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CHEMISTRY DEGREE RESEARCH PROJECT

HIGH MECHANICAL RESISTANCE GLASS CERAMIC TILES PREPARED FROM SOLID WASTES

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Abstract

The development of new glass-ceramic tiles by sinter-crystallization method have been investigated using solid wastes (ceramic polishing, soda-lime-silicate glass, eggshell, mussel shell and industrial sludge’s). Chemical compositions of wastes and glass-ceramic samples were studied by X-ray fluorescence (XRF) and thermal analysis (TG/DSC). Structural characterization by X-ray diffraction (XRD) measurement revealed the crystalline phases depending on process parameters. The morphology of glass ceramic samples was characterized by scanning electron microscopy (SEM/EDX). The apparent density values were between 1,47 and 1,79 g/cm^3. Flexural strength values range between 52,09 and 97,76 N/mm^2. The experimental compositions allowed reutilizing residues to produce high mechanical resistance glass ceramic tiles with suitable properties and environmental profits.

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1. Introduction

1.1. Industrial wastes

The increase of population under a social model based on producing and consuming bymaking a clear profit in the economy, generates very serious consequences at the environmental level [1]. The usefulness of products is not valued, and this generates a large number of wastes that end up being harmful to the environment and to health. This problem is present in the latest studies, which aim to develop production systems that reduce the generation of solid waste and that also have an added value as they can be reincorporated into the production chain.

In this sense, more sustainable models based on producing and consuming, but in an efficient way, are required. One model is the circular economy. As part of the European Green Deal, a new circular economy action plan was introduced in 2020 [2]. Supported by the "Roadmap to a Resource-Efficient Europe" it has as a priority to turn the EU into a low-carbon, resource-efficient, green and competitive economy [3]. The circular economy can be understood as the transformation of interconnected production and consumption systems into systems in which the value of products, materials and resources is retained in the economy for as long as possible and waste generation is minimized. This transformation involves industrial processes and product design, as well as the reconfiguration of business models. This economy is based on a green and sustainable industry [4].

To reduce waste, it is important to focus the economy on a six-pronged model: reduce, reuse, repair, remanufacture, recycle and recover. In addition, this will keep the resources extracted from nature to a minimum and make them last longer [5].

Waste containing heavy metals and the consumption of natural resources has a great impact on environmental sustainability. To take China as an example, in 2019, the overall solid waste industry generated 3.542 million tons of waste, of which only 1.949 billion tons were recycled. One of the challenges that is being addressed globally is the elimination of waste containing heavy metals, as they pose a serious problem to the ecological environment and human health. At present, the reuse of these wastes is being studied for the production of geopolymers, cement aggregates, concrete, ceramics, etc. Therefore, glass-ceramic materials produced from heat treatment are a good option to reduce waste [6].

As a consequence of the ceramic industry being one of the most important manufacturing areas in the world [7,8], the demand for products has increased, thus generating environmental problems. In Spain, Castelló is the locality where it focuses on the ceramic cluster. It is composed of more than a hundred tile manufactures, mainly tile factories but also producers of frits and glazes and spray-dried powder companies. More than 20.000 tons/year of residues are generated, creating a significant environmental impact [9]. The typical residues are: frit wastes, recycled glass, and chamotte, this last one rich in mullite. So, recent studies are looking at how to mitigate these problems by introducing waste into the market to create new materials [6,7].

Wastes can be raw materials as replacement of natural compounds for ceramics materials. For example, fly ash (FA), rice husk ash (RHA), blast furnace slag (BFS), water treatment sludge, polished tile waste, sludge and red mud, are some wastes with different chemical composition [10]. Many researchers show how these wastes replace total or partially natural resources in its composition. In refractory materials, the addition of wastes reaches better insulation behavior, porosity, and strength up to a limit [11–14]. Tiles are made of different types of clay, silica, feldspar, etc., that affect several environmental issues. Additionally, FA is used for preparing ceramic tiles and improve mechanical properties. Furthermore, FA is used to prepare low-temperature firing wall tiles [15–17]. Ceramic sanitaryware use a huge amount of natural compounds and the demand could be increased in the next few years. To reduce this, some studies show that introducing, for example, wall tile waste up to 10 wt. % reduces the thermal expansion coefficient, water absorption, high temperature deformation, and improves the strength of the fireclay products [18].

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Focusing on the recycling of materials, for example the case of glass wastes, less than 25%wt was recycled. This has led to numerous studies seeking to alleviate this problem by reintroducing this waste, for example, as a ceramic fluxe to reduce the temperature of the ceramic firing. The waste glass reduced 100ºC in the firing temperature of porcelain, reduce the temperature and the time of sanitaryware firing and accelerate the densification process of porcelain tile. In addition, it can improve the properties of the materials, for example, by reducing water absorption and increasing compressive strength in building bricks [19]. Another waste that can generate a great environmental impact is eggshell. This wastes creates major problems as it is one of the most consumed in the food industry [10,20]. Currently, the inertization, recovery and valorization of waste from urban and industrial waste are fundamental challenges to enhance environmental sustainability.

In case of glass-ceramic materials, silica-containing solid wastes have been studied. According to studies, FA is appropriate for making $CaO\text{-}Al_2O_3\text{-}SiO_2$ systems and is applicated on construction and decoration. Furthermore, iron-containing silica-based wastes are possible materials to fabricate glass-ceramic materials [21–23]. In addition, foam glass can be prepared with foaming agents like wool waste [24], eggshell wastes [25], and Li_2CO_3 [26].

1.2. Glass ceramic material

Glass-ceramic materials are formed by thermal processes that promote nucleation and controlled crystallization [23]. It is composed of polycrystalline inorganic solids and has a microstructure based on one or more crystalline phases and a residual glassy phase, inside which there are small crystals randomly oriented, without voids or microfractures.

Glass ceramics can be classified as non-porous materials that consist of tiny crystals uniformly distributed throughout the residual glassy phase. These crystals can be oxides, no-oxides and metals compounds. Glass ceramics could be obtained by heating the glass to elevated temperatures, where precipitation of solvated species occurs as long as the thermal energy is suitably to overcome the barrier of both nucleation and crystal growth [9]. The crystals in the glassy matrix are oriented randomly, their properties are independent of the direction of measurement. Thus, glass ceramics could be considered as isotropic materials. Their properties depend on the physicochemical properties of the glass, the crystalline phases present, the nature of the interface between each phase, the devitrified crystal size and, especially, the morphology of the two phases present [27].

Vitrification process has been demonstrated is an adequate processing method for inertize toxic and abundant residues and even to facilitate their recycling as secondary raw materials in ceramics and glasses industries [28]. Transforming of starting glasses after vitrification into glass-ceramics by controlled thermal treatment is possible to reach immobilizing of a wide range of industrial wastes (mineral residues, sludges from dumps, slags, ashes, …). Besides, the low cost and great availability of waste make these glass-ceramics materials very attractive from an economical and technological point of view, so synthetic high-performance materials with broad applications in construction and civil engineering can be obtained from residues.

The theoretical tendency towards crystallization can be evaluated by the ternary diagrams of Ginsgerg, Raschin-Tschetveritkov and Lebedeva, shows in Fig. 1 [23].

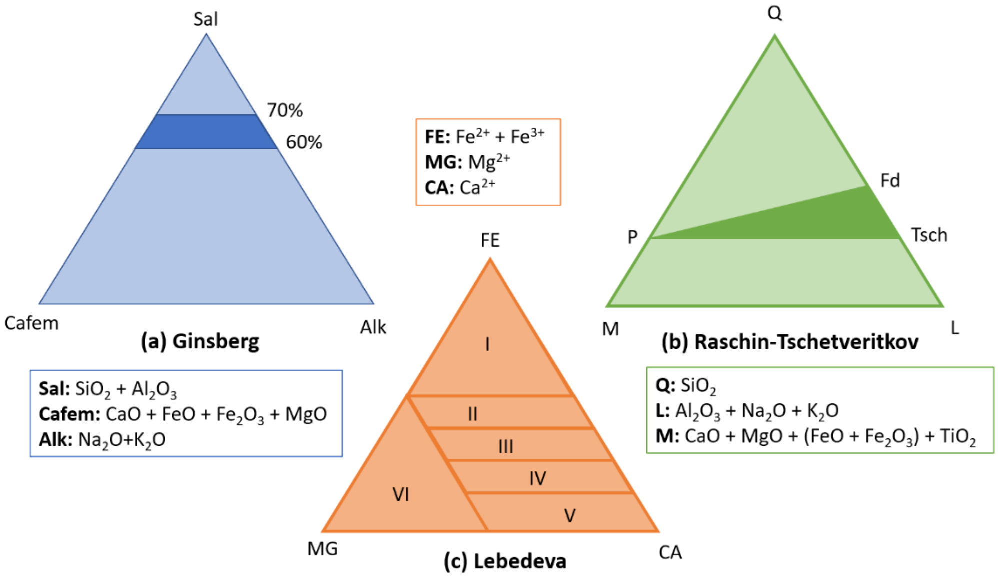

Figure 1. *Ternary diagrams of theoretical devitrification.*

The Ginsberg diagram differentiates three zones: at the 60-70% of salt, the glass has a tendency to devitrify. Above this zone, the material becomes too stiff and below it there is an excess of modifiers that destabilize the structure.

The Raschin-Tschetveritkov diagram shows a zone bounded by the points P (pyroxene), Fd (feldspar) and Tsch (Tschermark molecule $(Ca_2)(Mg_3Al_2)(Al_2Si_6O_{22})(OH)_2)$ which has a tendency to devitrify. Above this zone, there is an excess of quartz which makes the material more viscous and so complicates crystal formation. Below this zone, there is a tendency for olivine precipitation.

The last diagram consists of 6 different zones in which II, III and IV have a tendency to devitrify and different phases predominate. This diagram has been achieved thanks to the result of the previous one and includes the effects associated with the presence of structural modifiers, which are the divalent cations of iron, calcium and magnesium.

The 3 diagrams are a theoretical view of the tendency of glasses to devitrify, but they are not a tool that exactly predicts what will happen. In addition, they do not include a large number of factors that can influence devitrification. These diagrams complement each other because of the Ginsberg diagram which shows the role of cations in crystallization, while the others inform about the nature and sequence of crystallization.

The most commonly used methods to produce glass-ceramic materials from wastes [29] are summarized in table 1 [30]. The conventional method can be divided into two: the conventional and the modified method. They differ in that the crystallization in the conventional method is done in one step and in the modified method, in two steps. This is because, in the first case, there is no overlap between nucleation and crystalline growth, while in the other there is overlap. Both have small homogeneously distributed crystals and the final product has good quality. In addition, the conventional method uses nucleating agents to increase efficiency (lower temperature and processing time).

In petrurgical method, nucleation and crystal growth take place during cooling and this causes large size glass, because is difficult to control size during the cooling. Thus, this method is more economical and environmentally friendly. However, it produces materials with low quality and less structural homogeneity. Finally, powder sinter-crystallization is the method that will be used in this project. This method has a previous grinding and pressing stage and it doesn’t have annealing stage. The products obtained by this method are opaque and have limitations in size and shape.

Table 1. *Methods to produce glass-ceramic materials.*

Method	***Stages***	***Characteristics***
Conventional 2 stage method	*No overlap between nucleation and crystal growth: 2 stages*	*· Small homogeneously distributed crystals* *· Good quality product* *· More used*
Modified conventional method	*Overlap between nucleation and crystal growth: 1 stage*	*· Small homogeneously distributed crystals* *· Good quality product* *· More used*
Petrolurgical	*Nucleation and crystal growth during cooling*	*· Large size glass* *· Less structural homogeneity* *· More economical and environmentally friendly* *· Low quality product*
Powder sinter-crystallization	*Pre-grinding stage* *No annealing stage*	*· Opaque products* *· Size and shape limitation*

2. Objectives

The aim of this research work is the development of new high mechanical resistance glass-ceramic of new glass-ceramic tiles by sinter-crystallization method using solid wastes (ceramic polishing, soda-lime-silicate glass, eggshell, mussel shell and industrial sludge’s).

In order to achieve this general objective described above, a series of specific objectives have been defined:

- Analysis of the wastes using X-Ray diffraction (XRD) and Differential Thermal Analysis/Thermogravimetric (ATD/TG).

- Formulation and development of high resistance glass ceramic tiles from solid wastes.

- Characterization of the glass ceramics tiles.

3. Experimental methodology

3.1. Formulation of glass-ceramic material

Glass ceramic tiles were prepared by sinter-crystallization method [28,31] using polishing ceramic wastes, glass cullet from the recycling glass sector, eggshell, mussel shell and sludge’s wastes. The formulations are listed in Table 2. The method consists of melting stage (1600ºC/2h) of the mixture of wastes (Nanetti TT117 furnance) followed by fast cooled without been neither shaped nor annealed to reduce stresses. Table 3 shows melting cycle conditions.

Glassy granules were obtained at room temperature. After, they have to be ground to become a powder. The resulting powder were press on rectangular compacts (2x7 cm^2) obtained by uniaxial pressing (37 MPa) (Figure 3a and 3b). The compacts were treated at 950ºC (20ºC/min) during 30 minutes. Table 4 shows devitrification cycle conditions.

Table 2. *Formulation of glass-ceramic supports.*

Sample	**Glass (% wt.)**	**Chamotte (% wt.)**	**$CaCO_3$ (% wt.)**	**Sludge (% wt.)**	**Eggshell (% wt.)**	**Mussel Shell (% wt.)**
A	50	20	30	0	0	0
B	50	20	0	0	30	0
C	50	20	0	0	0	30
D	50	20	18,5	11,5	0	0

Table 3. *Temperature cycle to melt the material.*

T initial (ºC)	**T final (ºC)**	**t (min)**
30	500	20
500	900	40
900	1600	60
1600	1600	180

Table 4. *Devitrification thermal treatment.*

T initial (ºC)	**T final (ºC)**	**t (min)**
30	500	5
500	500	16
500	950	20
950	950	30

3.2. Characterization techniques

The samples were characterized by using X-ray diffraction (XRD), X-ray fluorescence (XRF), differential scanning calorimetry and thermogravimetric analysis (DSC-TG), scanning electron microscopy (SEM) and making a mechanical strength measurement.

3.2.1. X-Ray diffraction (XRD)

The crystal structure was monitored by X-ray diffraction (XRD) using a D4 Endeavor, Bruker-AXS equipped with a Cu Kα radiation source. The samples were made at a voltage of 40kV and a current intensity of 20 mA and data was collected by step-scanning from 10º to 80º with step size of 0.05º 2θ and 1 s counting time per step.

3.2.2. X-Ray fluorescence (XRF)

Wastes and glass ceramic compositions have been studied by X-Ray Fluorescence (XRF) using an S4 Pioneer, Bruker, wavelength dispersive X-ray sequential spectrophotometer is used with a 4 kW X-ray tube with a Rh anode.

3.2.3. Differential scanning calorimetry and thermogravimetric analysis (DSC-TG)

Thermal analysis of was done using differential scanning calorimeter (DSC) and Thermo Gravimetric Analysis Mettler Toledo DSC model DSC2 heat flow type equipment. Data was collected from 25ºC to 1000 ºC.

3.2.4. Scanning electron microscopy (SEM)

Scanning Electron Microscopy (SEM) model JEOL 7001F attached with an energy dispersive X-ray analysis (EDX) was employed to study the morphology and elemental composition of the samples. INCA 350 Oxford software was used for the analysis of the results.

3.2.5. Mechanical strength measurement (flexural strength)

The mechanical strength is measured with a HOYTOM three-support flexometer with a separation of 61 mm. The value is obtained using eq. 1.

$$RMCA\left(\frac{N}{mm^2}\right) = \frac{3}{2}x\frac{F_{máx}(N)\ x\ L_{rec}(mm)}{L_z^2\ (mm)\ x\ l_y\ (mm)} \qquad \text{(eq. 1)}$$

$$\frac{N}{mm^2} = 10'1972\frac{Kg}{cm^2}$$

4. Results and discussion

4.1. Wastes characterization

The XRF results of wastes are shown in Table 5. Glass wastes are rich in silica, sodium and calcium oxides. Ceramic wastes exhibit alumina/silica ratio 3:1 and lower alkali oxides. In contrast, eggshells and mussel shells present a typical $CaCO_3$ composition. Finally, sludge is composed of phosphate, alumina, potassium oxides and lower metal oxides (Cu and Fe). Furthermore, it shows a small amount of lead.

Table 5. *Chemical analysis of glass, ceramic waste, eggshells and mussel shells by XRF.*

Sample	**Na_2O**	**Al_2O_3**	**SiO_2**	**P_2O_5**	**SO_3**	**MgO**	**K_2O**	**CaO**	**BaO**	**TiO_2**
Glass	12,51	0,85	73,27	0,01	0,20	3,75	3,75	8,95	-	0,05
Ceramic waste	4,41	19,60	70	-	-	-	1,67	1,00	-	0,64
Sludge	0,23	25,70	0,59	48,40	0,83	-	19,8	0,56	-	0,03
Eggshell	0,19	0,05	0,33	0,25	0,41	0,52	0,11	51,2	-	-
Mussel shell	0,41	0,05	0,23	0,05	0,20	0,21	0,05	52,8	-	-

Sample	**MnO**	**Fe_2O_3**	**ZrO_2**	**ZnO**	**PbO**	**SrO**	**Cl**	**Br**	**CuO**	**[a]LOI**
Glass	-	0,10	-	-	-	-	-	-	-	-
Ceramic waste	-	0,34	0,17	-	-	0,05	-	-	-	1,08
Sludge	0,02	2,21	-	0,03	0,05	-	0,06	-	2,24	-
Eggshell	-	-	-	-	-	0,05	0,09	-	-	46,54
Mussel shell	-	-	-	-	-	0,11	0,05	0,05	-	45,86

[a]LOI (Loss on ignition) – consists of heating a sample of the material at a specified temperature, allowing volatile substances to escape, until its mass ceases to change.

Figure 2 shows the TG-DSC curves of the thermal treatments of the solid wastes between 25 and 1000ºC at 5ºC/min heating rate. The black curve refers to thermogravimetric analysis and the blue curve to differential scanning calorimetry analysis. In Fig. 5(a, b, c and d), one apparent endothermic stage is observed between 700 and 900 ºC according to the DSC curve which can be attributed to the decomposition of the carbonate into calcium oxide and carbon dioxide [32]. In Fig. 5(a), the endothermic stage corresponds directly to mass loss event in the TG curve and is less than 0,50%. In Fig. 5(b, c, d), the endothermic stage corresponds directly to 47-48% mass loss event in the TG curve [33–35].

Finally, in Fig. 5(e), two apparent endothermic stages are observed according to the DSC curve. First, at 100ºC due to water loss. So, at 700ºC caused of the decomposition of carbonate into calcium oxide and carbon dioxide. TG curve shows the 25% water mass loss that occurs until 200ºC, which remains constant. There are more endothermic stages at 900 and 1100ºC that are attribute to the decomposition of the metals presents in the sludge, as seen in chemical composition at Table 5. However, in TG curve, the loss mass is constant, so this decomposition is insignificant.

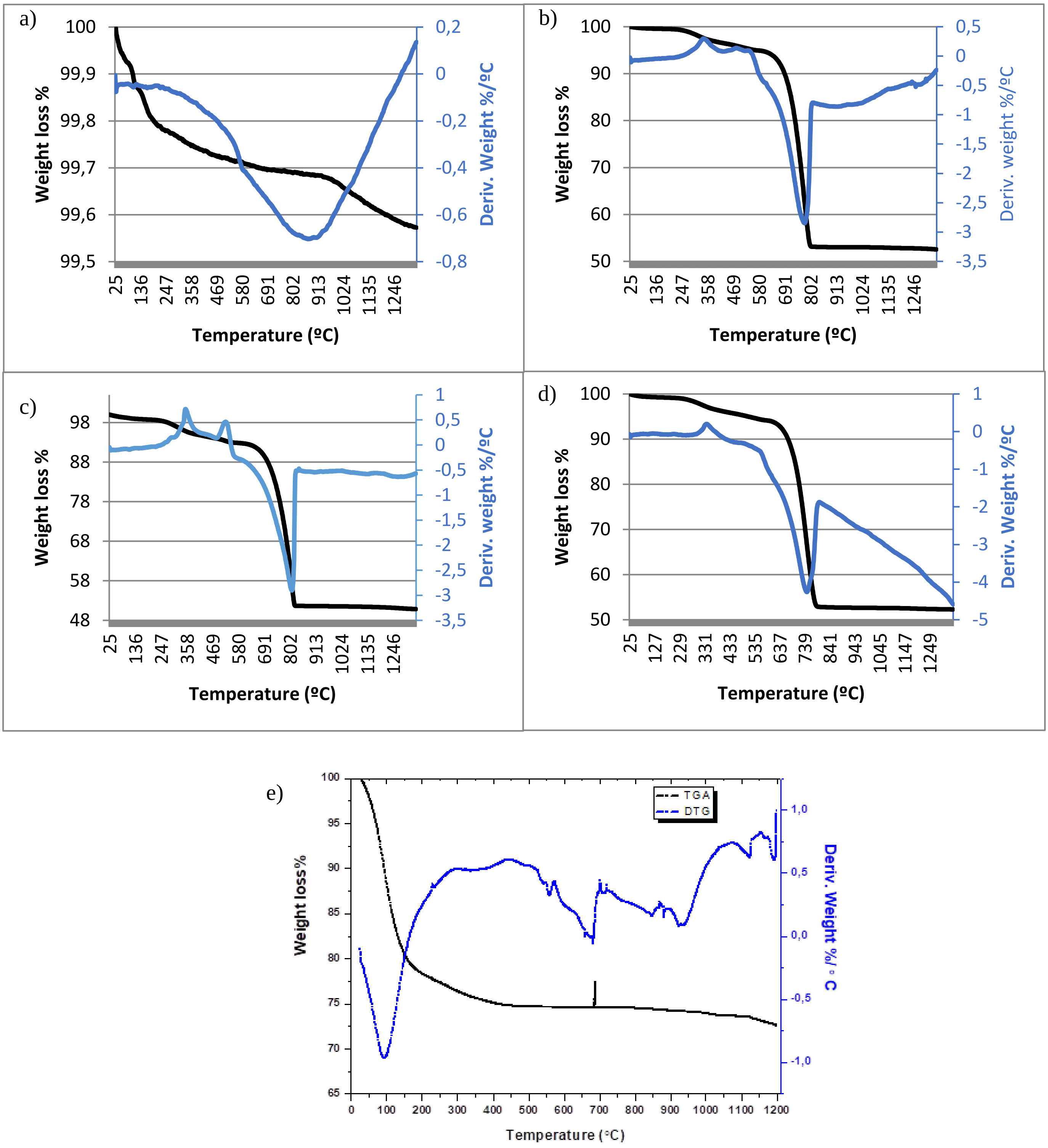

Figure 2. *TG-DSC of a) glass, b) ceramic waste, c) eggshell, d) mussel shell and e) sludge*

4.2. Characterization of glass-ceramic substrates

Fig. 3(a, b) shows the humidified sample before pressing and the sample after pressing. Fig. 3(c), the three replicates of the samples described in Table 2 before the thermal devitrification cycle are observed.

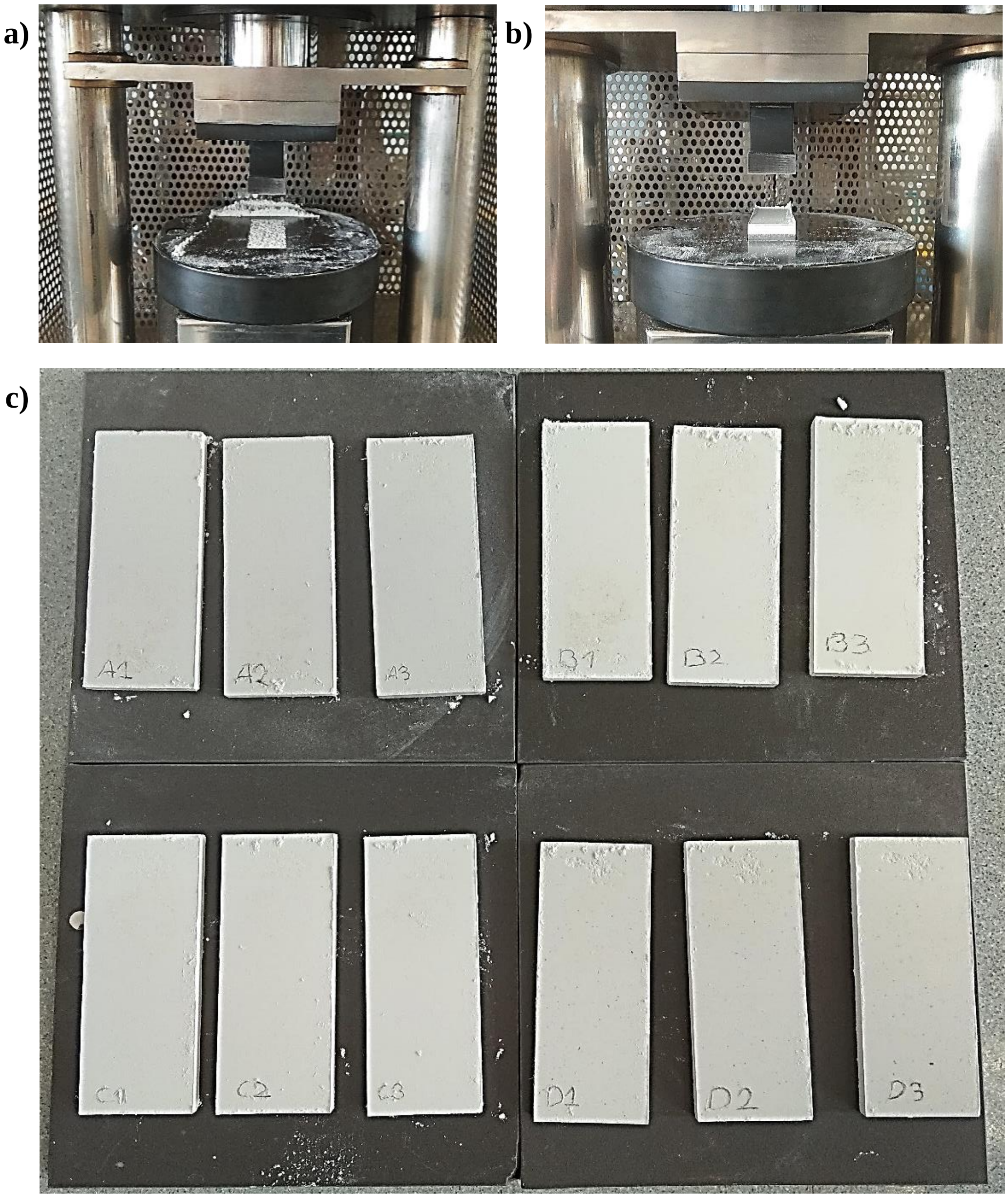

Figure 3. *Glass ceramic tiles compositions a) before pressing; b) after pressing; c) resulting tiles before thermal devitrification treatment.*

The glass-ceramic compositions were displayed in table 6. About the chemical composition, it is expected the devitrification of crystalline phases belonging to the more common simplified CaO-Al_2O_3-SiO_2 ternary system. This prediction is based on the ternary diagrams shows in Fig. 1. Based on these and knowing the chemical composition, it is expected that crystallize in the ternary system discussed above.

Table 6. *XRF of glass ceramic samples A, B, C and D.*

Sample	**Na_2O**	**MgO**	**Al_2O_3**	**SiO_2**	**SO_3**	**K_2O**	**CaO**
A	6,18	1,75	4,70	51,72	0,15	0,85	33,02
B	6,44	1,89	4,63	52,65	0,10	0,87	31,70
C	6,45	1,71	5,64	52,93	0,05	0,89	30,61
D	6,29	1,73	6,68	53,01	3,54	0,35	24,28

Sample	**TiO_2**	**Fe_2O_3**	**CuO**	**CoO**	**ZnO**	**SrO**	**ZrO_2**	**Total**
A	0,25	0,38	-	0,02	0,02	0,03	0,07	99,13
B	0,24	0,33	-	0,01	0,02	0,03	0,07	99,07
C	0,26	0,34	0,01	-	0,01	0,06	0,07	99,01
D	0,27	0,61	0,26	-	0,02	0,03	0,07	99,96

The X-ray diffractogram of glass ceramic samples treated at 950ºC during 30 minutes are shown in Figure 4. The samples A, B and C shows well define intense peaks corresponding to sodium calcium aluminum silicate (JCPDS card No 20-0020) crystalline phase. Sample D shows low crystallinity in contrast with the other samples.

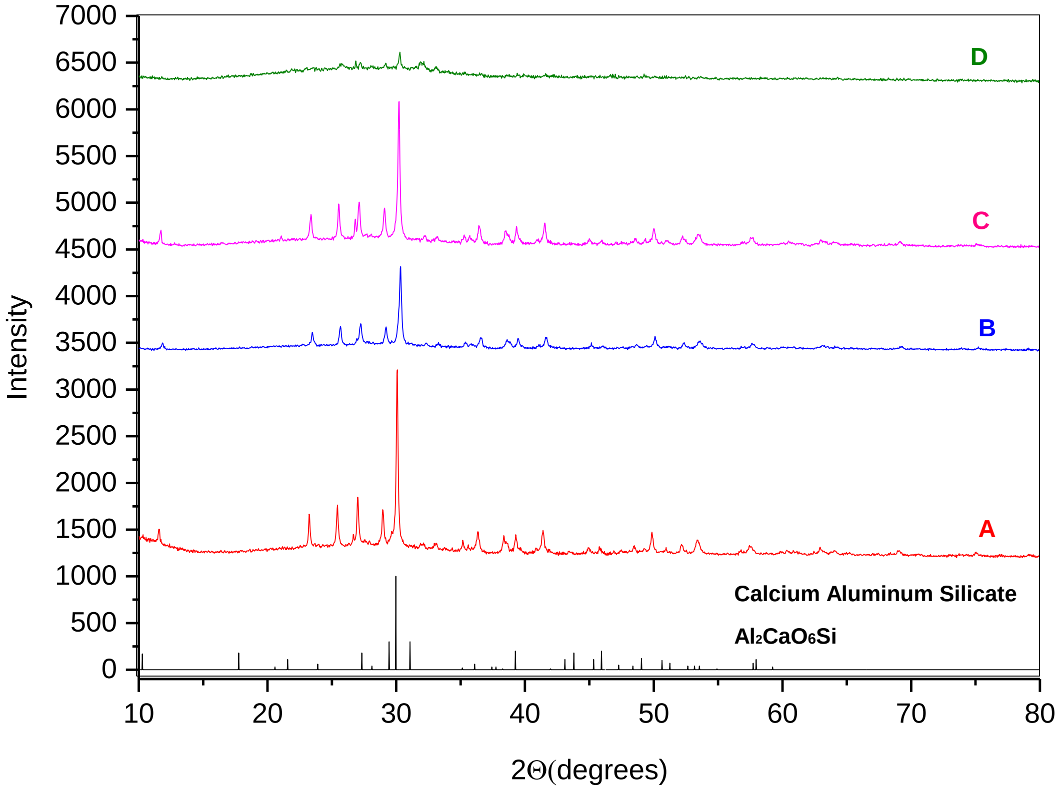

Figure 4. *DRX of vitroceramics materials A, B, C and D.*

About microstructural morphology, the corresponding SEM micrograph shows the presence of crystals uniformly distributed throughout the residual glassy phase produced by the controlled crystallization of precursor glass.

Small rectangular crystals distributed along glassy matrix were observed in samples A and B, as seen in Figure 5. Rectangular shaped crystals are observed in figure 11(c) that correspond to the phases obtained by XRD, presenting a high distribution of the same on the surface. Figure 11D shows minor crystallinity according to XRD analysis.

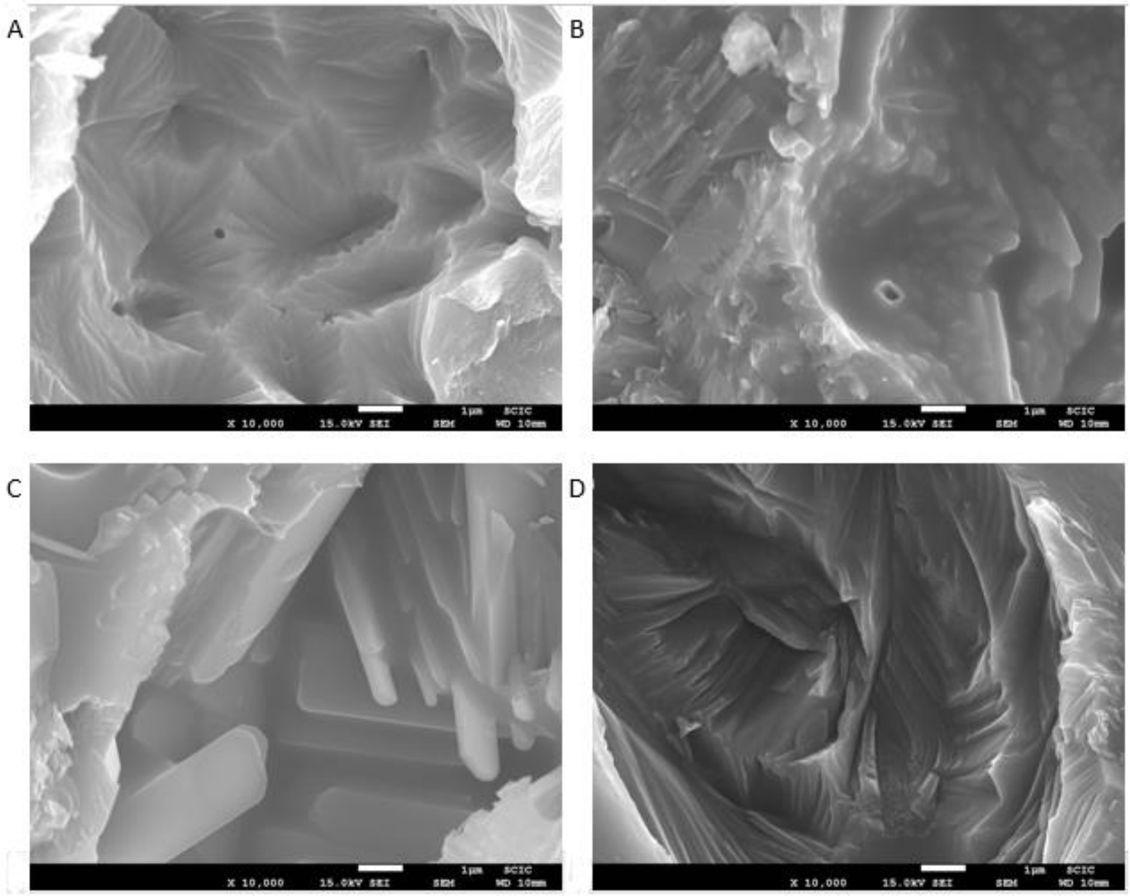

Figure 5. *SEM of glass-ceramic samples A, B, C and D.*

The variations on apparent density, flexural strength (FS) and force (F) are displayed in Table 8. These parameters are essentials to control the quality of the final product, because it has a ceramic application, being susceptible to cover floors and walls.

Table 7 shows density values with average value of 1,64 g/cm^3 at 950ºC. This value is lower and is obtained at lower temperatures than in the case of porcelain stoneware ceramic tiles [28], which reaches an only apparent bulk density of 2.40 g/cm^3 at 1200ºC.

The flexural tensile strength of fired pieces is based on the 3-points method and has been measured at maximum sintering temperature. Thus, the result corresponding to the glass ceramic is higher (82,91 N/mm^2) [36] than conventional porcelain stoneware tile which exhibits a value near 57 N/mm^2, been glass ceramic suitable data to be used as ceramic tile, according to the UNE-EN-

ISO 10545-4. These results are favored by the higher mechanical strength of glass ceramics with reduced thickness (< 4,5 mm).

Table 7. *Parameters of glass ceramic samples before thermal treatment.*

Ssample	**Weight (g)**	**Lx (mm)**	**Ly (mm)**	**Lz (mm)**	**D (g/cm^3)**
A1	21,14	80,71	30,46	5,31	1,6194
A2	19,96	80,62	30,33	4,95	1,6491
A3	21,43	80,61	30,49	5,14	1,6963
B1	19,09	80,37	30,27	4,39	1,7875
B2	18,90	80,84	30,26	4,66	1,6580
B3	19,98	80,81	30,40	5,33	1,5259
C1	20,27	80,61	30,44	4,94	1,6722
C2	20,90	80,56	30,28	5,82	1,4721
C3	21,02	80,59	30,38	5,27	1,6291
D1	20,79	80,71	30,26	5,23	1,6276
D2	22,12	80,64	30,44	5,46	1,6504
D3	21,14	80,39	30,24	5,30	1,6408

Table 8. *Fs and F of glass-ceramic samples after thermal treatment.*

Sample	**Ly (mm)**	**Lz (mm)**	**R (Kg/cm^2)**	**R (N/mm^2)**	**F máx (N)**
A1	26,09	4,27	966,65	94,80	492,8
A2	25,95	4,17	855,74	83,92	414,2
B1	25,85	3,98	941,59	92,34	416,2
B2	25,75	4,08	822,54	80,66	378,2
C1	25,65	4,31	967,02	94,83	494,4
C3	26,14	4,31	996,91	97,76	519,0
D1	25,80	4,40	681,58	66,84	364,6
D3	25,67	4,59	531,19	52,09	308,0

Glass-ceramic samples are shown in Fig. 6, this being already the final glass-ceramic material. As it can see, samples A, B and C present white color, and sample D the sample, turquoise due to metals contains in its composition, shows in the XRF.

Figure 6. *Glass-ceramic material with compositions A, B, C and D.*

5. Conclusions

Several glass ceramic tiles were prepared using solid wastes. Samples A, B and C shown crystals corresponding to sodium calcium aluminum silicate. However, sample D exhibits minor crystallinity and therefore worst mechanical properties.

Highest mechanical resistance result was obtained for sample C (97 N/mm2) forming large crystals as can been observed in SEM micrograph.

A high resistance glass ceramic tile from different wastes as raw materials was achieved which displays better technological properties than conventional porcelain stoneware tile. This composition implies also a reducing in the sintering firing with 250ºC of decreasement with respect to the conventional porcelain stoneware tiles, which can be corroborate with the testing at pilot and industrial scale in continuous production process.

Finally, this material has been achieved with a lower density than the conventional porcelain stoneware tile and with a reduced thickness. This fact allows to obtain a environmentally friendly material with low weight an suitable for technological applications.

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