO ,
 - between 0 % and 9 % of SrO ,
 - between 1 % and 5.5 % of Na_2O ,

- between 1 % and 5 % of K_2O ,
- between 0 % and 2% of B_2O_3 ,
- between 0 % and 14 % of ZrO_2 ,
- and between 0% and 5 % of MgO , BaO and ZnO .

5

6. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of SiO_2 is between 49 % and 60 %.

10 7. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Al_2O_3 is between 17 % and 25 %.

15 8. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Al_2O_3 is between 19 % and 23 %.

20 9. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of CaO is between 6 % and 12 %.

10. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of CaO is between 7.5 % and 11 %.

25

11. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Na_2O is between 1.5 % and 4 %.

30 12. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of Na_2O is between 2 % and 3.5 %.

13. Glass-ceramic material according to claim 5, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of K_2O is between 1.5 % and 4 %.
- 5
14. Glass-ceramic material according to the preceding claim, wherein the weight percent with respect to the end material expressed in terms of equivalent oxide of K_2O is between 2 % and 3 %.
- 10
15. Glass-ceramic material according to any of claims 1 to 14, wherein
- it further comprises zirconia crystals ZrO_2 or zirconium silicate crystals $ZrSiO_4$, where said crystals are distributed throughout the region of nanocrystals and vitreous phase which separate the microcrystals of the glass-ceramic material,
- 15
- and wherein the material displays a thermal conductivity between 0.31 and $0.45 \text{ Wm}^{-1}\text{K}^{-1}$.
16. Glass-ceramic material according to the preceding claim, wherein the zirconia crystals ZrO_2 may be in the form cubic, tetragonal or monoclinic.
- 20
17. Glass-ceramic material according to any of claims 15 or 16, wherein the zirconia crystals ZrO_2 have an average size of between 50 and 200 nm.
18. Glass-ceramic material according to claim 15, wherein the zirconium silicate crystals $ZrSiO_4$ have an average size of between 200 nm and 500 nm.
- 25
19. Glass-ceramic material according to any of claims 15 to 18, wherein the weight percent of the zirconia crystals ZrO_2 or of the zirconium silicate crystals $ZrSiO_4$ expressed in terms in equivalent oxide with respect to the total weight of
- 30
- the glass-ceramic material is between 2 % and 14 %.
20. Glass-ceramic material according to the preceding claim, wherein the

weight percent of the zirconia crystals ZrO_2 or of the zirconium silicate crystals ZrSiO_4 expressed in terms in equivalent oxide with respect to the total weight of the glass-ceramic material is between 2 % and 8 %.

- 5 21. Production process of the glass-ceramic material according to any of claims 1 to 20, comprising the following steps:
- a) melting at least one compound selected from the list comprising sassolite H_3BO_3 , quartz SiO_2 , dolomite $\text{CaMg}(\text{CO}_3)_2$, calcium carbonate CaCO_3 , zincite ZnO , kaolin $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, strontianite SrCO_3 , alumina Al_2O_3 , calcium
10 phosphate $\text{Ca}_3(\text{PO}_4)_2$, a zirconium compound selected from among zirconia ZrO_2 or zirconium silicate ZrSiO_4 and an alkali feldspar selected from among albite $\text{NaAlSi}_3\text{O}_8$ and anorthite $\text{CaAl}_2\text{Si}_2\text{O}_8$, or any combination thereof, at a temperature of between 1400 °C and 1550 °C, and fritting;
 - b) grinding the frit obtained in step a) with kaolin;
 - 15 c) forming the product obtained in b);
 - d) sintering the product formed in c) at temperatures of between 980 °C and 1280 °C.
22. Process according to the preceding claim, wherein the percentage of the
20 frit used in the grinding mixture of step b) is between 70 % and 96 wt%.
23. Process according to any of claims 21 or 22, wherein the percentage of kaolin is between 4 % and 15 wt% in step b).
- 25 24. Process according to any of claims 21 to 23, wherein step d) of sintering is carried out at temperatures of between 1100 °C and 1220 °C.
25. Process according to any of claims 21 to 24, comprising an additional
30 step e), after the step of sintering (d), of rectifying and polishing with abrasives.
26. Use of the glass-ceramic material according to any of claims 1 to 20, for the manufacturing of industrial, structural or ornamental ceramic products.

27. Use according to the preceding claim, for the manufacturing of floor tiles or glazes of floor tiles.
- 5 28. Use of the glass-ceramic material according to any of claims 1 to 20, as thermal insulator.
29. Use of the glass-ceramic material according to claim 28, as a component of a cool roof, cool room or cool façade.
- 10 30. Use of the glass-ceramic material according to any of claims 1 to 20, as whiteners-opacifier in paper industry, painting or polymers.
31. Use of the glass-ceramic material according to claim 30, wherein the glass-ceramic material comprises a milled powder with an average particle of 3-7 μm .
- 15

20

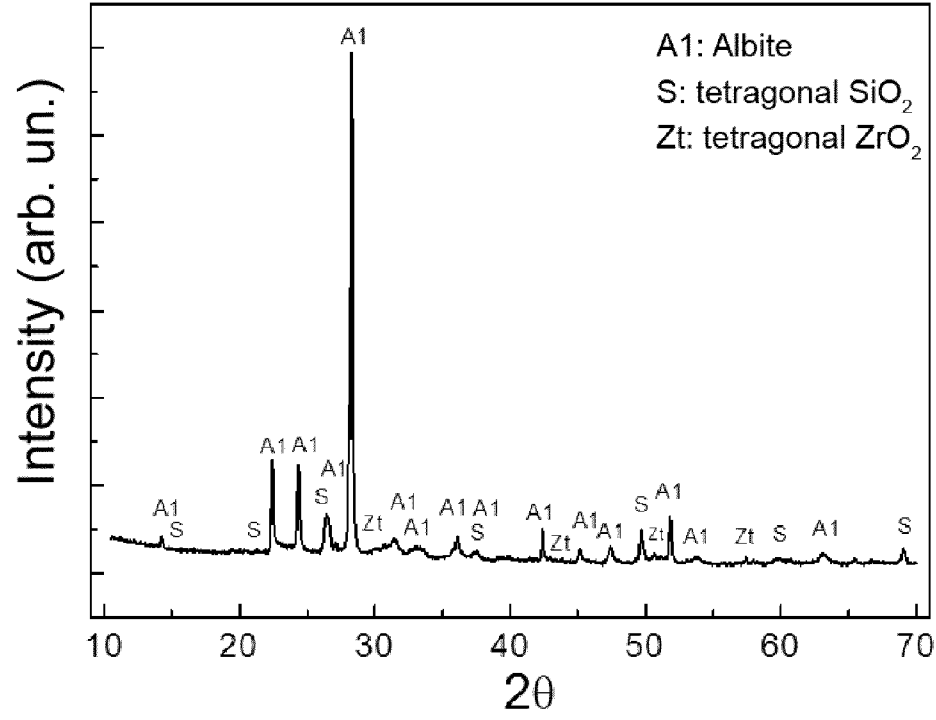


FIG. 1

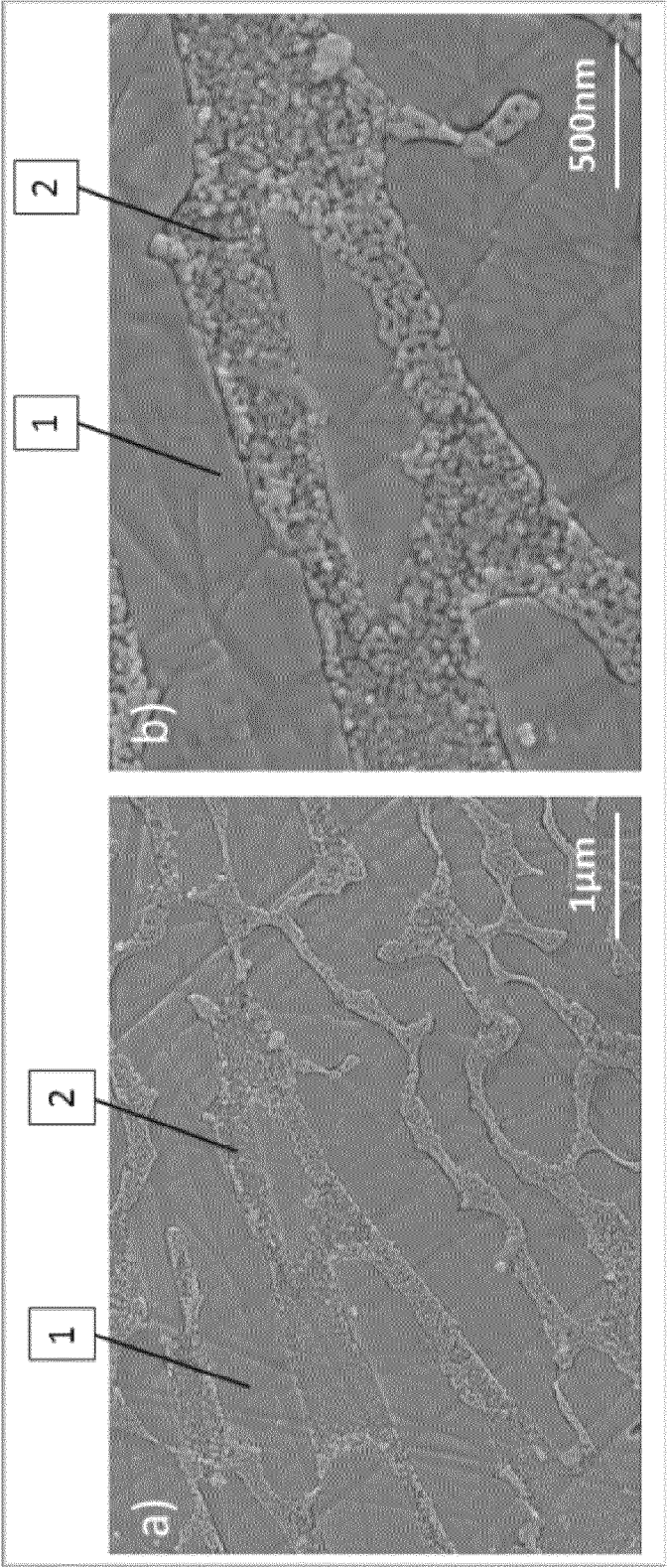
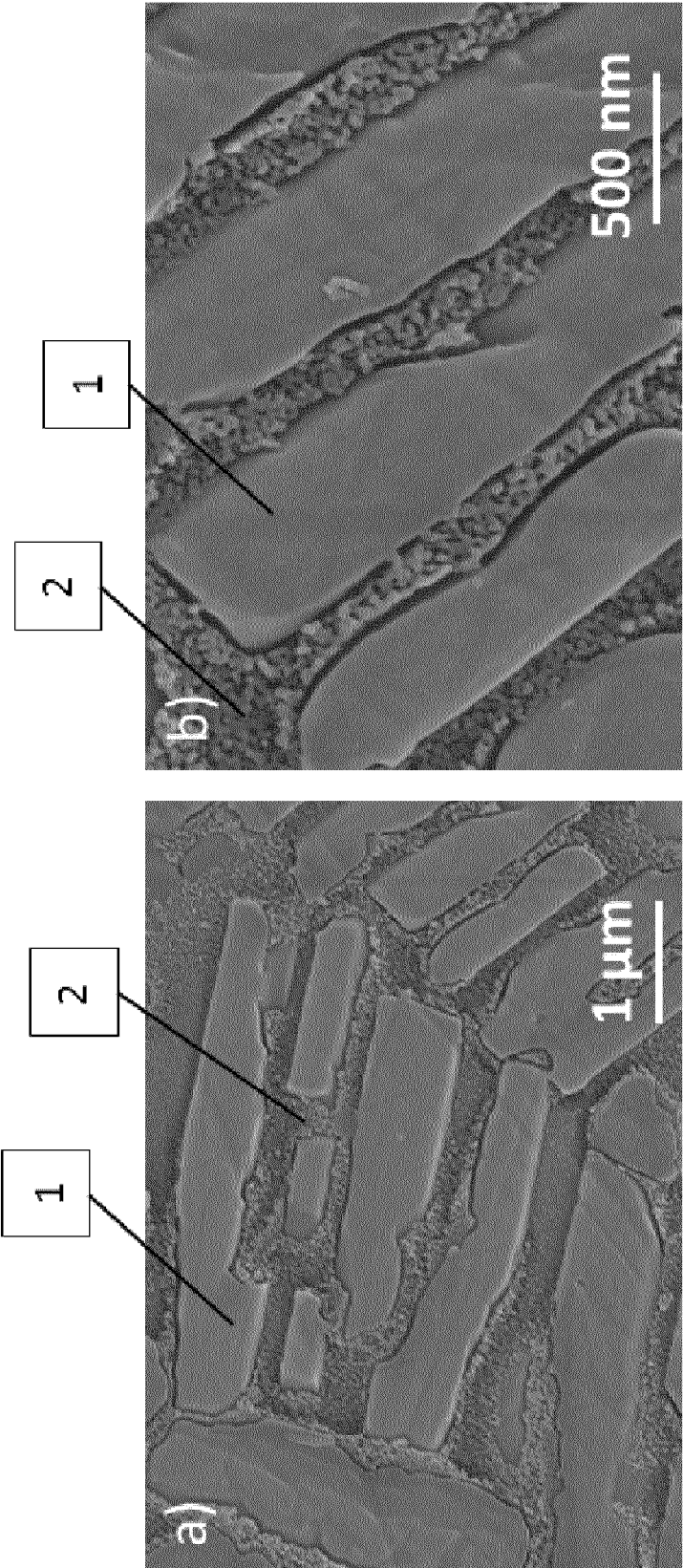


FIG. 2

FIG. 3



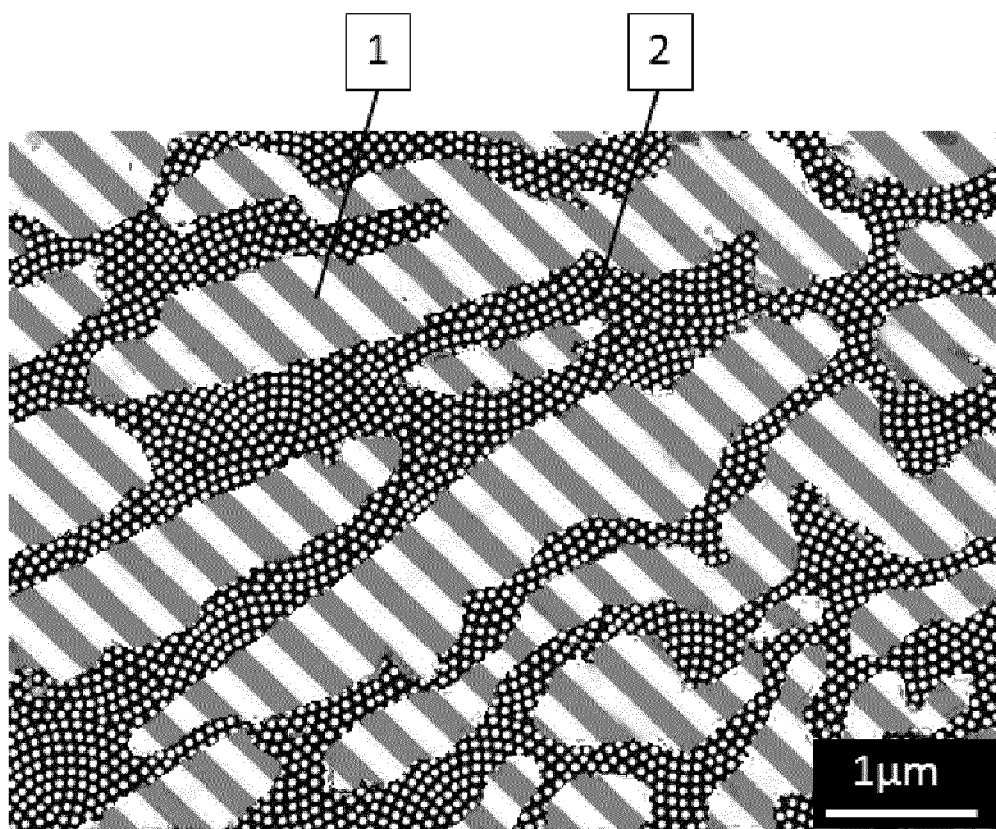


FIG. 4

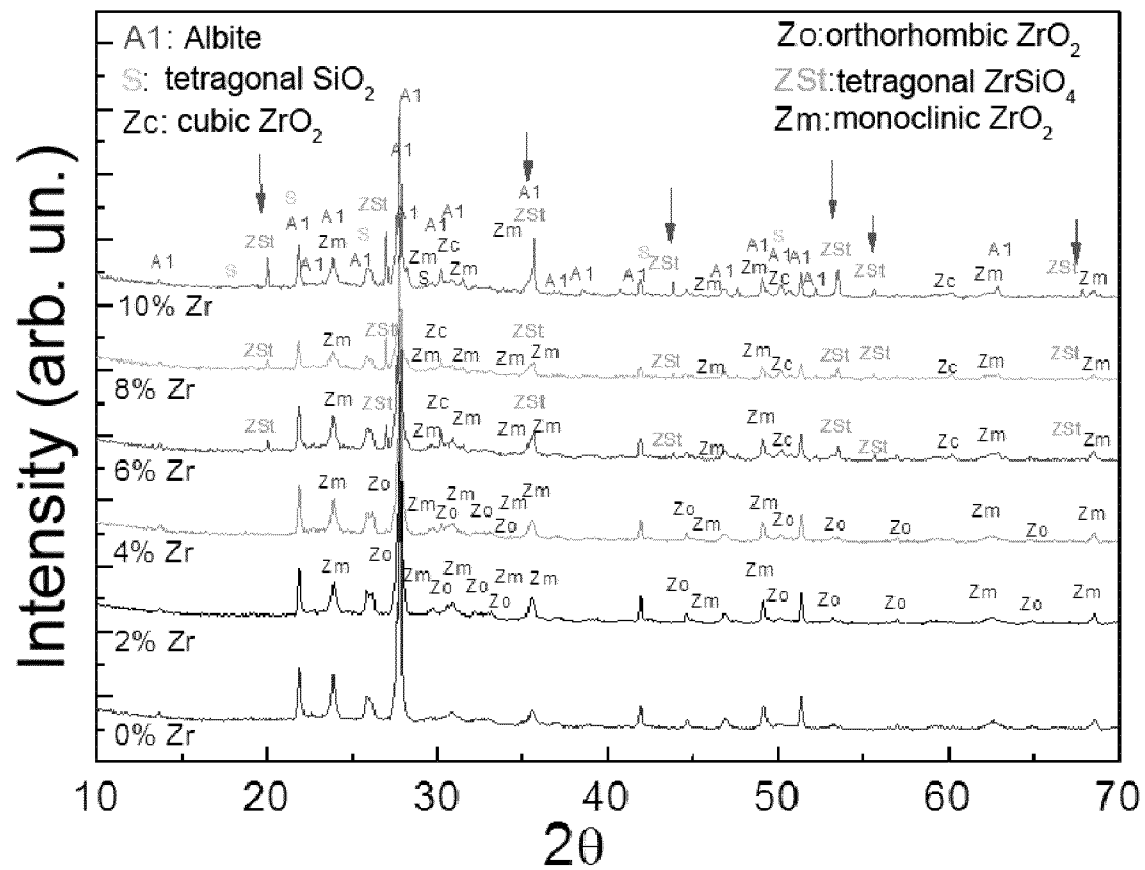
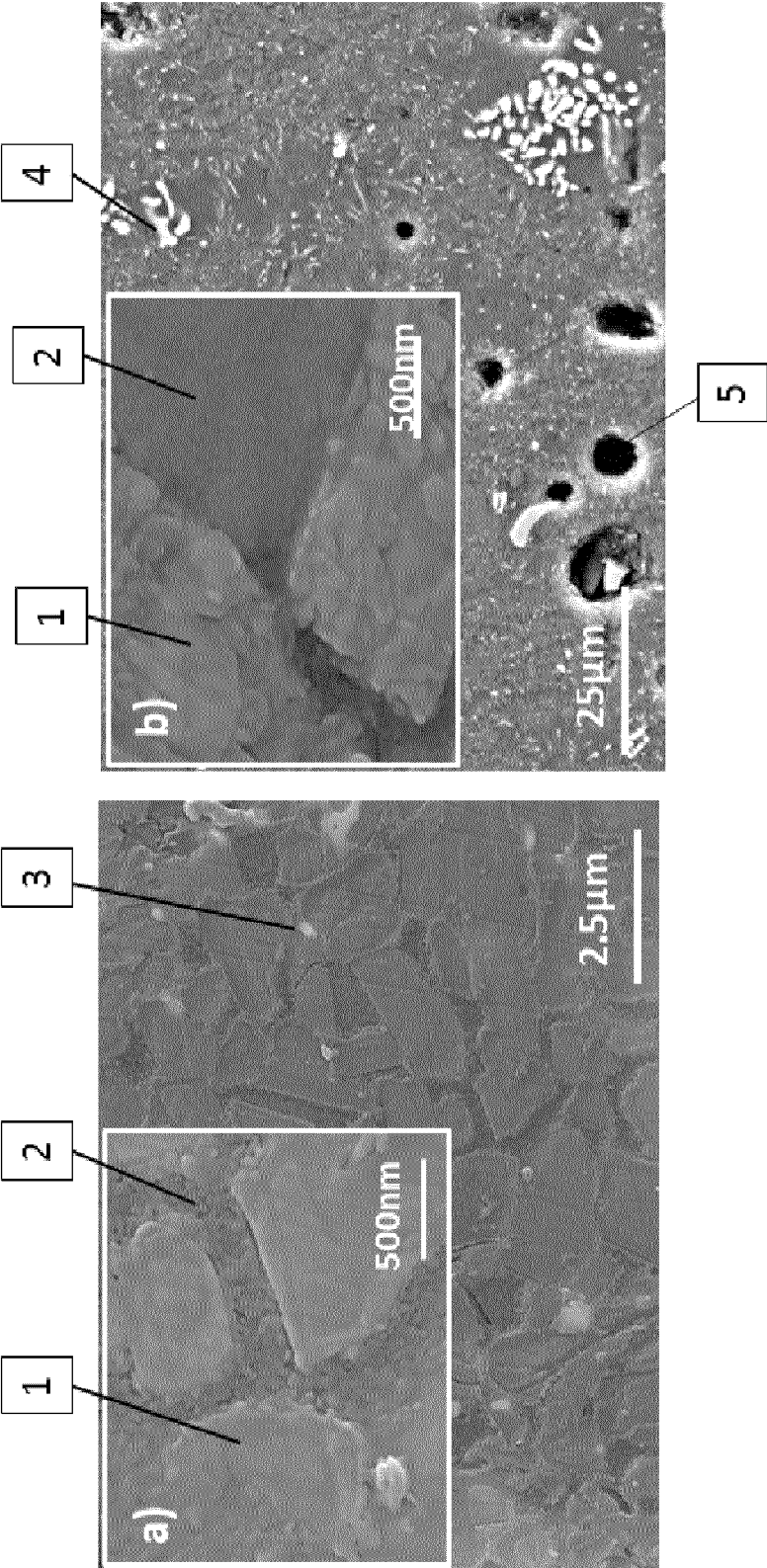


FIG. 5

FIG. 6



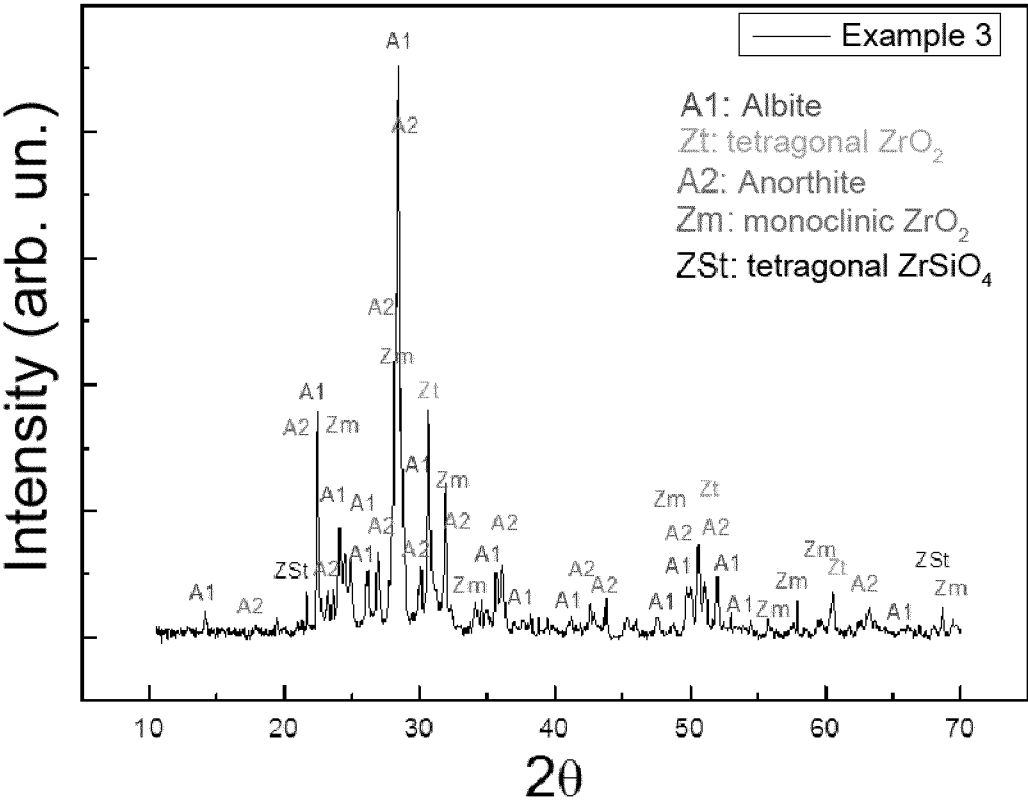


FIG. 7

FIG. 8

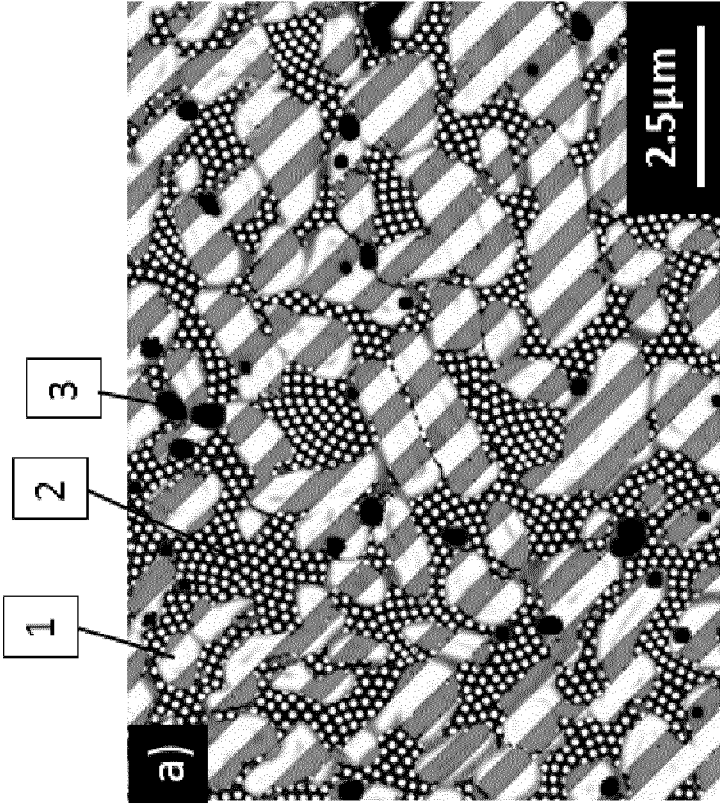
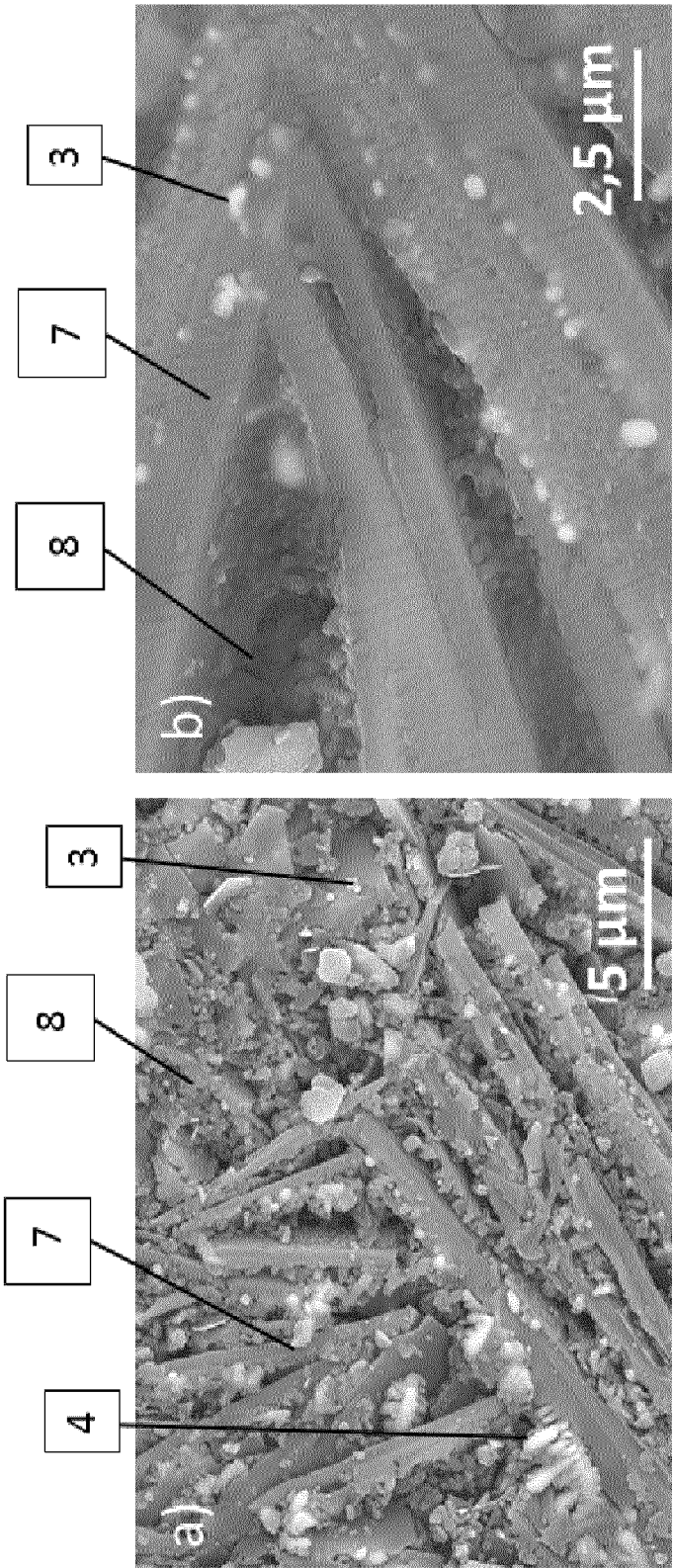


FIG. 9.



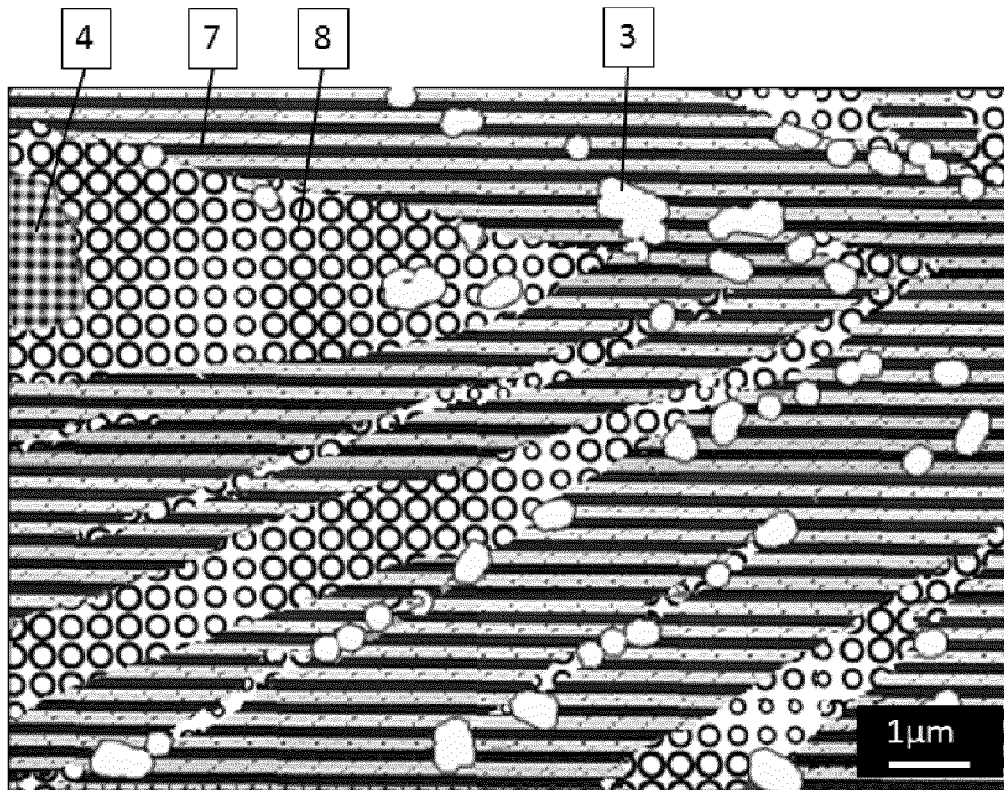


FIG. 10

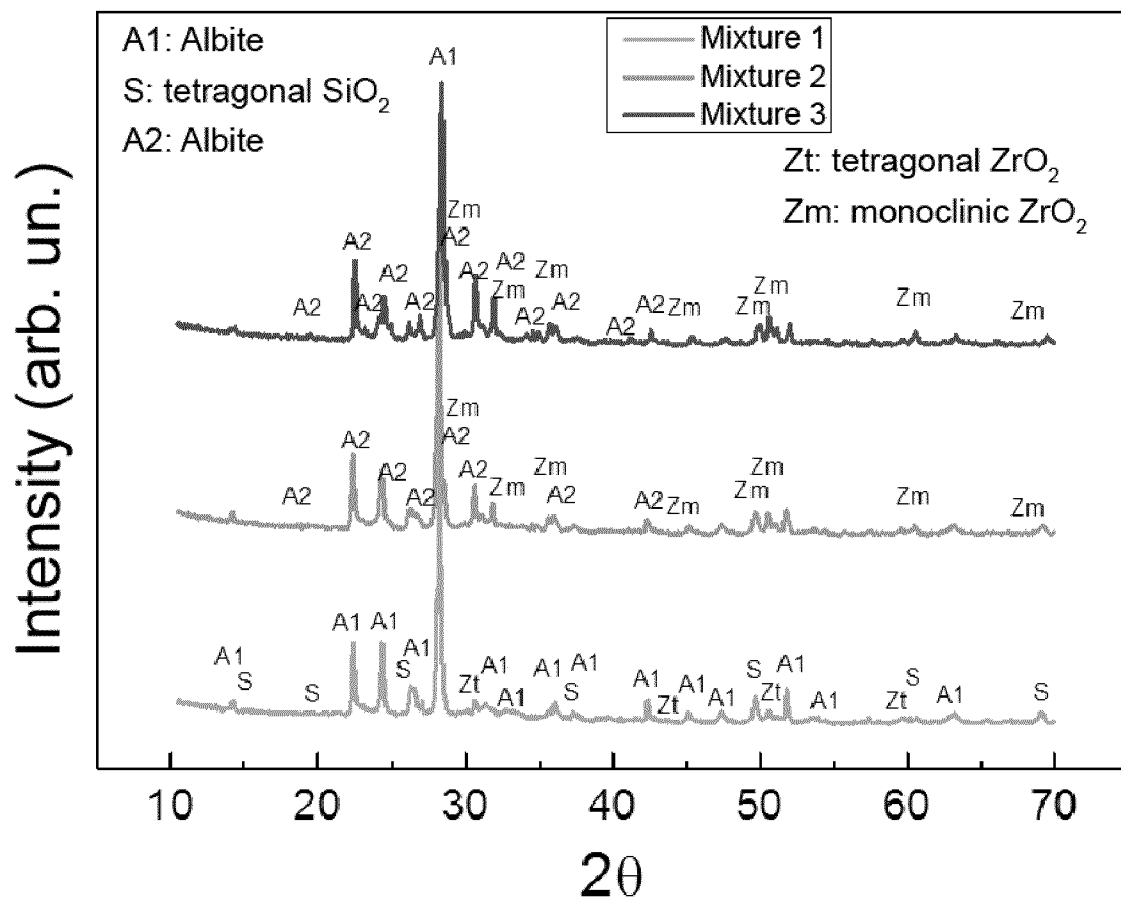


FIG. 11.

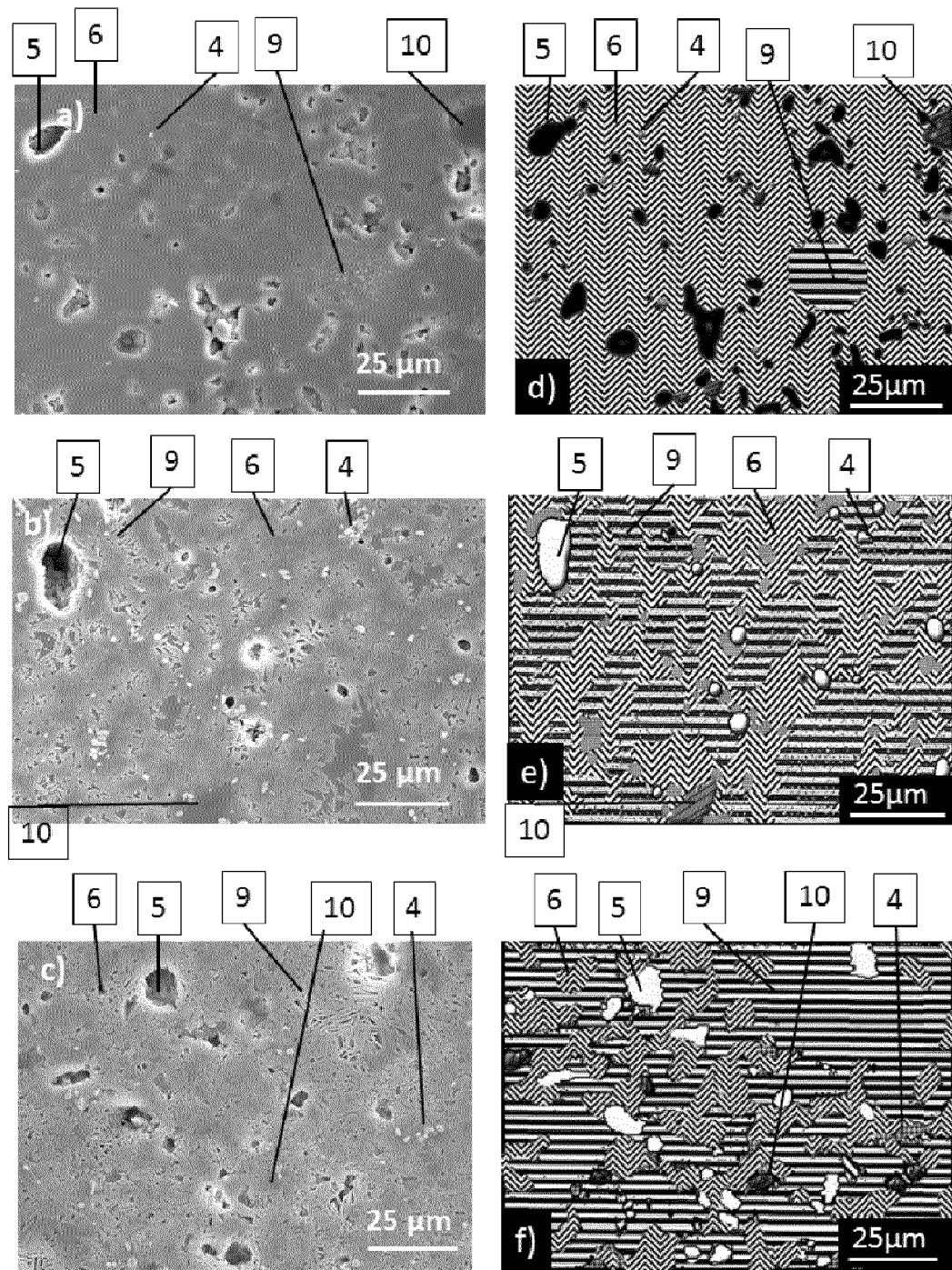


FIG. 12.

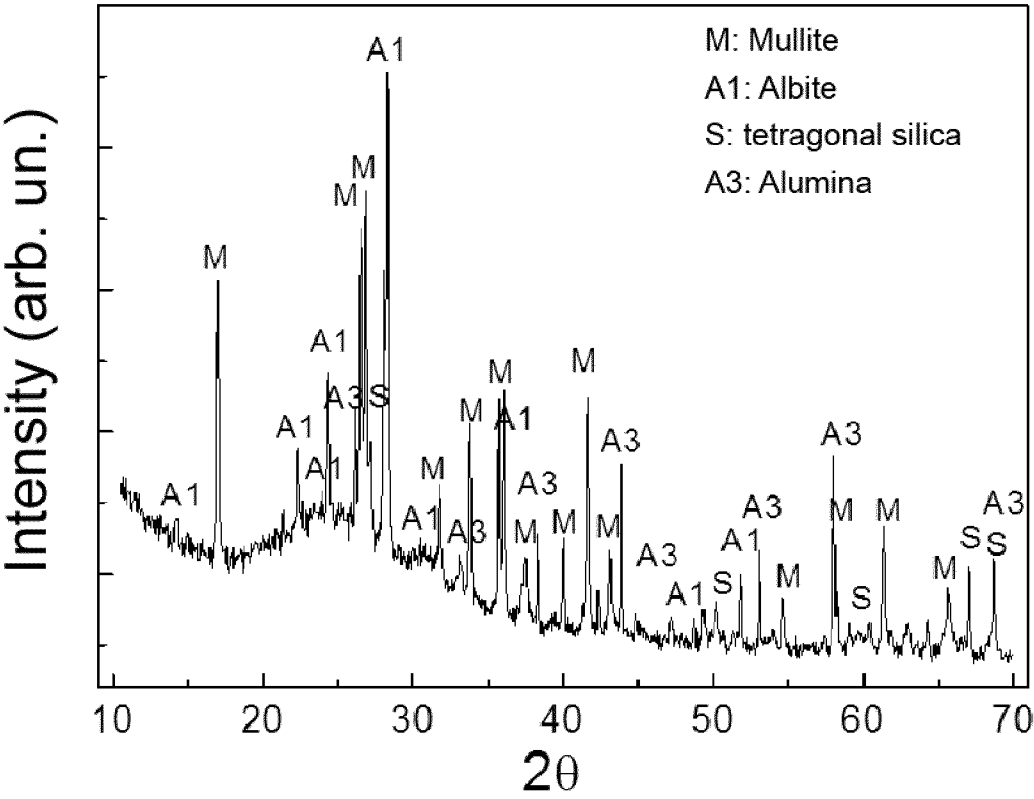


FIG. 13.

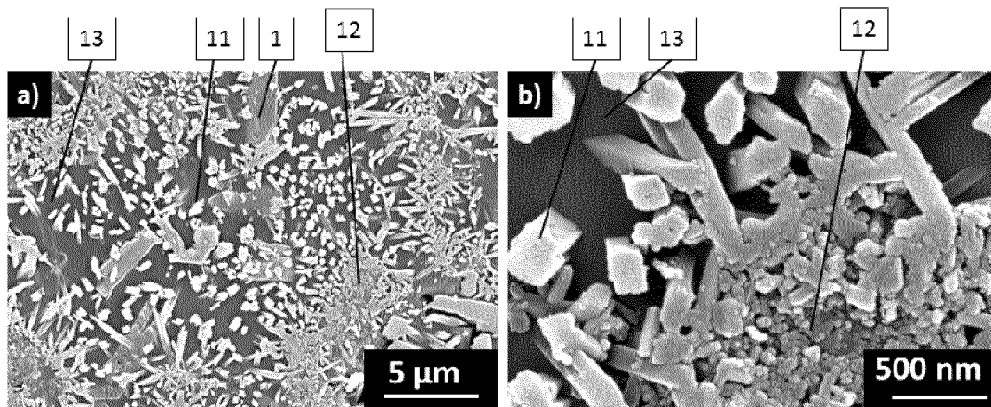


FIG. 14.

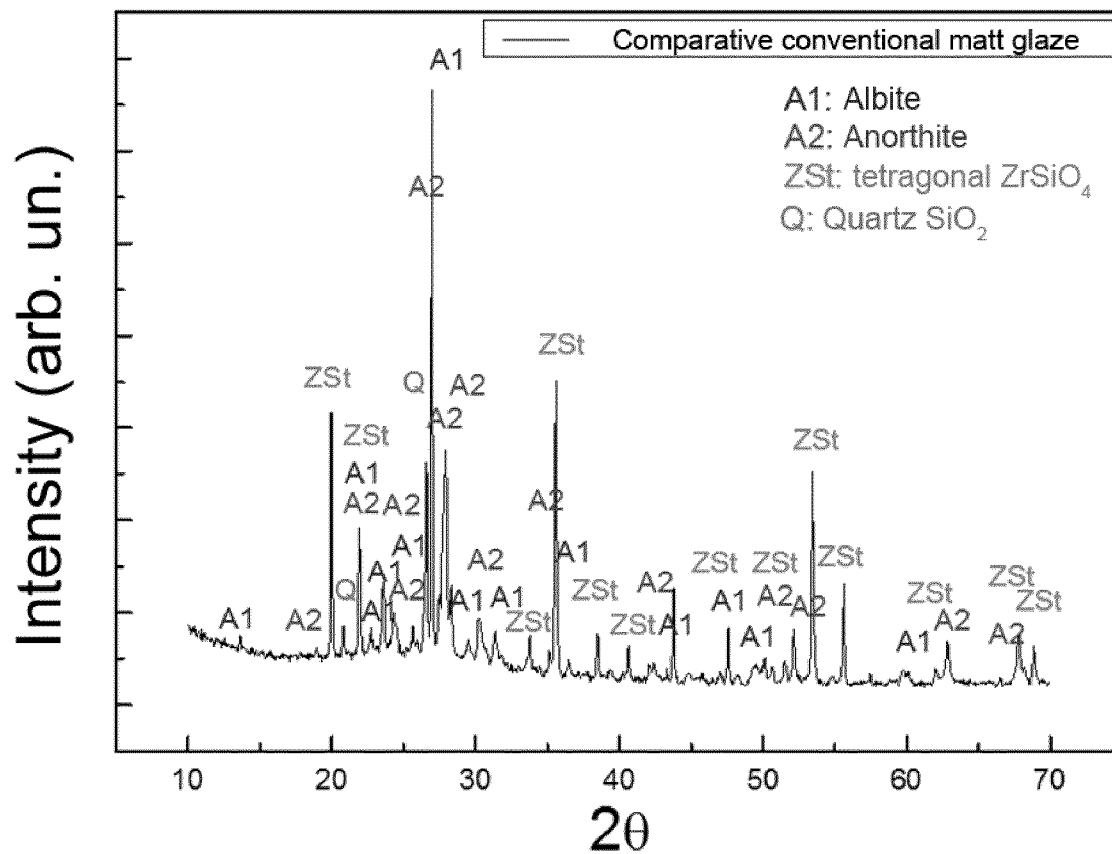
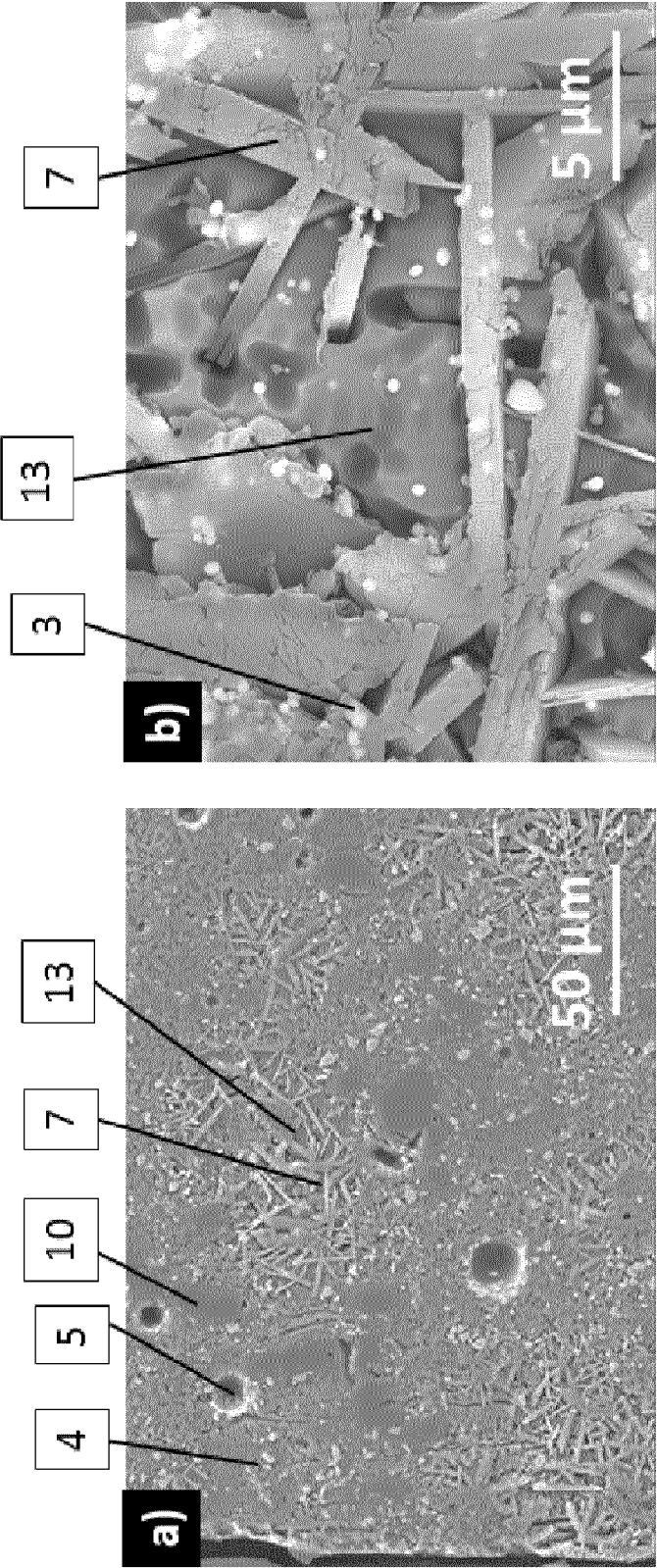


FIG. 15.

FIG. 16.



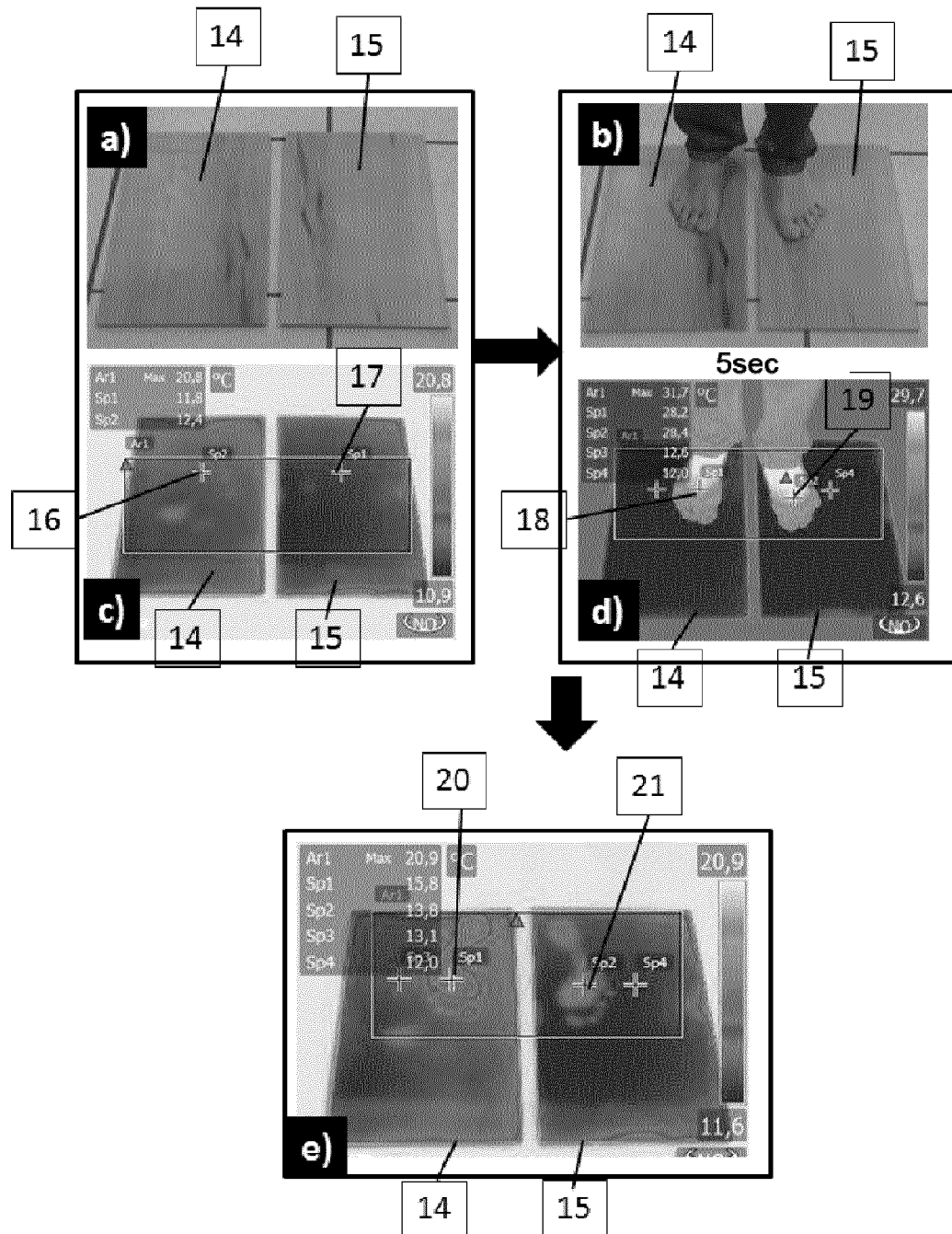


FIG. 17.

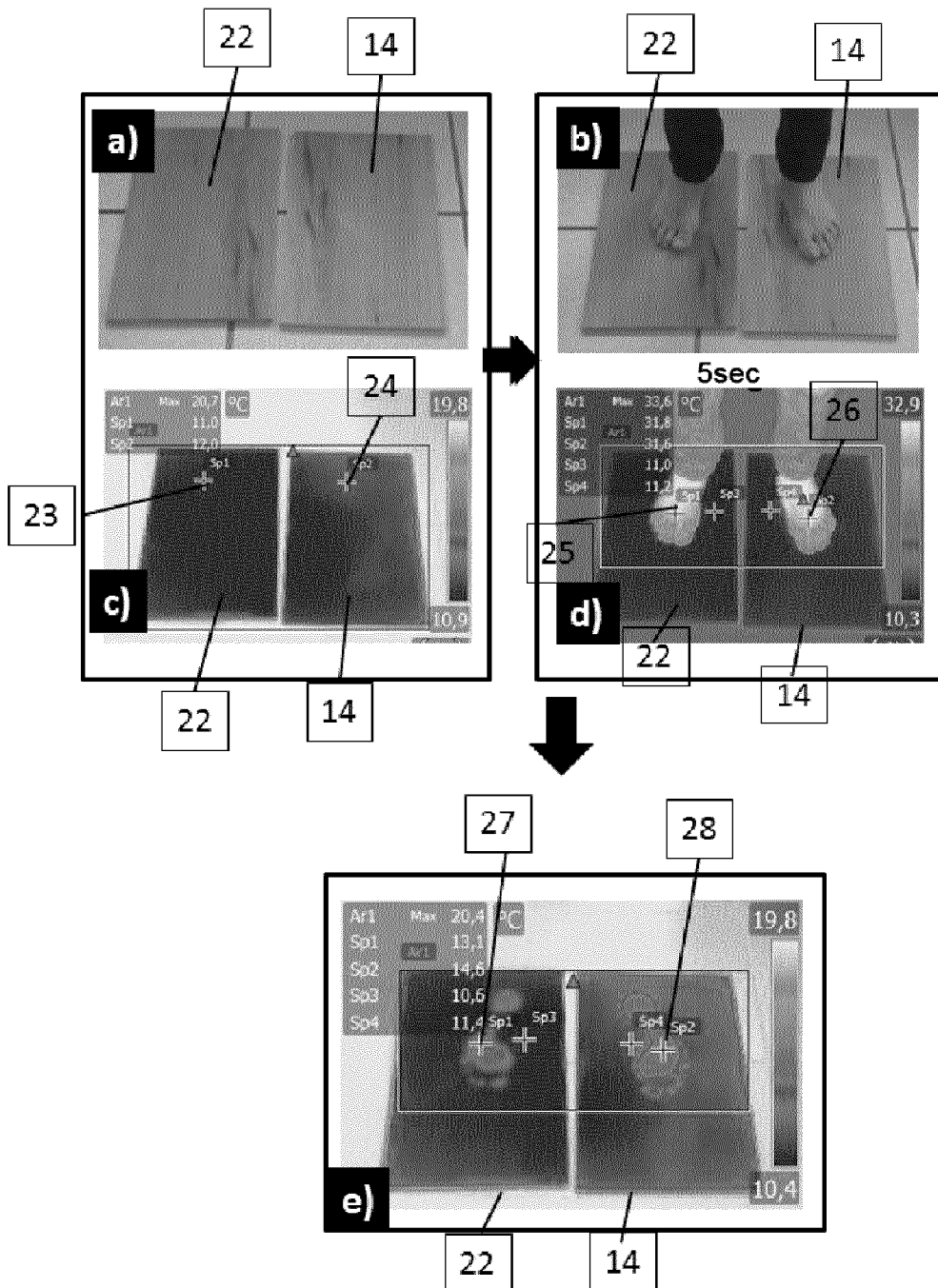


FIG. 18.

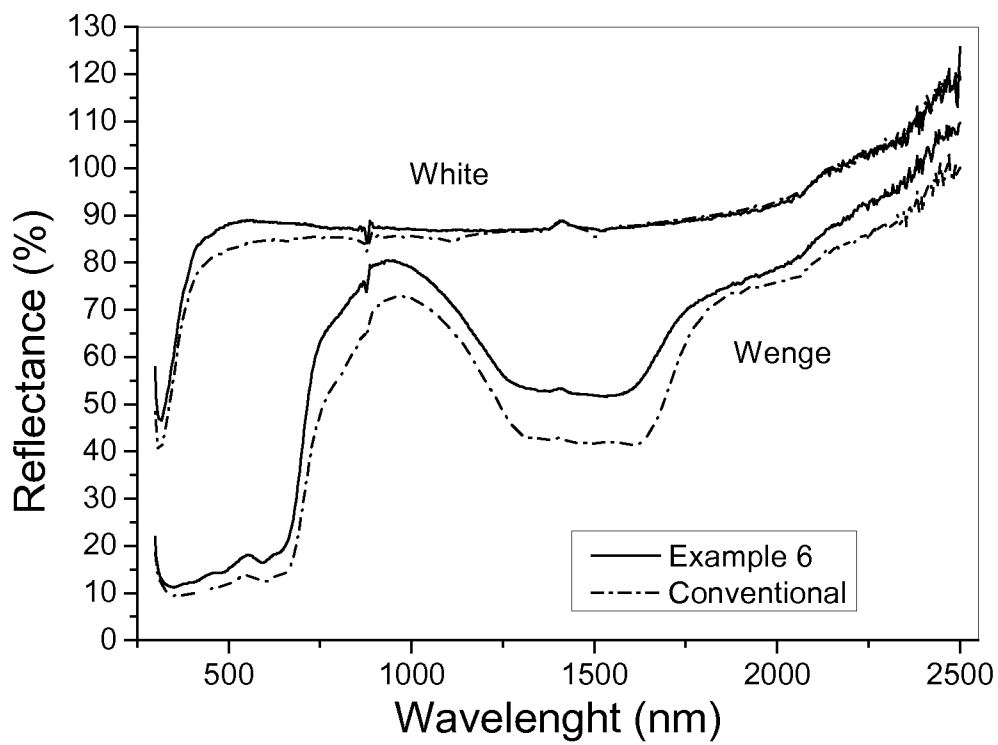


FIG. 19

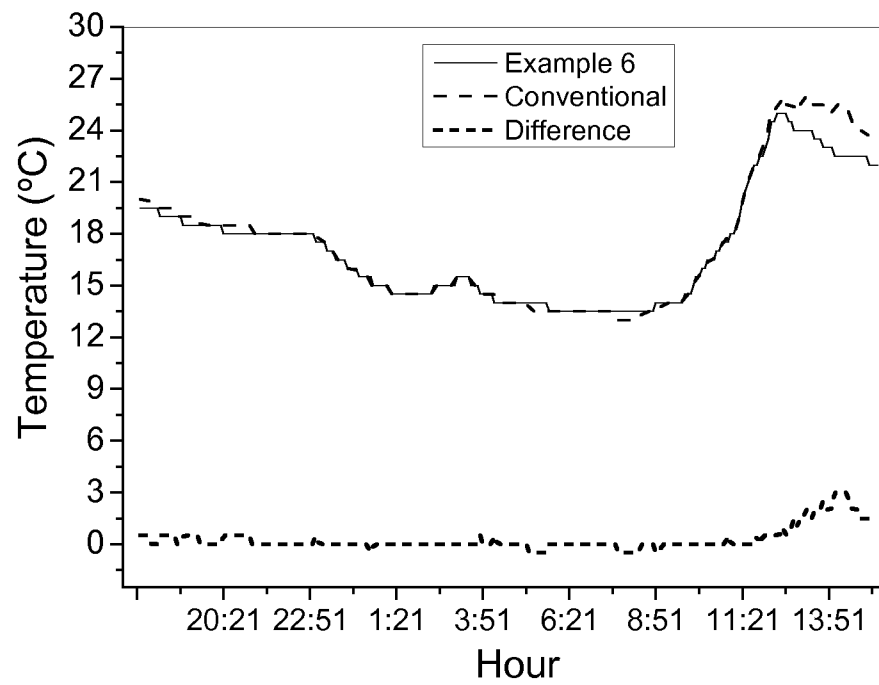


FIG. 20

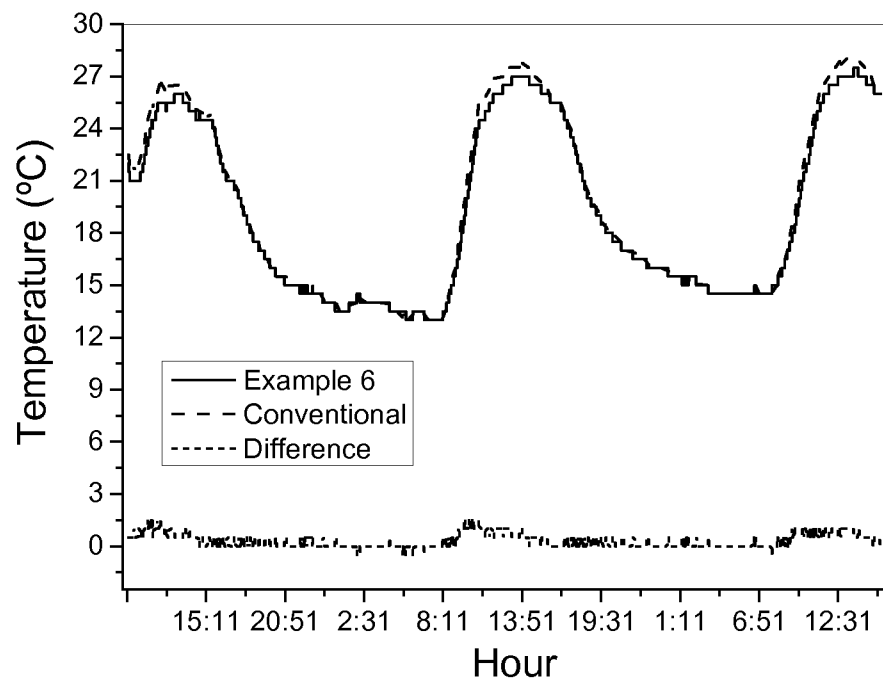


FIG. 21

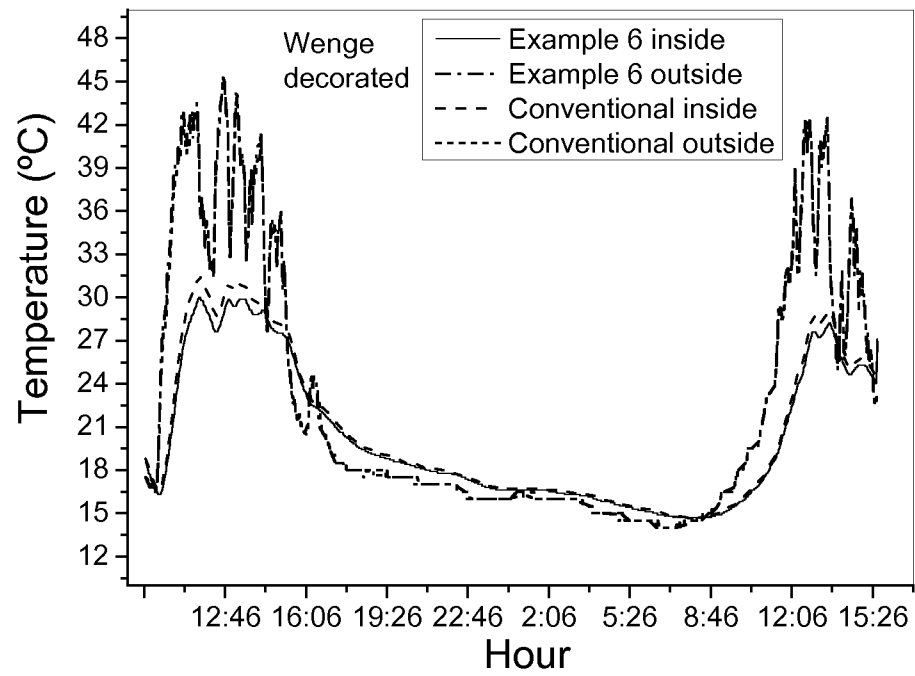
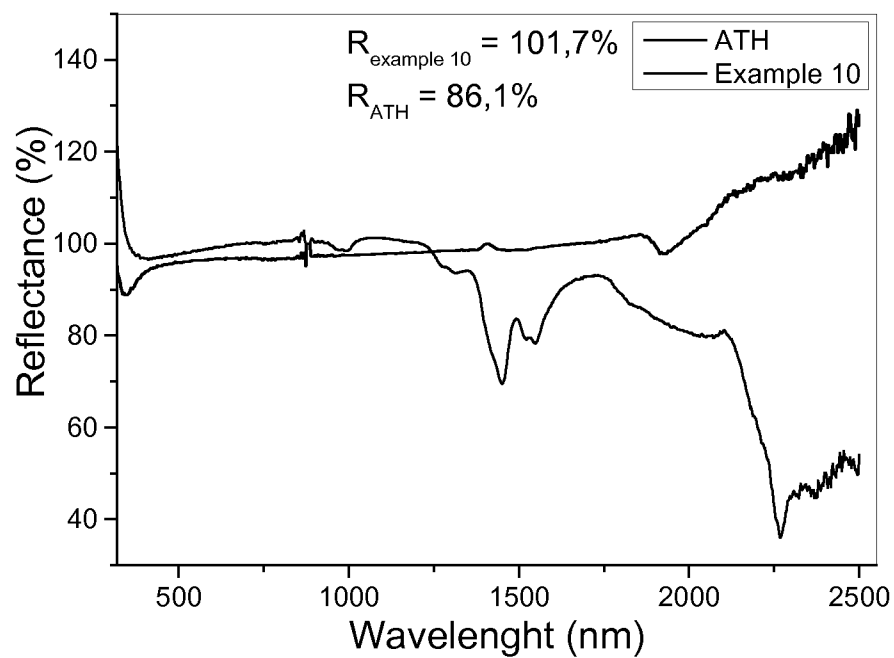


FIG. 22



FIG. 23

a



b

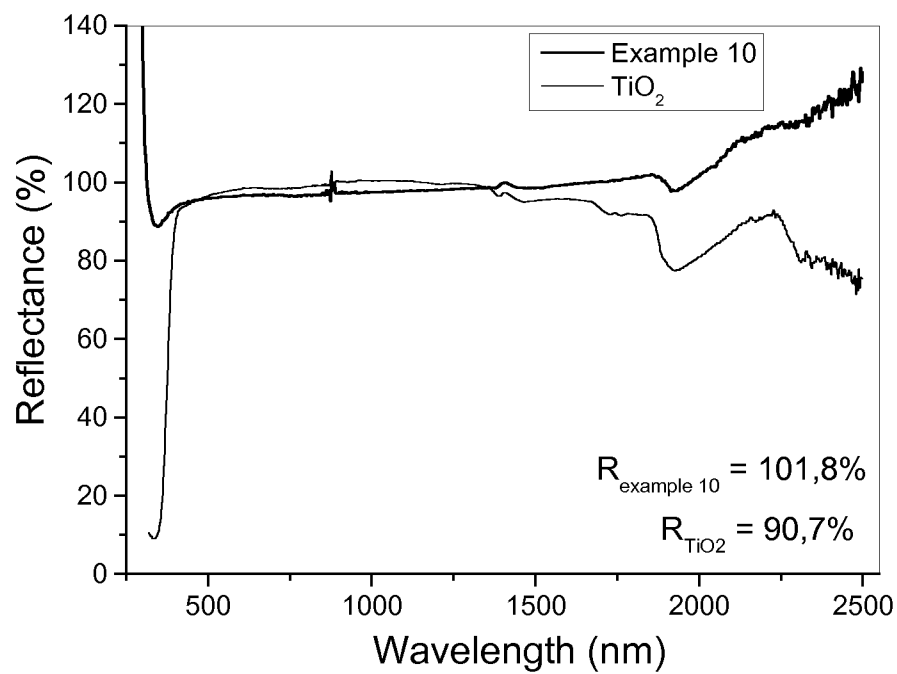


FIG. 24

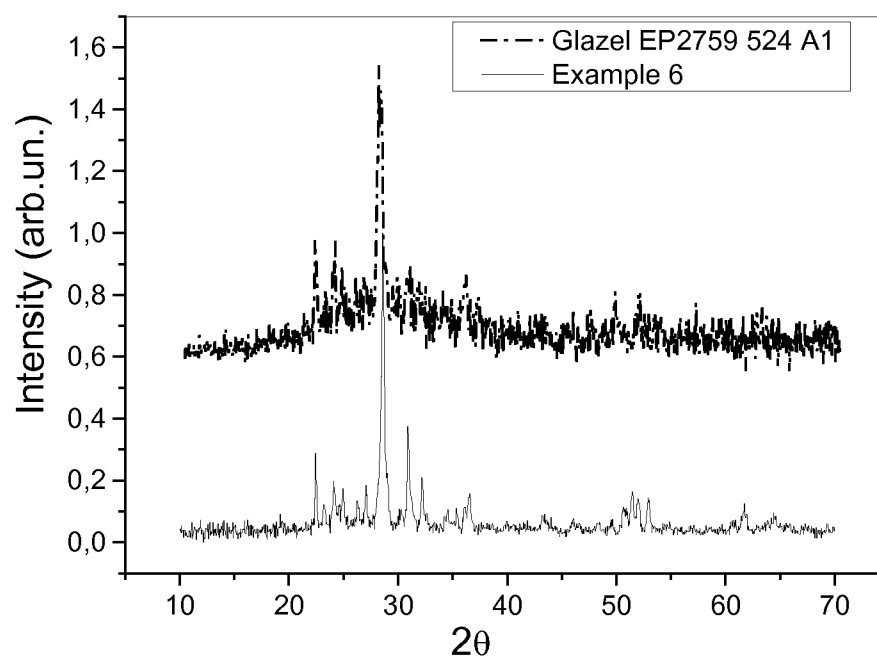


FIG. 25

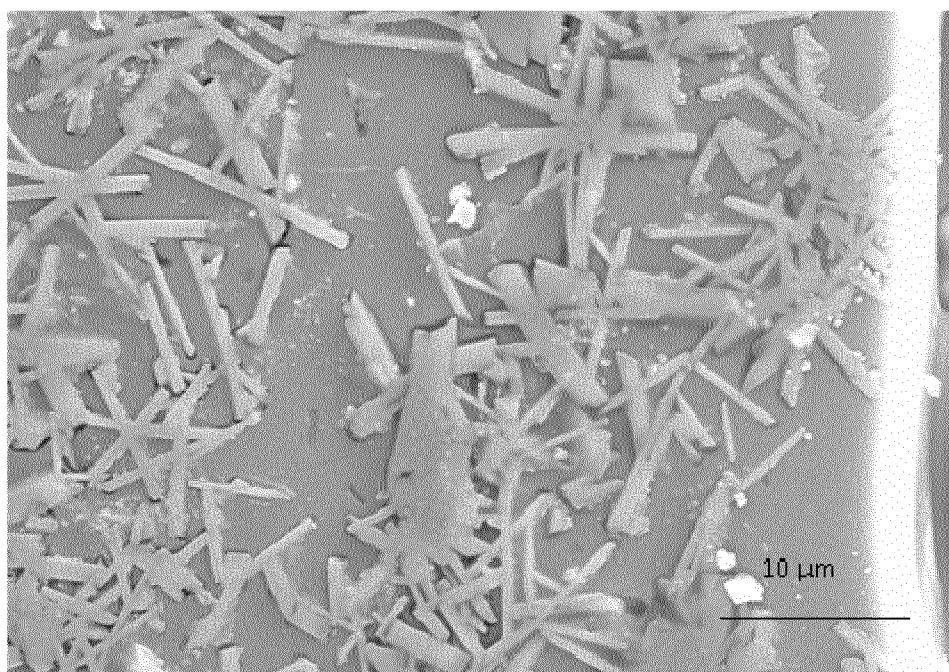


FIG. 26

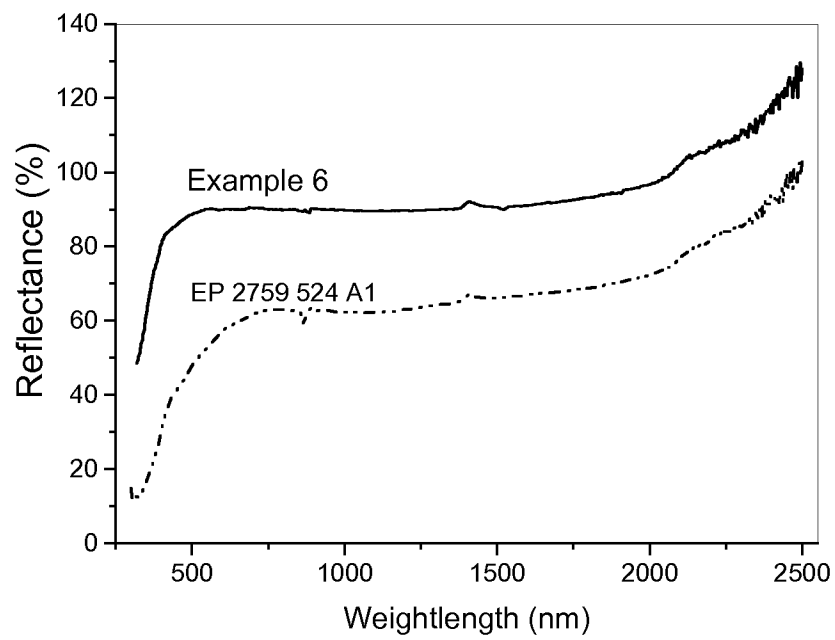


FIG. 27

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2016/051916

A. CLASSIFICATION OF SUBJECT MATTER		
INV.	C03C3/087	C04B41/86
	C03C10/00	
ADD.	C03C10/06	C03C10/10
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 C04B		
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) EPO-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	EP 2 759 524 A1 (CONSEJO SUPERIOR INVESTIGACION [ES]; KERAFRIT S A [ES]; NANOBIO MATTERS) 30 July 2014 (2014-07-30)	1-27
Y	[0004], [0014], [0022], [0049]-[0055], [0059]-[0065], [0090]-[0095], [0121]	28,29
X	ES 2 444 740 A1 (ESMALGLASS SAU [ES]) 26 February 2014 (2014-02-26)	1-27
Y	page 2, lines 19-p. 3, l. 25; p. 4, l. 8-26	28,29
A	US 5 200 369 A (CLIFFORD JOHN F [GB] ET AL) 6 April 1993 (1993-04-06) col. 1, l. 27-47; col. 4, l. 14-51	1-29
	-/--	
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 21 March 2016		Date of mailing of the international search report 01/04/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Deckwerth, Martin

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2016/051916

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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