


Sustainable porcelain ceramics production using local raw materials and recycled automotive glass

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The main objective of this research is the explanation of the replacement of feldspar limestone imported from Spain with recycled automotive glass, in order to reduce waste and promote environmental sustainability. Details and efforts of making porcelain ceramics from local raw materials such as quartz, kaolin and glass are also given. Replacing the feldspar with reclaimed automotive glass shows the effect of the Na₂O and CaO solvents contained in the glass on the sintering and crystallization of the studied porcelain. The results showed that the added glass contributes to the reduction of the density and the acceleration of the sintering process, by occupying the sites of the open spaces, observed in the samples not containing feldspars. By reaching a nonporous ratio at a temperature of 1000°C, the melting of the material is accelerated due to the dissolved oxides it contains, in addition to the linear shrinkage rate in samples that contain a lot of glass reaching the normal level of porcelain (about 12%) at low temperature compared to ordinary porcelain.

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1. Introduction

As soon as mankind became aware of ceramics, he began to study and develop it. Since ancient times, clay and clay materials were used only for the production of ceramics for household use. The use of these materials traditionally lasted until the discovery that they possess important mechanical and thermal properties that metallic materials do not possess.¹ Porcelain is considered one of the non-existent manufactured materials in nature. It is a material qualified as a solid, inorganic, non-metallic, multiphase composite (presence of crystalline and sometimes amorphous phases) that is intentionally obtained by thermal transformation of silicate materials.² The characteristics of sandstone in terms of hardness and durability exceed the characteristics of color whiteness and partial transparency, which is a mixture of kaolin, feldspar and silica. It is heat treated at a temperature below 1300°C.^{3,4} Its mechanical and thermal properties have been the subject of research for many physicists. The use of “porcelain stone” according to Yanyia⁵ is instrumental in the development of Chinese porcelain because sericite easily reacts at high temperatures with feldspars and kaolin.⁶ This promotes the formation of a uniform glassy matrix with improved translucency. In the west, the term “porcelain” designates a particular ceramic material which is a white, fine, closed, vitrified, homogeneous and translucent body fired between 1250°C and 1460°C. The fine, tight and compact paste is due to the use of kaolin clay. This siliceous clay, friable and not very plastic, is mainly composed of kaolinite ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$) and an aluminum silicate which comes from the decomposition of feldspathic rocks. It has the particularity of having few fluxes (K, Na, Mg), which means that it is a refractory clay. The shaped pieces thus undergo little shrinkage during firing and have good fire resistance. The absence or low amount of iron oxides also gives it a characteristic white color after firing.⁷ A new recipe involves the use of a different “china stone” to which kaolin is added.^{8,9} X-ray diffraction analyses have established that this new “china stone” is composed of a mixture of quartz, secondary micas and sodium feldspars (albite). Mainly due to its higher alkali content, bodies made from albite-rich “china stone” are less refractory, which could improve the fusibility of the body and thus facilitate firing. The mixing of the “china stone” and the “porcelain stone” is a very important step in the process. The mixing of “china stone” and kaolin increases the concentration of Al_3O_4 in the porcelain body (over 19%). This gives the porcelain body a greater plasticity which allows for easier shaping and molding of the ware.¹⁰ This mixture also provides a better firing behavior and therefore allows a higher firing temperature than with porcelain stone alone. The chosen weight percentages in the batch compositions were based on several factors. First, the ternary phase diagram of kaolin–quartz–feldspar at a temperature of 1300°C

provided guidance on the composition range suitable for preparing hard past porcelain. This diagram, as referenced in Refs. 11 and 12, indicated that the composition range for the raw body should fall within specific proportions. The recommended weight percentages, which include 30–60% kaolin, 10–40% quartz and 25–35% feldspar. The study mentioned in Ref. 13 aimed to investigate the physical and mechanical properties of the ceramic material by examining batch compositions. To align with the desired composition range and explore different compositions, the authors selected a specific combination of 45% kaolinite clay, 30% feldspar and 25% quartz. Our research is an attempt to prepare a new porcelain recipe by replacing feldspar with recovered automotive glass and the effect of Na_2O and CaO on the sintering and crystallization of this new porcelain. In order to improve the physical and mechanical properties, the presence of Na_2O and CaO accelerates the chemical reaction, which accelerates the sintering and crystallization process. This results in a better density, which largely depends on the sintering temperature, so the denser the material, the better its properties, and its porosity is very low, which is directly related to the density.

2. Methods Used in Preparation

All the constituent materials of the porcelain are ground with a grinder planetary for 5 h at a rotational speed of 250 tr/min. The latter works with pellets made of zirconia, whose diameter does not exceed 15 mm. The crushing process took place in the presence of water, where we obtained a colloidal solution. After completing the crushing process, we dried the results in an oven at a temperature of 150°C for 24 h. Then we crushed the product manually and then sifted it with a sieve with a diameter of $150\ \mu\text{m}$ to obtain a powder with homogeneous granules. We pressed the prepared samples into a mold of treated steel using a manual hydrostatic press device. The value of the mass that can be applied reaches 15 tons. As for the dimensions of the samples for the different types of powders studied, they are of constant diameter ($d = 13\ \text{mm}$) and similar weights. After compressing the samples, we processed them at different temperatures: 1000, 1050, 1100, 1150, 1200 and 1300°C , constant heating speed $10^\circ\text{C}/\text{min}$, and different sintering times: 15, 30, 60 and 120 min. For heat treatments; an ST-1800 MX-III oven with a maximum temperature of 1800°C with an automatic program and PANalytical (ISM) for X-rays diffraction and ZETIUM-type X-ray fluorescence (XRF) was used as an analytical technique to determine the chemical composition of the samples. We used Redfield model in order to obtain additional details of calculations. In this study, we

Table 1. The gravimetric composition of the different samples of glass.

Sample	Kaolin (%)	Quartz (%)	Feldspars (%)	Glass (%)
V00	50	20	30	00
V10	50	20	20	10
V20	50	20	10	20
V30	50	20	00	30

used four powders as raw materials, namely kaolin, quartz, feldspar and glass. Kaolin was obtained from Jebel Debbagh, on the outskirts of the city of Guelma, Algeria. It is characterized by its almost white color and a density estimated at about 2.53 g/cm^3 . As for the quartz, it was obtained from Tamanrasset in Algeria, and is a white stone. The feldspars are imported from Spain and are used in the manufacture of ceramics in addition to recovered automotive glass (Table 1).

3. Results and Interpretation

We report in Table 2 all results of chemical individuals and oxides present in Kaolan Jabal Dabbagh DD2 analyzed in addition to quartz, feldspars and recovered glass.

3.1. Shrinkage of the samples

In this research, we measure the shrinkage percentage of the samples and compare them at the same temperature with a difference in heat treatment time. The curves concerning the shrinkage of samples V00, V10, V20 and V30 at different sintering temperatures 1000°C , 1050°C and 1100°C and sintering times of 15, 30, 60 and 120 minutes are represented in Fig. 1.

The crystalline reorganization, the increase in the areas of contact between grains and the reduction in the dimensions of the pores then their disappearance, leads to a variation in the apparent volume, in the form of shrinkage. As soon as the temperature is sufficiently high, an internal reorganization of the disorder of each grain is ensured. The amorphous zones crystallize, this stage is called primary recrystallization.¹⁴

The percentage of samples shrinkage in concentrations (V00 and V10) increases as the temperature increases, which facilitates the shrinking process and attains the maximal value about 13%. As for samples with concentrations V20 and V30, their shrinkage is almost constant at all temperatures. Usually, porcelain shrinks between (12% and 20%) when the heat treatment is completed, but at normal temperatures the samples that contain in their composition glass have reached the level of natural shrinkage where the glass occupies the voids sites.

Table 2. The weight composition of raw materials chemicals.

Oxides	Kaolin DD2 (%)	Quartz (%)	Feldspars (%)	Glass (%)
SiO ₂	45.52	99.9	69	69.86
Al ₂ O ₃	38.75	0.027	17.5	1.08
FeO ₃	0.04	0.005	0.17	0.08
CaO	0.18	0.001	2.32	10
Na ₂ O	0.05	—	0.37	13.11
K ₂ O	0.03	0.002	10.22	0.03
MgO	—	0.001	—	1.55
P ₂ O ₅	—	0.001	—	—
SO ₃	—	—	0.16	0.38
TiO ₂	—	0.0002	—	—
L.O.I	15.44	0.01	0.42	—

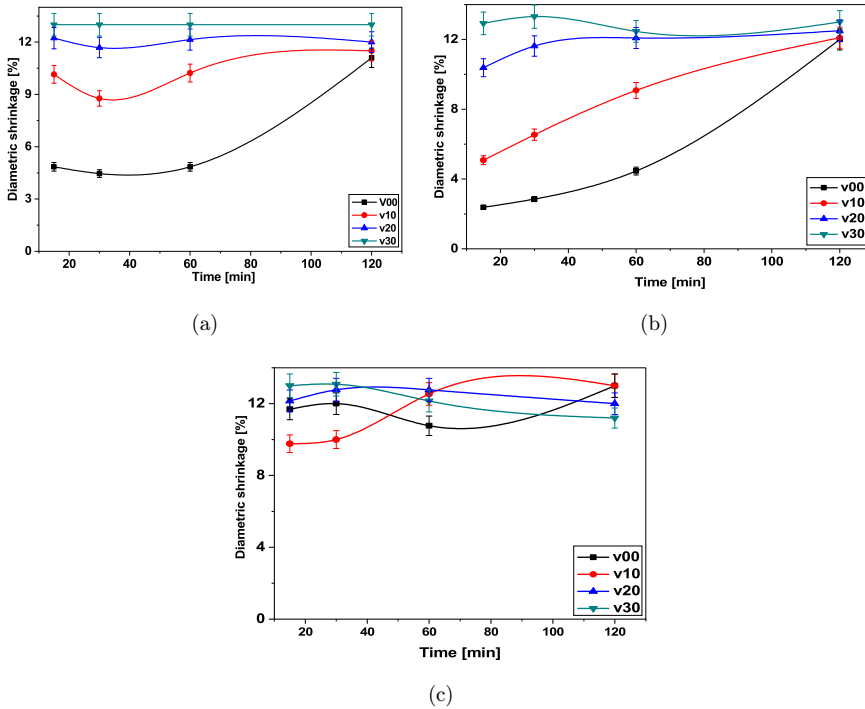


Fig. 1. (Color online) Diametric shrinkage as a function of the time for sample treated at 1000°C (a), 1050 (b) and 1100°C (c).

3.2. Volumetric mass

The volumetric mass of the samples was measured, as the samples V00, V10, V20 and V30 were compared in terms of the heat treatment time of 15, 30, 60 and 120 minutes at different temperatures of 1000, 1050 and 1100°C, as shown in Fig. 2. Practically, it shown that, at time less than 60 min, the volumetric mass is almost constant in V00 and V10 of the order of (2.6 g/cm³), but it is less in proportions when that contain a large amount of glass V20 and V30 about 2.5g/cm³ due to the formation of significant quantities of anortitein in the samples. This is related to the presence of CaO considered in the added glass with a relatively small volumetric mass compared to that of the other phases for the samples that contain glass in a large way (V20 and V30). The volumetric mass decreases due to their melting at temperatures slightly greater than 1100°C and attains the minimal value of the order of 2.1g/cm³, where the liquid phase will increase the samples' volume. The volumetric mass of V00 and V10 is almost constant because they were treated with relatively small temperatures compared to their melting temperatures (experimentally, we have seen that it melts at temperatures greater than 1300°C). Usually, the feldspars' presence indicates the gases formation that evaporate during calcification, leaving behind closed voids, which play a major role in reducing the volumetric mass.

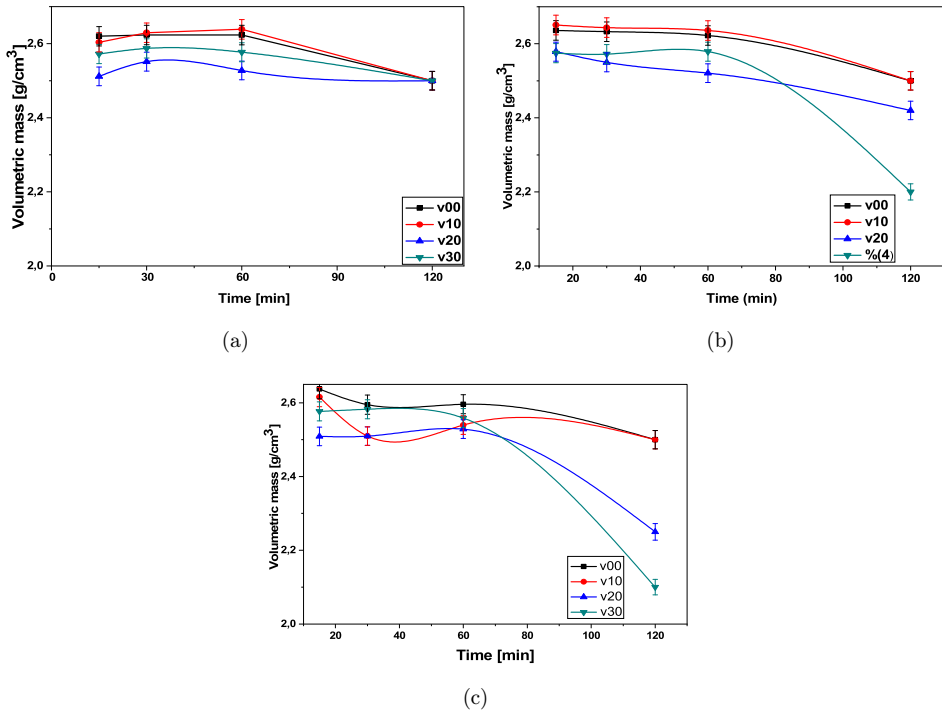


Fig. 2. (Color online) Volumetric mass as a function of time for sample treated at 1000°C (a), 1050°C (b) and 1100°C (c).

3.3. Porosity

The percentage of porosity was measured for samples treated at different temperatures (1000, 1050 and 1100°C) and at different times (15, 30 and 60 minutes). Figure 3 shows that the porosity gradually decreases and disappears as the percentage of glass added increases. The decrease in the proportion of open voids with the increase in temperature is due to the condensation of the material due to the contact area between the grains which increases. This enlargement is accompanied by a rapprochement of their centers. This is the start of shrinkage and the disappearance of the open porosity. The contact between the grains continued to grow, the star-shaped pores becoming spherical. Small pores disappear as a result of the escape of occluded (closed) gas bubbles. The large pores absorb the small ones and sometimes disappear by migration to the surface following the grain boundaries.¹⁴

For V20 and V30 samples, the glass forms in the liquid phase which leads to the closing of the open voids, accelerating the sintering process by decreasing the temperature by the effect of Na₂O. Figure 4 displays the XRD data of the different compositions of V00, V10, V20 and V30 sintered at 1100°C contained two phases anorthite and quartz. The increase in the amount of added glass resulted in a higher degree of crystallization of the anorthite phase is due to the high concentration of

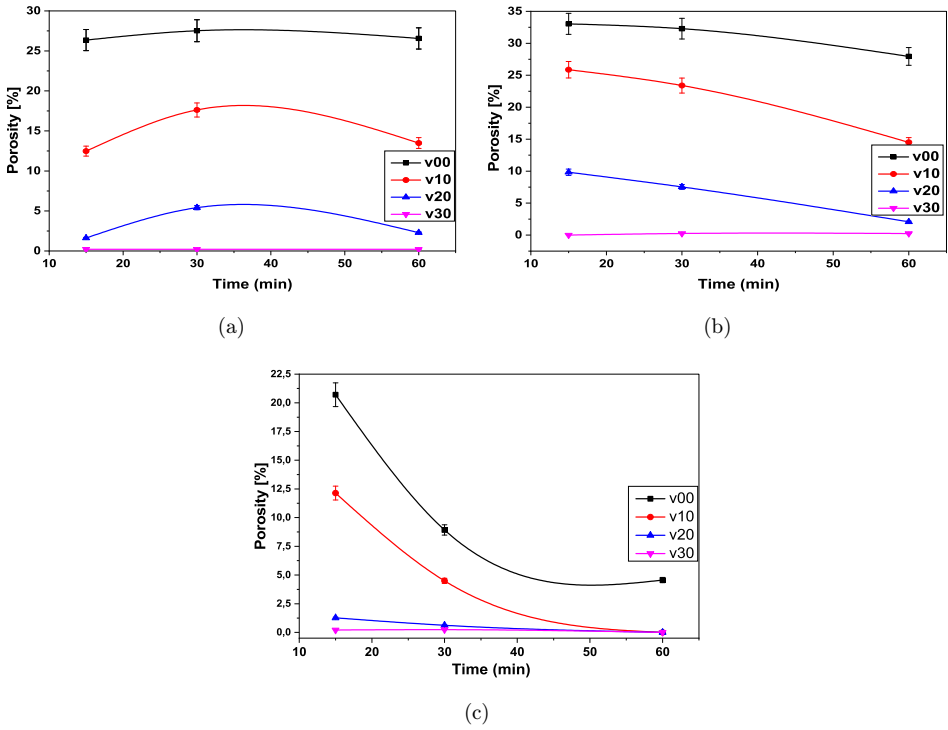


Fig. 3. (Color online) Porosity as a function of time for samples treated at 1000°C (a), 1050°C (b) and 1100°C (c).

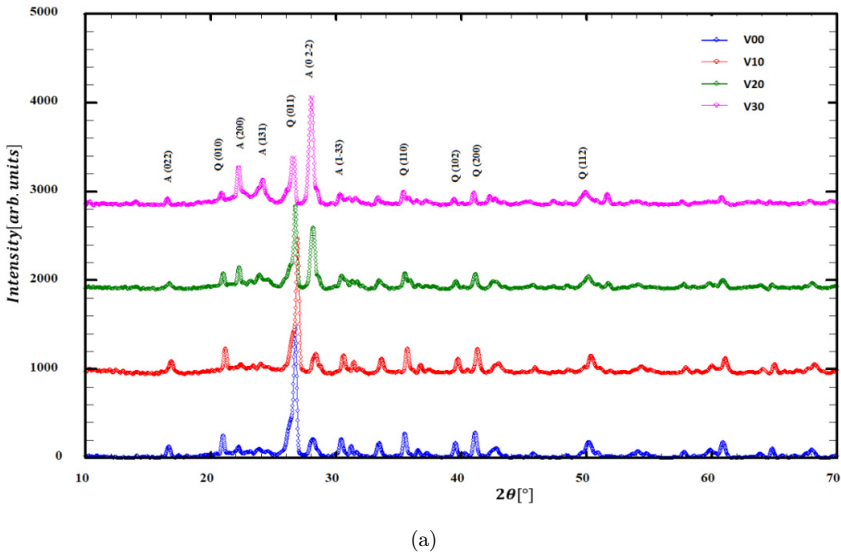
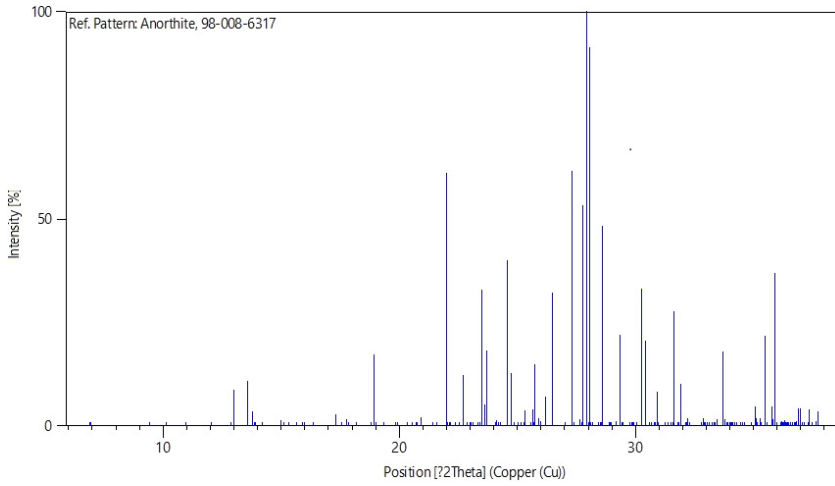
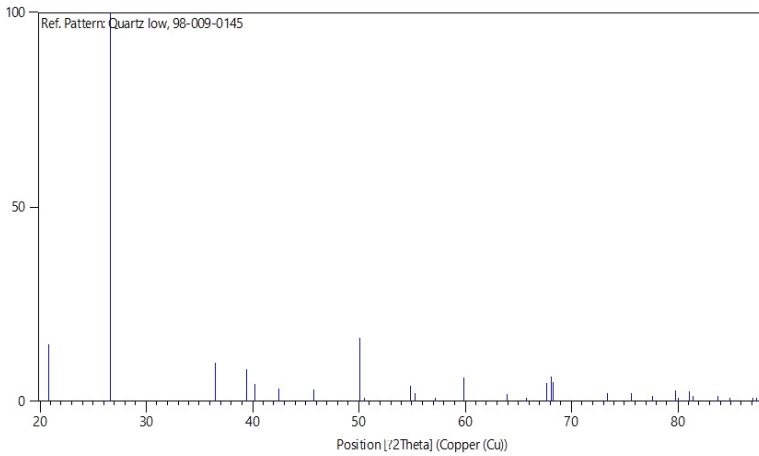


Fig. 4. (Color online) XRD pattern of V00, V10, V20 and V30 sintered at 1100°C (a), card numbers of anorthite 98-008-6317 (b) and Quartz 98-009-0145 (c).

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(b)



(c)

Fig. 4. (Continued)

CaO in the glass. This is attributed to the high proportion of CaO in the added glass, from which anorthite forms with one mole of CaO in addition to two moles of silica and one mole of alumina which are abundantly present in the feldspar compound.^{15,16} From the XRD curves, we deduce the improved results after Rietveld refinement, as presented in Table 3.

Based on the XRD results, the crystallite size was calculated using the following equation:¹⁶

$$D_p = K\lambda / B \cos \theta, \tag{1}$$

Table 3. Rietveld refinement results of V00, V10, V20 and V30 sintered at 1100°C.

Phase	Reference				V00				V10				V20				V30				
	Anorthite	Quartz	98-009-0145 ¹⁰	SiO ₂ Hexagonal	Anorthite	Quartz	Rietveld results	SiO ₂ Hexagonal	Anorthite	Quartz	Rietveld results	SiO ₂ Hexagonal	Anorthite	Quartz	Rietveld results	SiO ₂ Hexagonal	Anorthite	Quartz	Rietveld results	SiO ₂ Hexagonal	
Reference code	98-008-6317 ¹⁸	98-009-0145 ¹⁰																			
Chemical formula	CaAl ₂ Si ₂ O ₈	SiO ₂																			
Crystal system	Triclinic	Hexagonal																			
Space group	P -1	P 31 2 1																			
a ± 0.001(Å)	8.1750	4.916																			
b ± 0.001 (Å)	12.8730	4.916																			
c ± 0.001 (Å)	12.9019	5.409																			
Alpha (°)	85.771	90																			
Beta (°)	81.137	90																			
Gamma (°)	88.72	120																			
Volume of cell (Å ³)	1337.81	113.21																			

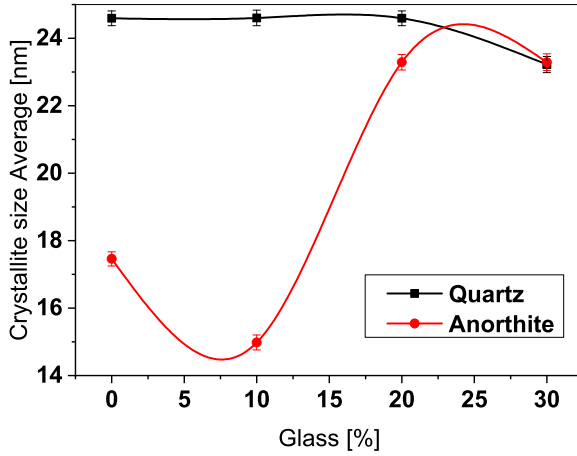


Fig. 5. (Color online) Crystallite sizes of anorthite and quartz as a function of glass percent for samples treated at 1100°C.

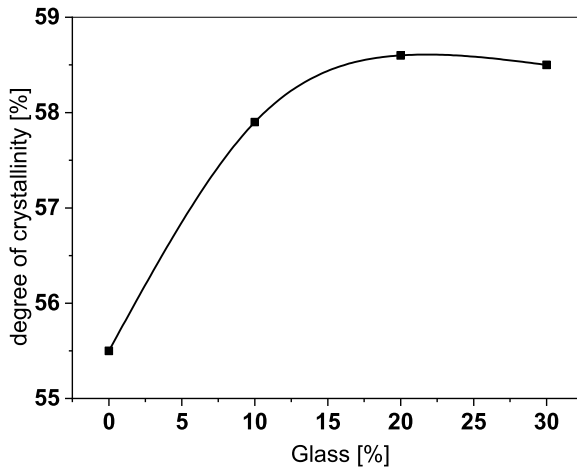


Fig. 6. Degree of crystallinity as a function of glass percent for samples treated at 1100°C.

where D_p is average crystallite size (nm), K is Scherrer constant. K is 0.94 for spherical crystallites with cubic symmetry, λ is X-ray wavelength, Cu $K\alpha$ average = 1.54178 Å, B is FWHM of XRD peak and θ is peak position, one-half of 2θ .

From Fig. 5, we determine the crystallite size for each phase and we find that the size for the quartz phase was around 24 nm. The results of Khamis *et al.*¹⁷ confirm this value. On the other hand, the crystallite size for the anorthite phase gradually increased from 18 nm up to 20% glass substitution, where it stabilized at 23 nm. On the other hand, we notice that the degree of crystallinity increases to reach 58.5% with an increase in the percentage of glass to 20% (Fig. 6).

4. Conclusion

The results showed that the added glass contributes to reducing the volumetric mass, and also accelerates the sintering process, by occupying the sites of open spaces. As we saw in samples that do not contain feldspars, reaching a nonporous ratio at a temperature of 1000°C, the glass accelerated the melting of the material due to the dissolved oxides which it contains. There is also a variation of anorthite in the samples and this is related to the presence of CaO. The percentage of quartz begins to melt gradually, this is due to its melting and the formation of the glassy phase. Its melting temperature decreases with an increase in the percentage of glass containing large proportions of dissolved oxides such as CaO (10%) and Na₂O (13%). The percentage of the vitreous phase gradually increases, this is mainly due to the dissolved silica of each of the quartz and anorthite. For the amorphous phase, it has been noticed that its percentage is high at temperatures around 1000°C, due to the non-crystallization of the compounds, and it begins to decrease with the crystallization of the phases. In addition, the linear shrinkage rate in samples contain a lot of glass reaching the normal level of porcelain (about 12%) at low temperatures. As the global demand for sustainable products continues to grow, the findings of these studies have the potential to drive significant changes in the ceramic industry towards a more sustainable future.

Competing Interests

The authors declare that they have no competing interests.

Authors' Contributions

M. Fatmi, A. Djelmi, H. Belhouchet and A. Faci designed, coordinated this research and drafted the manuscript. M.A. Ghebouli, K. Bouferrache, B. Ghebouli and T. Chihi carried out experiments and data analysis, Y. Slimani, N. Algethami, Saif A. Mouhammad and Sultan Alomairy conceived of the study, and participated in research coordination. All authors read and approved the final manuscript.

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