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A novel process of preparing glass-ceramics with pseudo-bioclastic texture

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Abstract

Water quenching-induced cracked-glass was used as parent glass to prepare glass-ceramics in this work. The cracked-glass panel was first heat-treated through two-step method, i.e. sintering for 1 h at 860 °C and subsequent crystallization for 1.5 h at 1080 °C, and then naturally cooled down to room temperature to be transformed into glass-ceramics. XRD and SEM observations confirm that the cracked-glass can be used as parent glass to deposit β-wollastonite crystals depending on crack crystallization mechanism. The volume densities, porosities and bending strengths of the glass-ceramics are respectively around 2.7 g/cm^3, 0.5% and 40 MPa. As compared with glass-ceramics prepared by conventional glass grain sintering process, the new type of glass-ceramics produced by CGC process shows pseudo-bioclastic texture and has less gas pore flaws, and may therefore become an alternative for materials of architectural decoration.

Keywords: Cracked-glass; Glass-ceramics; Crystallization; Pseudo-bioclastic texture

1. Introduction

Glass-ceramic materials are polycrystalline solids prepared by controlled crystallization of specific parent glass and have been widely used for architectural decoration purposes. In the 1960s, the so-called ‘‘slag-sitalls’’ glass-ceramics was produced by *rolling process* [1,2] in the former Soviet Union and mainly used as erosion-resistant and wear-resistant materials. The glass-ceramics of this type, however, does not possess any obvious textures at the surface. In 1971, another type of glass-ceramics, ‘‘Neopariés’’, with marble-like texture was successfully prepared by *Glass Grain Sintering* (*GGS*) *process* [3–6] and has since then been widely used in architectural decoration. However, although the marble-like texture can be obtained at the surface, gas pore flaws easily form during the sintering of glass grains with the particle sizes of from 1 to 7 mm as the parent glass.

A novel process of preparing glass-ceramics is proposed and tested by the authors, in which cracked-glass is used as parent glass that is then sintered and crystallized. The new process is named as *Cracked-Glass Crystallization* (*CGC*) *process*, a process of preparing glass-ceramics by the crystallization of glass panel with cracks induced by water quenching. The surface appearance of the glass-ceramics prepared by the CGC process, which is quite different from that of the products by the conventional GGS process, shows variable and composite textures, and looks like that of polished bioclastic rocks with remnants of plant fossils. Accordingly, glass-ceramics of this type is called by the authors as *pseudo-bioclastic glass-ceramics*. In this paper, the experimental work on the new process and the major characteristics of the new glass-ceramics product are reported.

2. Experimental

The flowchart of CGC process is shown in Fig. 1. Water quenching of the hot glass panel immediately after the formation operation is the key step, which results in significant amount of cracks in the glass. The cracked-glass panel is then heat-treated by the two-step method, first a lower temperature heat-treatment for sintering and then a higher temperature for crystallization.

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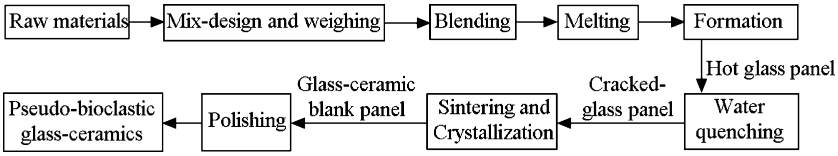

Fig. 1. Flowchart of CGC process.

The CGC process is essentially different not only from the conventional GGS process but also the rolling process. The parent glass used by GGS process is granular, and the glass grains are sintered and then crystallized depending on surface crystallization [7]. In contrast, the parent glass for rolling process is intact glass panel which is directly nucleated and crystallized relying on bulk crystallization induced by nucleating agents [8,9]. For CGC process in this work, however, cracked-glass is used as parent glass that is sintered and then crystallized following crack crystallization mechanism.

In this paper, the compositions for the three representative batches selected from nine screening experiments are given in Table 1 and discussed for the CGC process. The raw materials include minerals such as feldspar, quartz and limestone, as well as reagent-grade materials such as soda, boric acid, Sb_2O_3, $BaCO_3$, ZnO and Al_2O_3. For each batch, 4000 g raw materials were weighed and mixed and charged into high-aluminum crucible, and then melted for 2.5 h at 1500 °C. One part of glass melt was cast into 60 mm × 60 mm × 20 mm moulds pre-heated at 1000 °C and water-quenched immediately by spraying water on the hot glass panels kept in the moulds, and in this way cracked-glass panels were made and used as the parent glass for CGC process. To compare CGC with conventional GGS process, another part of glass melt was poured into water to form glass cullet that was then dried, crushed and sieved to obtain glass grains with particle sizes less than 5 mm as the parent glass for GGS process.

Part of the parent glass grains of all batches were ground into less than 0.74 μm powder. Differential thermal analysis (DTA) of about 20 mg parent glass powder was conducted with Netzsch STA449C apparatus, at a heating rate of 10 °C/min and in air atmosphere.

Parallel experiments were done on the as-prepared cracked-glass panels remaining in the moulds and the glass grains filled in new moulds with the sizes of 60 mm × 60 mm × 25 mm. Both were first heat-treated through two-step method, i.e. sintering for 1 h at 860 °C and subsequent crystallization for 1.5 h at 1080 °C, and then naturally cooled down to room temperature. The glass-ceramics prepared by using cracked-glass panels as parent glass were called CGC-GCs for short, and those by glass grains called GGS-GCs.

The crystal phases of all CGC-GCs and Batch 2 GGS-GCs samples were identified using X-ray powder diffractometer (XRD; D/Max-3B, Rigaku) with Cu Kα radiation, at 35 kV and 40 mA with 10 s scanning time. Scanning electron microscopy (SEM; JSM-35CF) was used to observe the microstructure of all CGC-GC samples that had been polished and etched for 30 s in 5% HF solution beforehand.

All CGC-GCs and GGS-GCs samples were cut into rectangular bars of 60 mm × 20 mm × 20 mm and 20 mm × 20 mm × 20 mm. The 60 mm × 20 mm × 20 mm bars were used for measuring four-point bending strengths with 40 mm external span and 20 mm internal span at a crosshead speed of 1 mm/min, and the 20 mm × 20 mm × 20 mm bars were used for measuring volume densities and porosities by the Archimedes method using water as the medium according to the national standard of PR China (GB/T9966.3-2001). Five specimens for each sample were tested and the data were averaged.

3. Results and discussion

3.1. Characterization of parent glass

The typical morphology of both parent glasses is shown in Fig. 2. It can be seen that the cracked-glass panel contains significant amount of *glass debris*, with different sizes and in a non-scattered state, and the cracks in the panel are actually interfaces of adjacent glass debris. Strictly speaking, the glass debris is essentially glass grain and the term *glass debris* is used here only to distinguish from the glass grains in GGS process.

The chemical compositions of as-received parent glass of all batches were tested and the result is given in Table 2. They are close to the classical chemical composition generally adopted in conventional GGS process [3] and belong to $CaO–Al_2O_3–SiO_2$ family. DTA curves are shown in Fig. 3. It can be seen that the exothermal peaks are sharp, indicating that the parent glass has strong crystallization capability.

3.2. Crystallization behaviour and mechanism of cracked-glass

The XRD patterns of all CGC-GCs and Batch 2 GGS-GCs samples were shown in Fig. 4. It can be seen that the XRD

Table 1
Compositions of three representative batches (wt.%)

Batch code	Feldspar	Quartz	Limestone	Na_2CO_3	Boric acid	Sb_2O_3	$BaCO_3$	ZnO	Al_2O_3
Batch 1	23.20	29.45	31.00	3.68	2.46	0.59	4.66	4.55	0.41
Batch 2	23.70	32.53	27.12	3.75	2.50	0.60	4.75	4.63	0.42
Batch 3	24.15	35.76	23.09	3.82	2.57	0.61	4.85	4.72	0.43

Table 2
Chemical composition of parent glass (wt.%)

Batch code	SiO_2	Al_2O_3	CaO	MgO	K_2O	Na_2O	Fe_2O_3	TiO_2	BaO	ZnO	B_2O_3	Others
Batch 1	55.43	7.45	19.85	0.13	2.00	3.25	0.10	0.06	4.18	5.10	1.20	1.25
Batch 2	58.32	6.40	17.20	0.12	2.06	3.48	0.09	0.04	4.17	5.26	1.19	1.67
Batch 3	61.39	6.07	14.45	0.11	2.20	3.47	0.07	0.03	4.27	5.26	1.17	1.51

reflections of CGC-GCs and GGS-GCs are similar and the major crystalline phase is β-wollastonite. In other words, cracked-glass panels can deposit β-wollastonite crystals as do glass grains.

The SEM images of all CGC-GC samples are shown in Fig. 5. The microstructure is characterized by spherical crystal particles, with single particle sizes of generally between 0.2 and 0.4 μm, and their aggregates are in the form of tree trunks. Noticeably, from Batch 1 to Batch 3, the density of crystal particles decreases with the decrease in CaO content, and the tree-trunk form of crystal aggregate is more obvious in Batch 3 CGC-GCs with the lowest CaO content.

The reason for the effective crystallization of cracked-glass could be explained by crack crystallization mechanism. During the fabrication of cracked-glass by water quenching method, the interaction between water and hot glass may induce the occurrence of active radicals (for example ≡Si–OH) and hetero-matters (for example silica gels) at the surface of glass debris [10], and the mineral impurities in water and dust of the air may be sorbed at the surface. The active radicals, hetero-matters, mineral impurities and dust can all act as the nucleating positions and lower the nucleation energy [10,11]; in addition, the glass debris belonging to $CaO–Al_2O_3–SiO_2$ family parent glass has a tendency of surface nucleation by itself. Accordingly, under the synergetic actions of the above factors, the surface of glass debris separated by the cracks in the cracked-glass panel will be heterogeneously nucleated during heat-treatment and then preferentially deposit initial crystals as seen in Fig. 6 where a magnified photo of the cross section of a CGC-GC sample partially crystallized only for 10 min at 1080 °C is given.

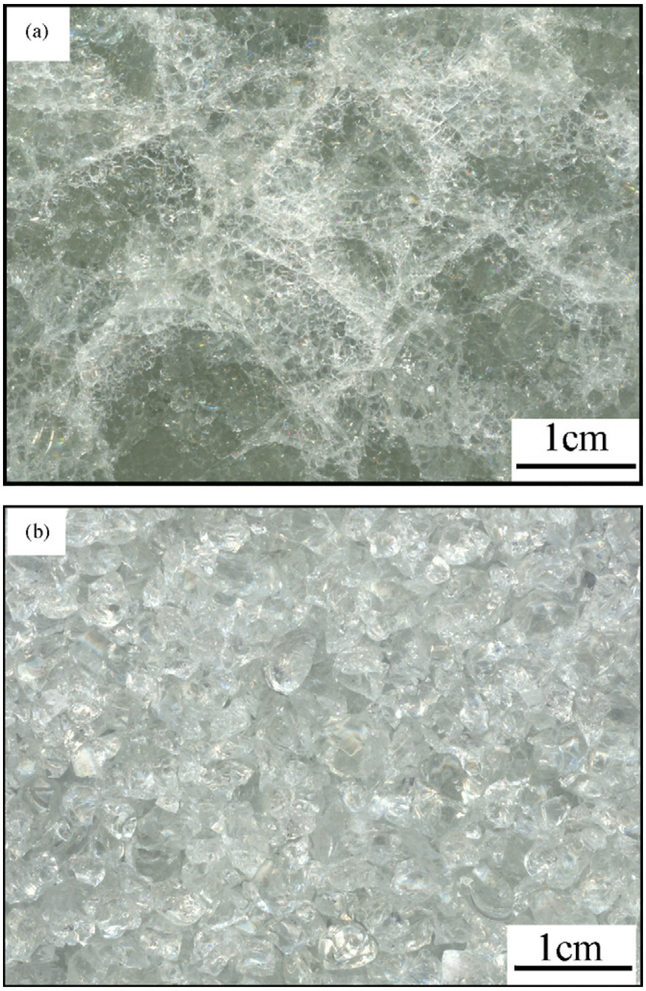

Fig. 2. Comparison of the morphology of cracked-glass panel (a) with that of glass grain aggregate (b), both from the same Batch 2 parent glass melt.

The growth of the initial crystals from the surface into the center of glass debris in the cracked-glass panel can be further explained by *dendritic growth mechanism of crystals* [12]. Under such effects as CaO loss and latent heat release during crystal growth, the initial surface crystals cannot grow evenly in all directions. Instead, the growth would be orientated along directions with abundant CaO supply and low latent heat release impact. When primary dendrite crystals deposit on the initial crystals and grow along the radial orientation of glass debris, the impacts of latent heat release and CaO loss are so weak that crystallization develops fast and the crystallinity is

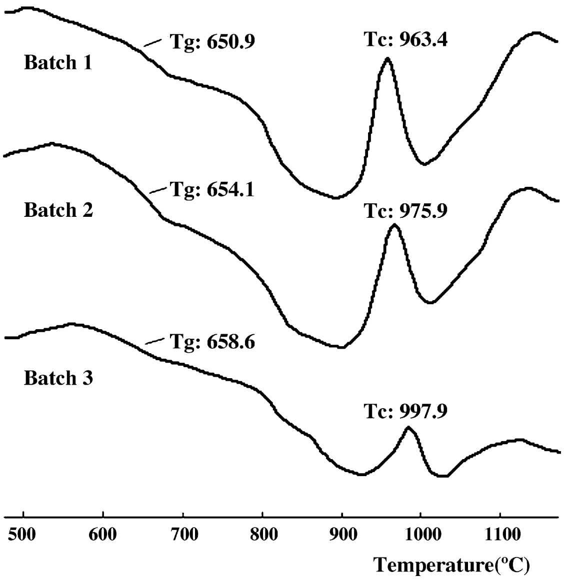

Fig. 3. DTA curves of different parent glasses with different CaO contents. From Batch 1 to Batch 3, the intensity of the exothermal peak decreases with the decrease in CaO content.

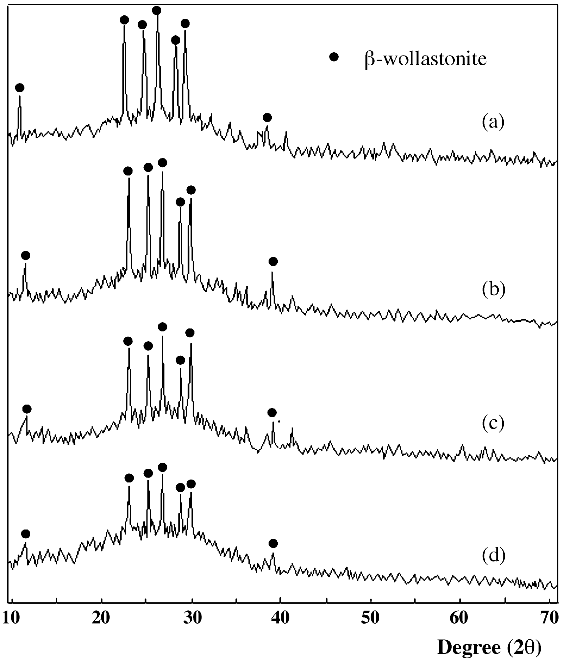

Fig. 4. XRD patterns of: (a) Batch 2 GGS-GCs, (b) Batch 1 CGC-GCs, (c) Batch 2 CGC-GCs and (d) Batch 3 CGC-GCs.

high. Later on, when secondary dendrite crystals are deposited on the primary dendrite crystals along the circumferential orientation of glass debris, the effects of CaO loss and latent heat release become stronger, and as a result, the crystallization proceeds slower and the crystallinity is lower. Accordingly, under the limited crystallization heat-treatment time (1.5 h in this study), the glass debris and the whole cracked-glass panel as well may not be bulk crystallized. The crystallinity differences between surface and interior as well as between radial and circumferential parts of the glass debris are thus formed as seen in Figs. 5 and 6. It should be noticed that it is the CaO content of parent glass that has great impacts on crystallinity difference and total crystallinity, as indicated by the DTA results (Fig. 3), XRD traces (Fig. 4) and the SEM images (Fig. 5).

3.3. Formation of pseudo-bioclastic texture

The pseudo-bioclastic texture on the CGC-GCs samples can be observed in Fig. 7a. The formation of the texture results from anisotropic crystallization and differential crystallinity of the glass debris as discussed above. Additionally, the color difference between white β-wollastonite crystal phase and

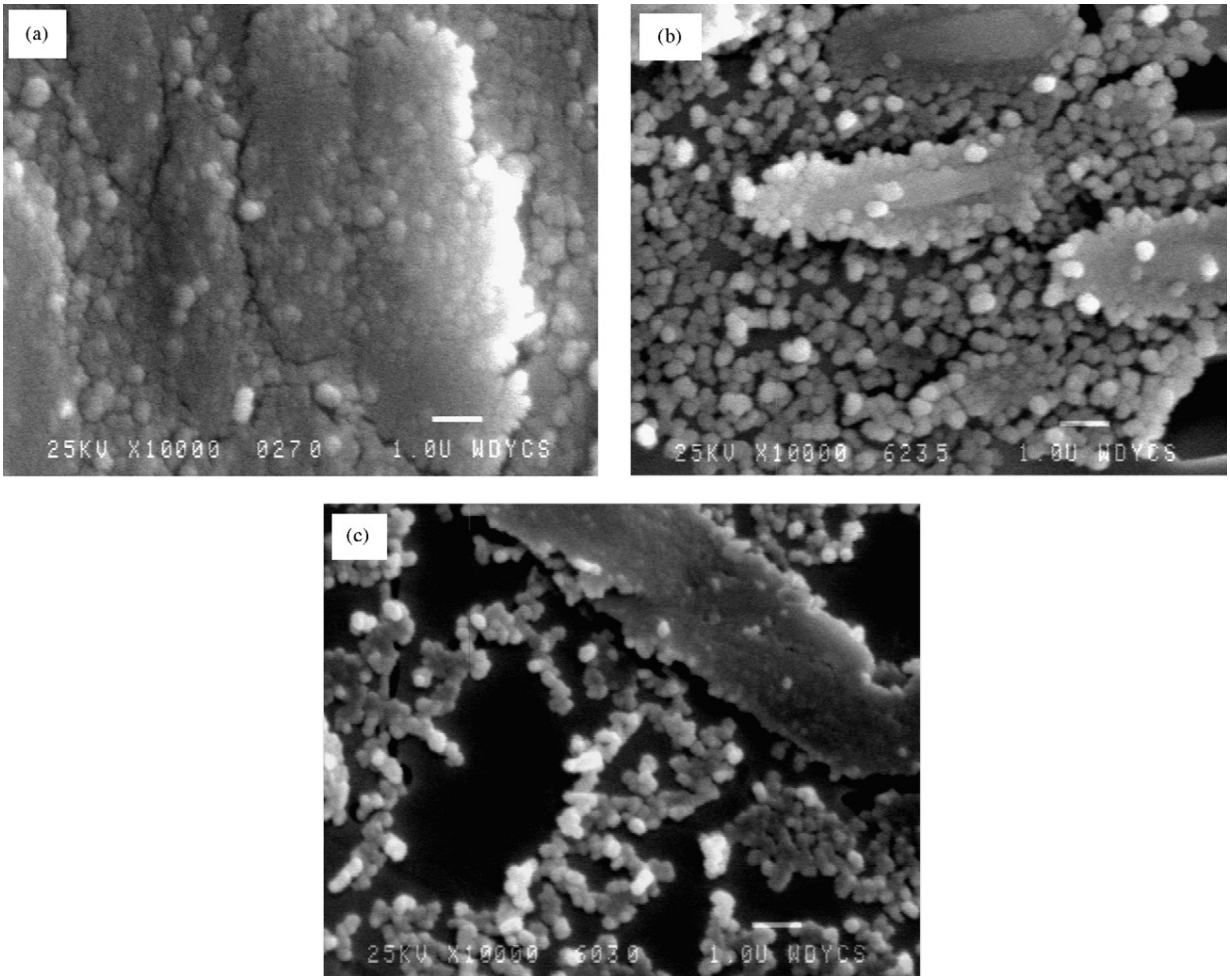

Fig. 5. SEM micrograph of: (a) Batch 1, (b) Batch 2 and (c) Batch 3 CGC-GCs.

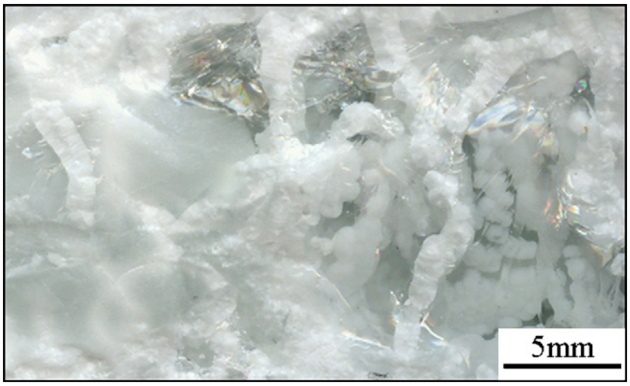

Fig. 6. Magnified view of the cross section of Batch 3 CGC-GCs partially crystallized for 10 min at 1080 °C. Preferential crystallization in the original cracks and then dendritic crystal growth tendency can be clearly seen.

the residual glass phase accounts for the visible appearance of the pseudo-bioclastic texture. The pseudo-bioclastic texture of the CGC-GCs, different from the granular texture of the glass-ceramics (Fig. 7b) produced by the conventional GGS process, makes CGC-GCs a potential alternative for materials of architectural decoration.

3.4. Properties of CGC-GCs

The physical and mechanical properties of all CGC-GCs and Batch 2 GGS-GCs samples are given in Table 3. The strength of CGC-GCs, though lower than that of GGS-GCs, meets the requirements of decorative building materials (more than 35 MPa, as required by National Standard of China). As a whole, the volume densities of CGC-GCs are higher than those of GGS-GCs, and the porosities over three times lower. The results clearly indicate that, using cracked-glass panel as parent glass to produce glass-ceramics by CGC process, the compactness of the product can be remarkably increased and gas pore flaw can be effectively controlled.

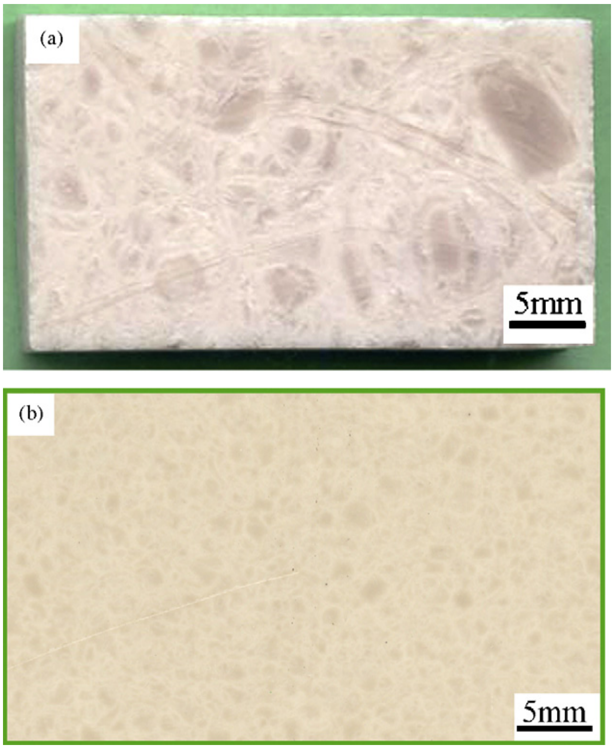

Fig. 7. Comparison of the surface appearance of Batch 2 CGC-GCs with the addition of MnO_2 as colorant (a) with that of the GGS-GCs bought from the market (b).

Table 3
Physical and mechanical properties of CGC-GCs and GGS-GCs

Samples	Volume density (g/cm^3)	Closed porosity (%)	Bending strength (MPa)
Batch 1 CGC-GCs	2.759	0.57	41.00
Batch 2 CGC-GCs	2.719	0.53	38.13
Batch 3 CGC-GCs	2.674	0.48	35.78
Batch 2 GGS-GCs	2.703	1.81	45.60

4. Conclusions

Water quenching-induced cracked-glass can be used as parent glass to prepare glass-ceramics by the CGC process. The compactness of the products can be remarkably increased and gas pore flaw effectively controlled as compared with those of the glass-ceramics from the conventional GGS process. One of the most remarkable feature of CGC-GCs is the pseudo-bioclastic texture. Therefore CGC-GCs are more suitable for floor and wall covering of buildings and a potential alternative for conventional decorative glass-ceramics.

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