THE GLASS-CERAMIC PROCESS: AN ALTERNATIVE FOR MANUFACTURING TILES FROM HIGH PERCENTAGES OF INORGANIC WASTES

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1. ABSTRACT

The Solid State Chemistry Research Group in the Inorganic and Organic Chemistry Department at Universitat Jaume I is studying the value enhancement of industrial wastes by the vitrification technique, which favours their homogeneity. This paper presents an overview of the existing industrial methods for fabricating glass-ceramic material from wastes. In particular, the investigation focuses on the experimentation of the sinter–crystallisation method and of the petrurgical method, with a view to designing glass-ceramic tiles using wastes from the recycled glass sector and from the thermal power station in Andorra (Teruel). The selection of the two methods is based on the important energy savings they provide and they ease of performance. The study presents an example of waste valorisation using the sinter–crystallisation method.

2. INTRODUCTION

Glass-ceramic materials are defined as polycrystalline inorganic solids produced by the controlled vitrification/crystallisation of certain glass precursors, generally induced by nucleating agents. These agents are responsible for favouring nucleation and they may be metals (Au, Ag, Pt, Pd) or non-metals such as TiO_2, P_2O_5, and ZrO_2. They are made up of a structure characterised by the presence of one or more crystalline phases and a residual glassy phase, it being possible to obtain crystallinity between 0.5 and 99.5%. The crystalline phases are determined by randomly oriented small crystals in the residual glassy phase, without any voids or micro-fractures or any other type of porosity, so that the number of crystals, their growth rate and their final size are controlled by the thermal treatment to which the glass precursor is subjected [1-4].

Although the devitrification process is considered to have been discovered by the French naturalist, physicist, and technologist Réaumur (1683–1757), the phenomenon was not consolidated until the mid 20th century, thanks to the work of the famous inventor and chemist Dr Stookey (1915–2014), who accidentally discovered glass-ceramic material as a result of the overheating of a furnace in which it was intended to precipitate photosensitive silver in glasses belonging to the binary system $Li_2O{\cdot}SiO_2$ [5].

The vitrification process constitutes an alternative for the treatment of mainly inorganic wastes, such as the waste and scrap from the ceramic sector, because it is able to significantly enhance the chemical homogeneity of extremely heterogeneous mixtures that may even contain toxic and hazardous heavy metals, achieving appropriate compositional stability of the system. This vitrification process, followed by the corresponding thermal treatment for crystallisation, allows glass-ceramic tiles for construction to be manufactured [6-10].

For the manufacture of glass-ceramic material, the two main existing industrial fabrication routes are based on bulk crystallisation, starting with a glass, and on the sinter–crystallisation of the glass in the form of a compact powder. Preliminary bulk crystallisation of the glass by hot forming can be performed in several ways: either through the petrurgical method, crystallising during controlled cooling, or using the conventional glass-ceramic process, which involves rapid cooling to the annealing temperature to remove glass stresses, followed by another additional thermal treatment step to generate nuclei that give rise to crystal growth. This step may consist of a single stage or of two stages, a nucleation stage and a crystal growth stage, depending on the type of starting composition and the product to be made. With regard to sinter–crystallisation, this process involves cold forming of the glass powder, following the traditional ceramic route, such that the pressed pieces are subjected to thermal treatment for nucleation and crystal growth, which allows crystals to appear on sintering the solid compact [11-14].

Figure 1 shows micrographs of the structure of a glass-ceramic material, of a glass, and of a ceramic material (porcelain tile), obtained by scanning electron microscopy (SEM). It may be observed that the glass exhibits a single phase of an amorphous nature, whereas the glass-ceramic and the ceramic materials exhibit different crystalline phases. The glass-ceramic material displays small crystals of a similar morphology, randomly arranged in a residual phase without any porosity, whereas the ceramic material (porcelain tile cross-section) exhibits a great variety of crystals of different nature, together with a considerable quantity of closed porosity.

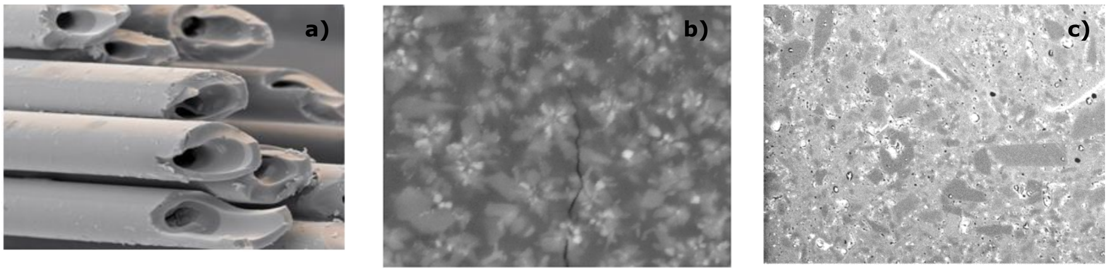


Figure 1. *SEM micrographs of different materials: a) glass tubes, b) glass-ceramic material and c) porcelain tile.*

The most notable advantages of glass-ceramic materials include forming flexibility, the possibility of designing nanostructures for specific applications, and practically zero porosity. In addition, they allow materials that combine a great variety of properties required for multiple technological applications to be processed. Thus, for example, dental applications combine properties of high hardness and mechanical strength with translucency, biocompatibility and chemical durability [15-16].

In the context of traditional flat ceramics, the use of glass-ceramic glazes on porcelain tiles to obtain non-slip tiles involves the consolidation of this type of material in the ceramic sector [17-25].

3. PRODUCTION METHODS

3.1. CONVENTIONAL METHOD (2 STAGES)

The conventional method, known as such because it is the most widely used method in glass-ceramics manufacture, starts with raw materials fusion at high temperatures, above 1500ºC, so that the melt, lightly cooled, undergoes hot forming (between 1000 and 1300ºC) using moulds or roller lamination, as shown in Figure 2. The formed glass is then rapidly cooled to 700ºC, after which it is subjected to a slow cooling or annealing process to avoid residual stresses arising in the glass, thus yielding a sufficiently resistant glass at ambient temperature.

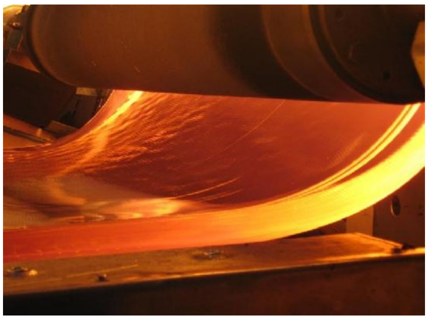


Figure 2. *Image of molten glass forming by roller lamination.*

The glass is subsequently subjected to a devitrification process, which, in this case, consists of two different stages: nucleation and crystal growth, as shown in Figure 3. The glass is thus heat-treated at its characteristic nucleation temperature for a given time, after which heating is increased to the appropriate temperature for growth of the previously nucleated crystals for a specific time, depending on the material to be treated and the targeted end product.

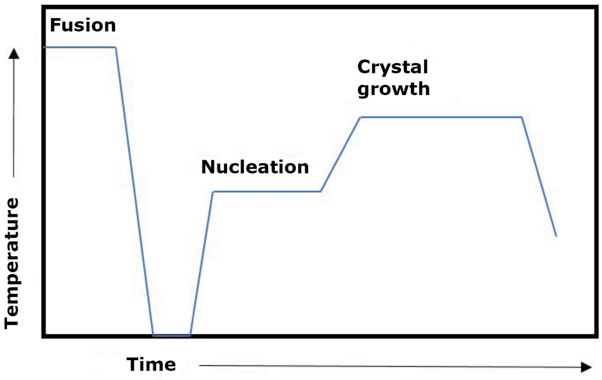


Figure 3. *Thermal cycle of the conventional 2-stage method for the production of glass-ceramic materials.*

In this case, bulk crystallisation occurs, as the crystals grow inside the mass, creating a random distribution of small crystals that contribute great homogeneity to the material, providing an end product with high added value, which is why this method is the most widely used one in industrial practice. Figure 4 schematically illustrates the devitrification of a glass precursor by the nucleation and crystal growth process.

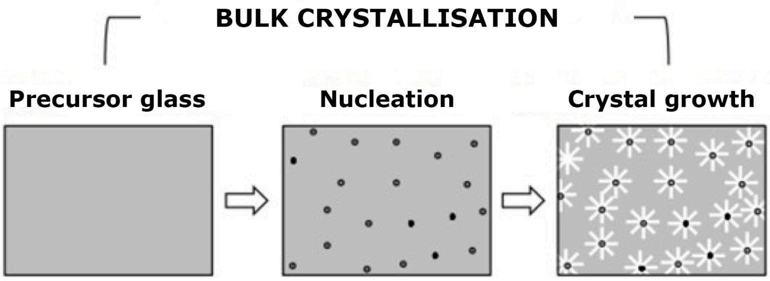


Figure 4. *Scheme of bulk crystallisation.*

It is may be noted that, in this case, from a kinetic viewpoint, two thermal treatment stages are required because the maximum rates of nucleation and of crystal growth take place at different temperatures, so that they do not overlap, as may be observed in Figure 5. The nucleation rate depends not only on the likelihood of stable nuclei formation, but also on the diffusion of the different components needed for nuclei development. Similarly, the crystalline growth rate is also affected by chemical component transport to the developing crystal, which is directly related to melt viscosity.

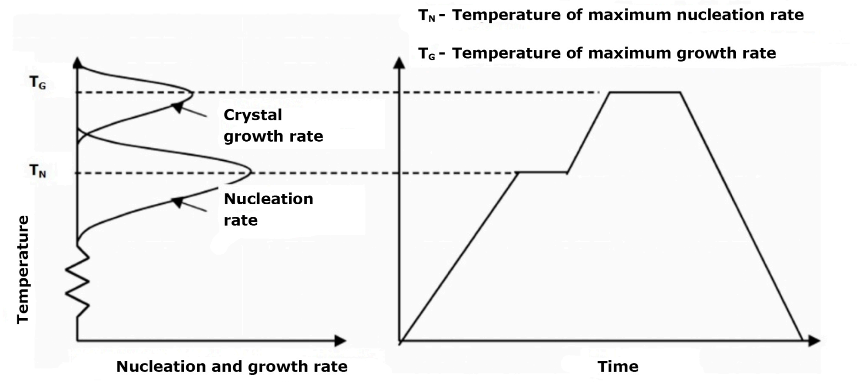


Figure 5. *Variation of the nucleation and crystal growth rates in glasses as a function of the degree of undercooling, corresponding to the conventional 2-stage method.*

The mechanisms that produce nucleation in a glass can be of a homogeneous type, if nucleation takes place from the components in the melt, or of a heterogeneous type, if nucleation develops from particles of a different chemical composition or at the interfaces determined by the surfaces bounding the molten glass mass.

An example of an industry that uses this method is the kitchen top manufacturing industry.

3.2. MODIFIED CONVENTIONAL METHOD (1 STAGE)

This method entails a modification of the above conventional method and is designed for cases of glass precursors in which the two stages of nucleation and crystal growth take place in similar temperature ranges, as may be observed in Figure 6. The figure shows that both curves exhibit a wide overlapping area, so that a single heat-treatment stage is sufficient to cause the glass precursor to crystallise or devitrify [26].

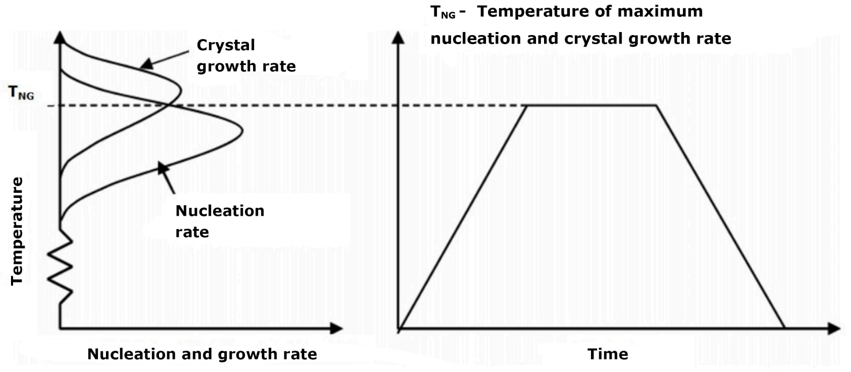


Figure 6. *Variation of the nucleation and crystal growth rates in glasses as a function of the degree of undercooling, corresponding to the conventional 1-stage method.*

Thus, on having a single heat-treatment stage, the modified conventional method becomes a more feasible route, energy-wise, than the two-stage method, though its use also largely depends on the composition of the starting glass precursor and on the end product to be synthesised.

3.3. PETRURGICAL METHOD

This method consists of obtaining glass-ceramic materials by thermal cycles similar to natural processes of mineral genesis, i.e. from the nucleation and crystal growth of a melt from its melting temperature to cooling to ambient temperature. Thus, glass is obtained by hot forming, as in the conventional methods. Figure 7 shows a representative scheme of the petrurgical method.

The process requires strict control of the starting chemical composition, which must favour the obtainment of melts in which phases can crystallise that allow isomorphic substitutions, as melt devitrification will depend on the capability of the constituents to organize themselves and to form stable crystal structures.

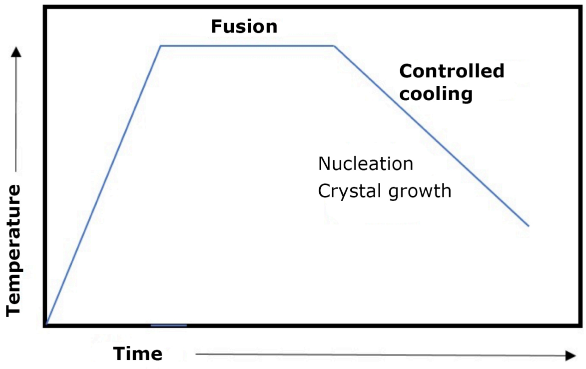


Figure 6. *Typical thermal cycle of the petrurgical process.*

As might be expected, this method can be more economical than the conventional methods described above, as no subsequent thermal treatment is required. In this case, however, control of nucleation and crystallite size is quite complex, so that end products are not obtained with as much added value as in the conventional methods. However, the method's environmental advantage invites further research and development.

3.4. SINTER–CRYSTALLISATION METHOD OF GLASS POWDER

This method also starts by fusing the raw materials but, in this case, the glass is quenched in air or cold water without glass forming, yielding irregularly shaped glass at ambient temperature, as shown in Figure 8. These granules are then milled to obtain a glass powder ready for cold forming by different techniques such as pressing using a uniaxial press, casting, or extrusion. From this point on, the process follows the traditional ceramic route.

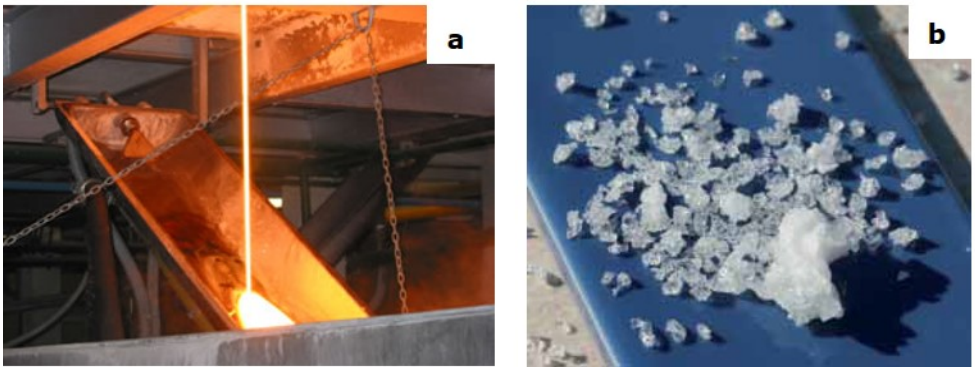


Figure 7. *a) Melt quenching process. b) Sample of glass granulate obtained by quenching.*

After cold forming, the pieces are dried and then subjected to a firing cycle, in which powder sintering takes place, reducing internal porosity, while nucleation and crystallite growth start simultaneously. It is important to take into account the rate of viscous flow sintering and the crystallisation rate, and the interaction between both processes. When both processes occur such that densification and crystallisation occur concurrently in the same temperature range, it is possible to obtain high-density glass-ceramics. Thus, the optimisation of the composition and the sintering temperature allow different microstructures and, consequently, products with different properties to be designed. However, this process is limited by the size and form of the components. In this case, surface crystallisation occurs on the glass powder particles.

4. VITRIFICATION AS AN ALTERNATIVE FOR FABRICATING TILES FROM HIGH PERCENTAGES OF INORGANIC WASTES

The vitrification process is able to significantly increase the chemical homogeneity of very heterogeneous mixtures that may even contain toxic and hazardous heavy metals, achieving sufficient compositional stability in the system and thus modulating end-product properties.

It was in the former Soviet Union in the 1930s that glass-ceramic tiles were first made from blast furnace waste by the petrurgical method.

Since then, numerous glass-ceramic materials have been marketed, such as “Slagsitall” (wollastonite and anorthite crystallisations), “Slagceram”, and “Slagkyston”, and even preindustrial products such as “Silceram”, based on pyroxene, their main applications being directed to the field of abrasion resistant materials (industrial hall roofs, façades, abrasion resistant coverings, high-temperature insulations). Thus, the low cost and the availability of revalorised raw materials make these types of materials very appealing from an economic viewpoint [27].

At present, the immobilisation, recovery and valorisation of wastes from the incineration of urban and industrial wastes are fundamental challenges for fostering environmental sustainability and, in addition, they are relatively economic.

The interest in these products lies in their relatively low manufacturing cost, compared with that of advanced ceramics. Glass-ceramic materials can be formed using a great variety of economical processes, and though energy consumption cannot be avoided owing to the need for high-temperature sintering, savings can be achieved by simplifying the thermal treatment process and using industrial wastes as raw materials.

The Solid State Chemistry Research Group in the Inorganic and Organic Chemistry Department at Universitat Jaume I, directed by Professor Juan B. Carda, pursues the development of ceramic tiles from wastes from the recycled glass sector and from the thermal power station in Andorra (Teruel). Using the sinter–crystallisation method, highly densified glass-ceramic tiles have been obtained with very promising mechanical properties, which could usefully be incorporated into indoor as well as outdoor environments, including environments exposed to heavy traffic of people and machinery. On the other hand, the possibility is also being studied of optimally controlling crystal growth during cooling in order to be able to use the petrurgical method, which is much less expensive in terms of energy consumption.

5. SUMMARY OF THE EXPERIMENTAL RESULTS OF THE REVALORISATION OF A FRIT WASTE FOR THE SYNTHESIS OF GLASS-CERAMIC MATERIAL

A frit waste from a glaze producer, exhibiting the chemical analysis indicated in Table 1, determined by XRF, was revalorised by means of the sinter–crystallisation method of the glass powder.

% by weight	Na_2O	MgO	Al_2O_3	SiO_2	K_2O	CaO	TiO_2	Fe_2O_3	ZrO_2	BaO	BaO	PbO	ZnO	L.O.I.
FRIT WASTE	10.40	0.00	3.96	57.70	1.84	20.30	0.00	0.00	0.10	0.54	0.54	0.27	1.09	3.14

Table 1. *XRF chemical analysis of the frit waste expressed as oxides in % by weight*

After powder pressing, drying, and final thermal treatment at different temperatures for different times, test pieces were obtained that exhibited two crystalline phases, namely wollastonite and calcium sodium silicate, as shown in Figure 9:

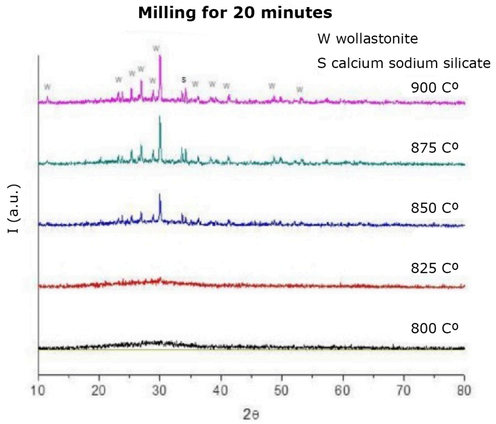


Figure 8. *Diffractograms of test pieces prepared from powder milled for 20 minutes in a planetary grinding mill.*

Table 2 shows the progression in crystal formation from 800ºC to the maximum sintering temperature of 900ºC with a residence time of 2 minutes. It may be observed that crystal growth of the arising phases developed on raising the temperature, as shown in the scanning electron microscope (SEM) micrographs. The EDX chemical analyses indicate a rise in the CaO percentage as temperature rose, tending to approach the theoretical formula of wollastonite (48.3% CaO and 51.7% SiO_2), though the microanalyses are a mixture of the two crystalline phases detected by XRD.

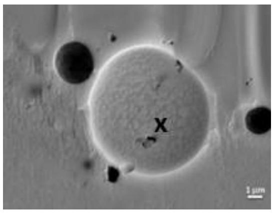
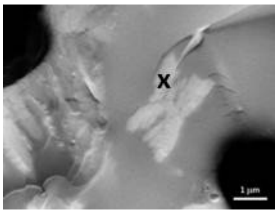
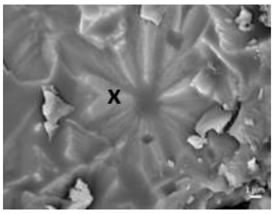
a	**b**	**c**
 x **800ºC**	 x **850ºC**	 x **900ºC**
Na_2O 11.72 Al_2O_3 2.68 SiO_2 63.06 K_2O 1.46 CaO 20.40	Na_2O 5.9 Al_2O_3 2.62 SiO_2 60.26 K_2O 1.13 CaO 30.09	Na_2O 4.39 Al_2O_3 1.61 SiO_2 60.99 K_2O 0.74 CaO 32.27

Table 2. *SEM micrographs and microanalysis of the test pieces synthesised at different temperatures: a) synthesised at 800ºC, b) synthesised at 850ºC and c) synthesised at 900ºC. Microanalyses expressed in % by weight.*

6. CONCLUSIONS

The vitrification process is a feasible alternative for revalorising industrial wastes because, in addition to favouring their homogenisation, it allows tiles of a glass-ceramic nature to be manufactured, using the different fabrication methods available: conventional methods with 1 or 2 stages, the sinter–crystallisation method, and the petrurgical method. The Solid State Chemistry Research Group in the Inorganic and Organic Chemistry Department at Universitat Jaume I is pursuing the fabrication of glass-ceramic tiles from industrial wastes (recycled glass and wastes from thermal power stations) by means of the sinter–crystallisation method and the petrurgical method, as these are the most respectful of the environment. This paper presents a summary of the experimental results obtained on using a frit waste to obtain crystalline phases by the sinter–crystallisation method.

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