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Effect of Different Concentrations of Titanium Oxide (TiO_2) Addition on the Crystallization Behaviour and Some Properties of Alkaline Earth Aluminosilicate Glass-Ceramics

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Abstract: Glass-ceramics in the CaO-MgO-Al_2O_3-SiO_2 quaternary base glass system was produced via melting technique using feldspar, limestone and magnesite as sources of starting materials. Glass-ceramics production involves making a base glass, annealing and cooling to room temperature and then reheating the base glass to nucleation and crystal growth temperatures. Characterization of the produced glass-ceramics was carried out using a scanning electron microscope (SEM). The effects of the crystallization process on some properties such as hardness, chemical durability in acid and alkali media of samples were determined. The results portrayed that glass-ceramic samples to which various amounts of TiO_2 (2,4,6,8 and 10 wt.%) were incorporated showed the formation of crystalline phases dispersed in the matrix of their respective residual glassy phases. Significant improvement in hardness, as well as minimum weight loss, were recorded for all the glass-ceramic samples. On the contrary, the glass samples did not crystallize despite subjecting them to heat treatment, their hardness values were low and they were not resistant to acid (1M HCl) and alkali (1M NaOH) attacks. The inability of TiO_2 addition to fully transform them into glass-ceramics remains a shortcoming. However, the glass-ceramic samples obtained from this study can be used for tiling works.

Keywords: Base glass, Crystallization, Glass-ceramics, Durability, Hardness

I. Introduction

Glass-ceramics are polycrystalline, solid materials prepared by controlled nucleation and crystallization processes [1]. Crystallization is the process by which a regular crystalline array is generated from a glassy structure [2]. The material is prepared by controlled crystallization of glass through different processing techniques such as double-stage and sintercrystalliztion among others. Glass-ceramic material is characterized by at least one type of crystalline phase dispersed in a residual glassy phase [3]. The idea of transforming glass into a crystalline material was initiated by Reamur in the early 17th century but he was not able to achieve the transformation process. However, in the 1950s S.D Stookey made the breakthrough and therefore expanded the theory of phase-separation [4]. The material consists of a small volume fraction of glass surrounding each crystal grain. The crystallization process is generally affected by a nucleating agent via two mechanisms [5]. During the first (nucleation stage), the glass is held for a period of time at a temperature that promotes the formation of microcrystals throughout the bulk of glassy material. During the second (crystal growth) stage, the temperature is increased to allow the growth of nuclei [6]. Alkaline-earth-aluminosilicate base glass systems had been studied extensively for decades, but there is the need to modify their properties. Excellent properties are achieved through base glass composition, nucleating agent and heat treatment schedule. To improve the crystallization processes, the incorporation of a nucleating agent in the glass composition is required because is the powerful driving force for nucleation and crystallization

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processes [2]. According to [7] and [8], titania [TiO_2] is known to be the best nucleating agent in the fabrication of aluminosilicate glass-ceramics via a double-stage heat treatment schedule. Similarly, [3] reported that TiO_2 minimizes the viscosity of molten glass at high temperatures and this promotes efficient crystallization processes.[7], further reported that TiO_2 has a significant effect on the transition temperature (T_g) of the CaO-MgO-Al_2O_3-SiO_2 base glass system as T_g decreases significantly with an increase in TiO_2 incorporation. There are a wide variety of nucleating agents for different glass-ceramic systems and the most common are; TiO_2, ZrO_2, P_2O_5 and Fe_2O_3 among others [9]. According to [5], glass-ceramic without nucleating agent possesses low mechanical properties. Liquid phase separation occurs first in glass-ceramics when TiO_2 is added as a nucleating agent, then crystalline phases would form with high density. TiO_2 is very effective as a nucleating agent because of its high ionic field strength that enhances phase separation as well as improves heterogeneous nucleation rate [8]. The incorporation of TiO_2 as a nucleating agent to the base glass decreases transition temperature, increases the homogeneity of the melt, promotes high-density nucleation and the formation of uniform crystals size [3,8,10]. The amount of TiO_2 in a wide range of glass-ceramics ranged from 2-20 wt%. However, when added to the composition in large amounts, TiO_2 becomes a major part of the glass composition [8]. The basis of controlled crystallization lies in efficient nucleation which results in the formation of fine-grained and uniform microstructure without voids or other porosity [10]. Glass-ceramic materials are superior to corresponding base glasses, conventional ceramics, metals and even organic polymers because they can be cast and pressed without dimensional changes or dislocation. Furthermore, they can be produced en-mass by using glass forming techniques such as casting, moulding, pressing and drawing among others to make complex shapes free from internal inhomogeneity [10]. Nevertheless, fewer research data about CaO-MgO-Al_2O_3-SiO_2 glass-ceramics with titania (TiO_2) as a nucleating agent were carried out and readily available locally [3, 6, 9, & 11] and this justifies the research work. Therefore, the aim of this study is to determine the role of different concentrations of TiO_2 in the crystallization of calcium-magnesium-aluminosilicate base glass system and also determine some chemical and mechanical properties of the samples produced.

II. Materials and Methods

The starting materials for this study are feldspar, limestone and magnesite. Each sample is sourced locally. Table 1-3 showed the chemical compositions of the starting materials as determined by XRF and Table 4 portrays the chemical composition of glass batches under investigation.

Table 1: Chemical Composition of the Matari Feldspar by XRF

Feldspar	K_2O	Na_2O	CaO	SiO_2	Fe_2O_3	Al_2O_3	Cr_2O_3
Wt.%	11.33	2.75	0.12	67.32	0.10	17.54	0.01

Feldspar	P_2O_5	ZrO_2	MgO	V_2O_5	NiO_2	Cu_2O	MnO_2	LOI
Wt.%	0.35	0.01	>0.01	<0.01	<0.01	0.02	0.02	0.14

Source: [3]

Table 2: Chemical Composition of Kalambaina Limestone by XRF

Limestone	CaO	MgO	Fe_2O_3	Al_2O_3	MnO_2	TiO_2	P_2O_5
Wt.%	53.08	0.73	0.55	0.75	0.03	0.04	0.11

Limestone	V_2O_5	ZrO_2	NiO_2	Cu_2O	SiO_2	Na_2O	Cr_2O_3	LOI
Wt.%	<0.01	0.01	<0.01	<0.01	3.38	<0.01	<0.01	42.00

Source: [3]

Table 3: Chemical Composition of Tsakesimptah Magnesite by XRF

Magnesite	CaO	MgO	Fe_2O_3	Al_2O_3	MnO_2		TiO_2	P_2O_5
Wt.%	9.77	63.3	2.86	4.86	0.08		0.4	0.05
Magnesite	SrO	ZrO_2	NiO_2	SO_3	Rb_2O	Na_2O	K_2O	SiO_2
Wt.%	0.05	0.013	0.015	0.08	0.083	0.09	0.74	17.7

Source: [3]

Table 4: Chemical Composition of Glass Batches in Oxide Form (wt %)

Glass No.	SiO_2	Al_2O_3	CaO	MgO	K_2O	TiO_2	NaCl	Fe_2O_3	Trace(oxides)
Glass 1	52.00	16.00	18.00	8.00	2.00	0.00	0.30	2.50	1.2
Glass 2	52.00	16.00	16.00	8.00	2.00	2.00	0.30	2.50	1.2
Glass 3	52.00	16.00	14.00	8.00	2.00	4.00	0.30	2.50	1.2
Glass 4	52.00	16.00	12.00	8.00	2.00	6.00	0.30	2.50	1.2
Glass 5	52.00	16.00	10.00	8.00	2.00	8.00	0.30	2.50	1.2
Glass 6	52.00	16.00	8.00	8.00	2.00	10.00	0.30	2.50	1.2

A. Preparation of Primary Glass Samples

Local feldspar, limestone, magnesite, chemical grades TiO_2 and NaCl were used as starting materials for this study. Feldspar sample was collected randomly at Matari feldspar deposit in Soba LGA of Kaduna State, limestone was sourced from Kalambaina limestone deposit in Wamakko LGA of Sokoto State, and the magnesite was obtained from Tsakesimptah magnesite deposit in Gombi LGA of Adamawa State. TiO_2 was incorporated as a nucleating agent in the order of 0, 2,4,6,8 and 10 wt% per 200 g of glass batch. The instrumental analyses of the starting materials for this study are portrayed in Tables 1, 2, and 3. Also, the chemical compositions of the prepared glass batches are shown in Table 4. Each batch was weighed and thoroughly mixed by a Ball mill at Multipurpose laboratory ABU to ensure homogeneity, and then melted in a crucible using an electric muffle furnace BST/MF/1800 at a temperature ranging from 1450-1600ºC for 3 hours. The glass melt was stirred at a regular interval of 20 minutes to achieve homogeneity. Each molten glass was poured into a casting mould as a rod and then transferred into a muffle furnace for annealing at 600ºC to minimize residual stress. Thereafter, the glass rods were allowed to cool gradually to room temperature at a heating rate of 3 ℃ per minute.

B. Heat Treatment of Glass Samples

Six (6) glass samples were subjected to controlled heat treatment via a two-stage process. 450-900ºC were used as nucleation and crystal growth temperatures respectively. Each sample was held for 1,2,3, & 4 hours during the soaking time to allow nucleation and crystallization processes. After the heat treatment, the furnace was switched off and samples were cooled to room temperature.

C. Analysis of Samples using Scanning Electron Microscope (SEM)

The microstructures characteristics of the samples heat-treated for 2 hours were carried out using a scanning electron microscope (JEOL JSM-7500F). The surface of each sample under study was polished and etched by immersion using Keller's reagent prior characterization.

D. Hardness Test on Samples

6 samples were subjected to heat treatment using 450-900 ^{o}C as nucleation and crystal growth temperatures respectively. Each sample was soaked for 1-4 hours, thereafter, hardness measurement on each sample was carried out using Micro Hardness Tester Model MV1-PC that has a square based diamond pyramid and stress of 0.3 Kgf was applied to each sample.

E. Effects of Acidic and Alkali Media on Samples

6 samples of known weights were subjected to varying soaking times for 1- 4 hours and then immersed in 1M HCl at 70^{o}C for 24 hours. The samples were washed with distilled water and oven-dried at 110^{o}C for 1 hour. Thereafter, each sample was reweighed to achieve the mass after immersion. Similarly, the same technique was applied to evaluate the chemical durability of 6 samples immersed in 1M NaOH aqueous solution at 70^{o}C for 24 hours.

F. Apparent Density Measurement

The measurement of density was performed using the Archimedes method which is in accordance with the ASTM C 373-88 standard [13]. The Apparent density of each sample was calculated using the below expression:

$$\text{Apparent density} = \frac{D}{W-S} \quad g/cm^3 \qquad (1)$$

where,
D = Weight of sample in the air (g).
W = Weight of sample soaked in distilled water (g).
S = Weight of sample suspended in distilled water (g).

G. Porosity Measurement

Porosity is a measure of the void. It measures the total amount of empty space in material and expresses as a percentage the relationship of the volume of the open pores in the specimen to its exterior volume. P is calculated using the following expression:

$$\text{Porosity (P, \%)} = \frac{Vp}{Vt} \times 100$$

(2)

Where,
VP =volume of void or pore
Vt= Total volume

H. Determination of Water Absorption

The measurement was carried out in accordance
with the ASTM C 373-88 standard test method for water absorption in glass-ceramic materials [12]. Each dry sample was oven-dried at 105℃ until a constant mass was achieved. The sample was cooled to room temperature and its weight was recorded as M_1. The sample was completely immersed in distilled water at 30℃ for 24 hours. The sample was removed from the water and a damp clean cloth was used to remove traces of water and reweighed as M_2. The percentage for water absorption of each sample was calculated using the following equation:

$$\text{Water Absorption (A, \%)} = [(M_2 - M_1)/M_1] \times 100 \quad (3)$$

where;
M_1 = Dried weight of sample
M_2 = Saturated weight of sample
A, % = Water absorption

III. Results and Discussion

The present study was carried out to determine the effect of TiO_2 incorporation on calcium- magnesium aluminosilicate base glass system as well as to evaluate some chemical, mechanical and physical properties of glass and glass-ceramics samples produced. The crystallization processes were achieved conventionally via a two-step heat-treatment regime that composed of nuclei formation and subsequent crystal growth achieved at varying holding times [1-4 hours]

Plate 1 is the SEM image of glassy material that was subjected to heat treatment for 2 hours. The SEM micrograph displays a single glassy phase due to the absence of crystallization because the base glass composition lack nucleation catalyst(TiO_2). Otherwise, the single glassy phase is the control of the study. Similarly, Plates 2-6 represent the SEM micrographs of glass-ceramic samples to which different amounts of TiO_2 were incorporated and heat-treated for 2 hours duration. The SEM images in Plates 2-6 showed efficient crystallization processes achieved as a result of TiO_2 addition as a nucleating agent in the base glass composition. Figure 1, shows results of variation of TiO_2 addition and heat treatment time on the hardness of samples understudy

The results revealed that all glass samples have shown low hardness. However, the results have shown significant improvement in hardness due to the gradual addition of TiO_2 from 2-10 wt% and variation of heat treatment time from 1-4 hours. This trend is expected because the hardness of glass-ceramic samples is increasing as a result of the precipitation of a wide range of crystalline phases dispersed in the matrix of residual glassy phases [3]. The finding is inconsonant with the results of the following researchers [8,13] who indicated that incorporation of 2-10 wt% TiO_2 as nucleating agent is sufficient to induce efficient crystallization which led to achieving excellent hardness.

Figure 2 presents the chemical solubility results of 6 samples subjected to heat treatment at varying heat treatment times (1-4 hours) and TiO_2 incorporation (0, 2,4, 6,8 and 10 wt%) in 1 M HCl acid.

It has been observed that all glass samples suffered leaching and dissolution in 1 M HCl

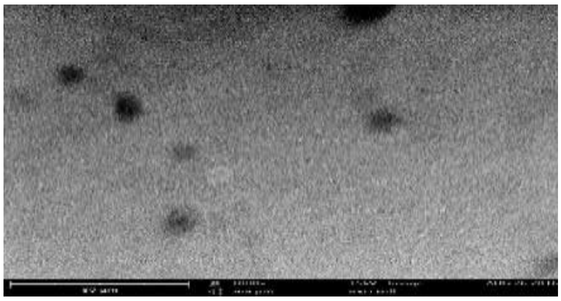

Plate 1: SEM image of 0 wt% TiO_2 heat treated for 2 hours

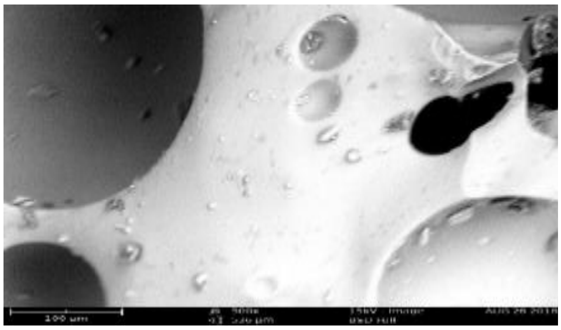

Plate 2: SEM image of 2 wt% TiO_2 heat treated for 2 hours

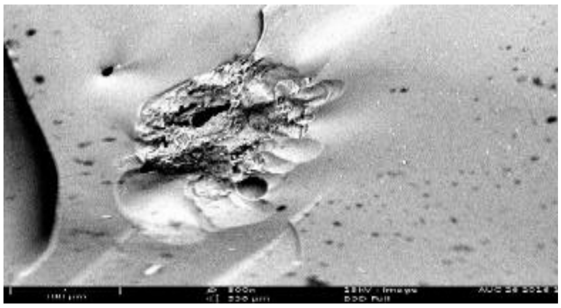

Plate 3: SEM image of 4 wt% TiO_2 heat treated for 2 hours

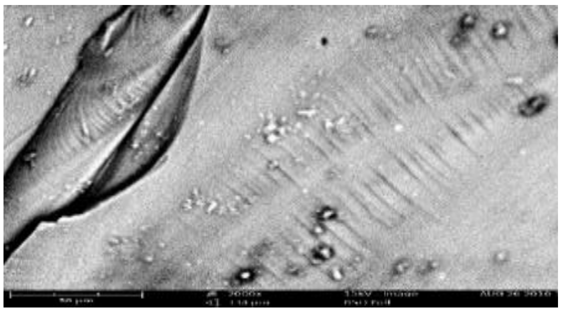

Plate 4: SEM image of 6 wt% TiO_2 heat treated for 2hours

due to degradation of network structure [15]. Acids generally attack fluxing agents (Na_2O, K_2O) in glass dissolving them by substituting

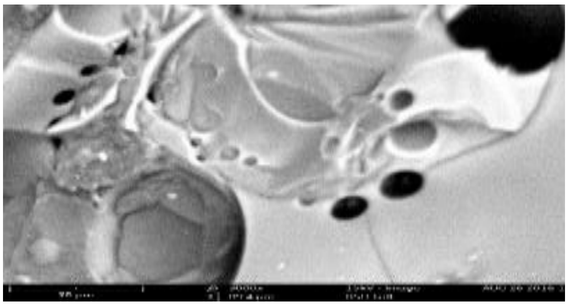

Plate 5: SEM image of 8 wt% TiO_2 heat treated for 2 hours

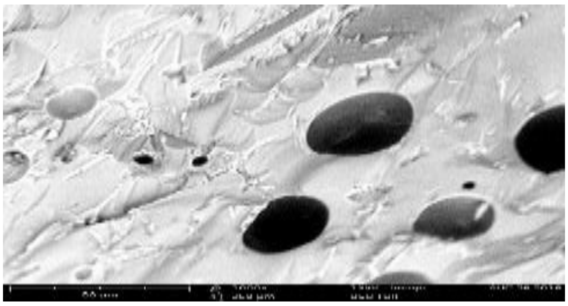

Plate 6: SEM image of 8 wt% TiO_2 heat treated for 2 hours

H^+ ions for the alkali ions thus opening up the silica skeletal structure [14]. However, decreases in weight loss were recorded on glass-ceramic samples to which varying amounts of (1-4 hours). The resistance to acid attack was due to the presence of a large volume of phases assemblage distributed in the matrix of residual glass [6]. Similarly, Figure 3 shows the chemical solubility results of 24 samples subjected to heat treatment at varying heat treatment times (1-4 hours) and TiO_2 incorporation (0, 2,4, 6,8 and 10 wt.%) in 1 M NaOH solution. Glass ceramic samples resists 1M NaOH aqueous solution attack. This result is expected because the presence of Ti^{4+} ions, as well as the formation of large volume of phases assemblage scattered in the residual glass, are driving forces for the hindrance of alkali attack [3]. On the contrary, the glass samples across suffered severe dissolution in 1 M NaOH solution due to degeneration of network forming structure.

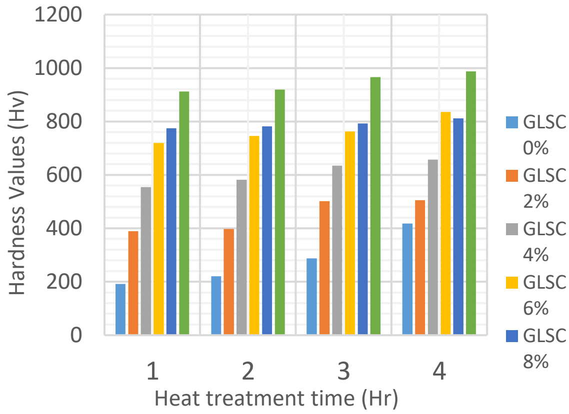

Figure 1: Effect of TiO_2 addition and variation of heat treatment times on hardness

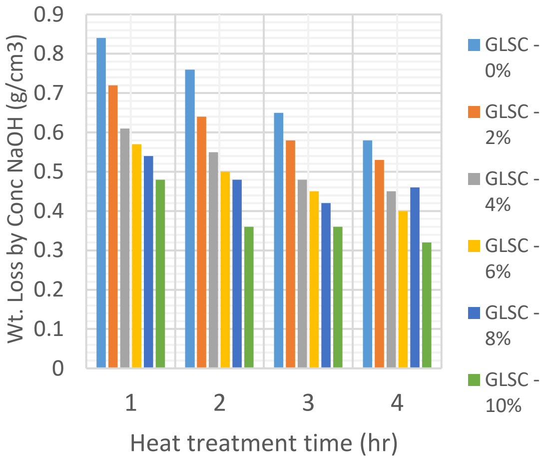

Figure 2: Effect of varying heat treatment time and TiO_2 addition on weight loss using 1M HCl solution for the various samples.

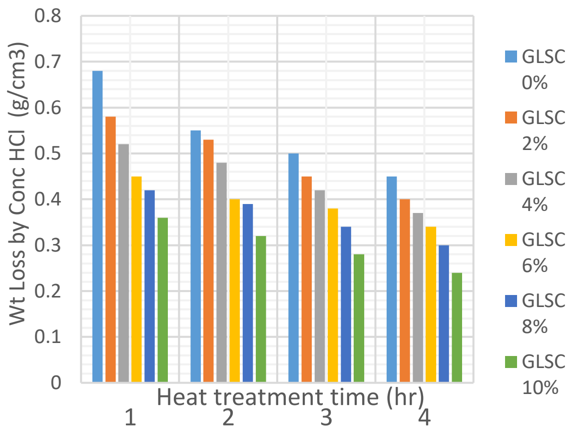

Figure 3: Effect of varying heat treatment time and TiO_2 incorporation on weight loss in 1M NaOH solution for the various samples.

TiO_2 was incorporated (2, 4, 6, 8 and 10 wt %) and heat-treated at various heat treatment time Figure 4 demonstrates apparent density results of 24 samples subjected to heat treatment at different heat treatment times (1-4 hours) and TiO_2 addition (0, 2,4, 6,8 and 10 wt%). All density values have shown a gradual increase as heat treatment time and titania addition are increasing progressively. Minimum density values were recorded on glass samples and this results from the absence of crystalline phases in the glass matrix [14]. However, density values of glass samples increased slightly as heat treatment time increases progressively. The slight increase in density was due to viscous flow formation resulting from prolonged heat treatment which eliminates or lower the concentration of inclusions thereby increasing the density values [3]. Nevertheless, an increase in density was recorded across the glass-ceramic samples as TiO_2 addition and heat treatment time are increasing progressively. This trend is expected because the density of the glass-ceramic sample is always larger than the density of its corresponding glass sample [16].

The difference in density was because of the In a similar manner, Figure 5 presents the porosity values of all the 24 samples under study at different heat treatment times and titania incorporation. The results showed that porosity decreases as heat treatment time and titania addition increased on all the samples. This is expected because glass-ceramics are non-porous materials as grains of crystalline phases were able to block up the pores present thereby decreasing the porosity. However, maximum porosity values were recorded on glass samples that were subjected to heat treatment time from 1-4 hours. Although, a slight decrease in porosity was noticeable. This results from the closure of some micro-sized pores due to prolong heat treatment time brought about by viscous flow formation [3].

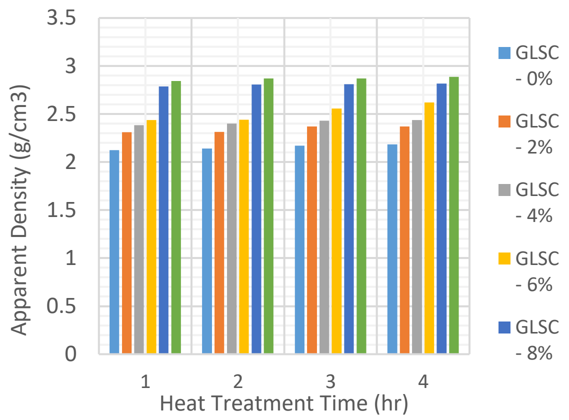

Figure 4: Effect of TiO_2 incorporation and heat treatment times on apparent density of various samples under study

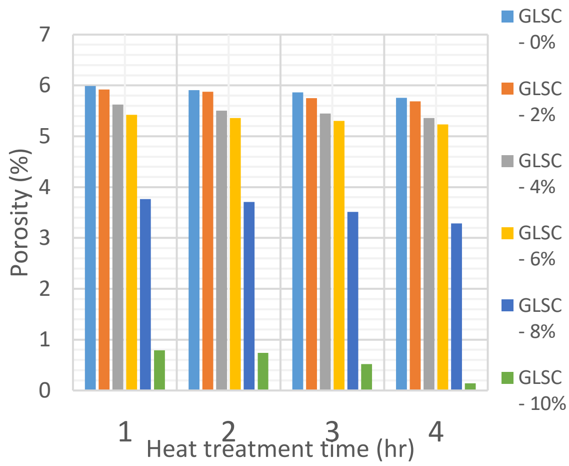

Figure 5: Effect of heat treatment time and TiO_2 incorporation on porosity of various samples.

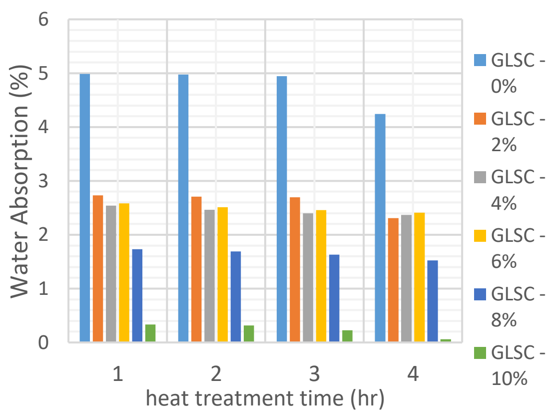

Figure 6: Effect of heat treatment time and TiO_2 addition on water absorption of various samples under study

However, minimum porosity values were recorded on glass-ceramic samples across the group and these results from the presence of a large amount of phases assemblage precipitated in the samples. In conclusion, maximum porosity values were recorded on glass samples. Conversely, minimum porosity values were observed on the corresponding glass-ceramic samples.

Figure 6 displayed water absorption values of 24 samples at a wide range of heat treatment time and TiO_2 addition. All water absorption values had shown a gradual decrease as heat treatment time and titania addition were increasing progressively. Low water absorption values were recorded across the glass-ceramic samples heat-treated from 1- 4 hours. This result is expected because the microstructure of glass-ceramics always consists of fine-grained phases assemblage dispersed in the matrix of residual glass which hindered propagating micro cracks as they cross grain boundaries [3]. However, maximum water absorption values were recorded on glass samples heat-treated from 1-4 hours. This is also expected because of micro-sized pores dispersed in the matrix of the glassy phase.

IV. Conclusion

Results of this study highlighted the effect of incorporating various concentrations of titania and heat treatment times on the crystallization of alkaline earth aluminosilicate base glass system (CaO-MgO-Al_2O_3-SiO_2). The results of the research portrayed that samples that have various amounts of TiO_2 (2,4,6,8 &10 wt.%) incorporated in the batch compositions and subjected to heat treatment at different soaking times showed the formation of crystalline phases dispersed in the matrix of their respective residual glassy phases, whereas, their corresponding glass samples have no crystalline phases due to lack of crystallization. Properties such as hardness, weight loss in acidic and alkali media, density, porosity and water absorption were investigated and the following conclusions are drawn:

1. Scanning electron microscope (SEM) displayed a regular distribution of a wide variety of crystalline phases dispersed in the matrix of residual glass-ceramics samples and the glass samples remain single phase due to lack of crystallization.
2. All glass samples in each set show low hardness, low density, poor resistance to acid and alkali attacks. They are slightly porous and absorb immersion liquid. This might be due to the lack of crystalline phases dispersed in the residual glass matrix.
3. An increase in hardness and density was noticeable on the gradual addition of titania and prolong heat treatment time. Similarly, a decrease in acidic and alkali attacks, as well as porosity and water absorption, were observed for all the glass-ceramic samples.
4. The glass-ceramic samples could be used for tiling and hardware resistance applications due increase in hardness, density, resistance to chemical attacks, low porosity and water absorption.

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