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# The Crystallization and Characterization of Calcium-Magnesium-Aluminosilicate Glass-Ceramics

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Abstract: Calcium-magnesium-aluminosilicate (CaO.MgO.Al<sub>3</sub>O<sub>3</sub>.SiO<sub>2</sub>) glass-ceramics was developed from the base glass system of the composition 52.00 wt% SiO<sub>2</sub>, 16.00 wt% Al<sub>2</sub>O<sub>3</sub>, 12.00 wt% CaO, 8.00 wt% MgO, 2.00 wt% K<sub>2</sub>O, 6.00 wt% TiO<sub>2</sub>, 0.30 wt% NaCl and 3.70 wt% in this study. The study focused attention on the crystallization of CaO.MgO.Al<sub>3</sub>O<sub>3</sub>.SiO<sub>2</sub> base glass system using 363°C & 663°C as nucleation and crystal growth temperatures respectively, and 1 - 4 hours as soaking time. The composition was melted at 1600°C for 3 hours in a muffle furnace and the molten glass was cast into rods, annealed at 600°C for 1 hour and finally cooled to room temperature. Due to the presence of impurities in the starting materials, the glasses produced have a brownish physical appearance. Base glasses were crystallized into glass-ceramics using double-stage heat treatment schedule, and XRD and SEM were used to characterize the produced samples. The XRD identified the crystalline phases precipitated in the residual glass matrix of the sample soaked for 4 hours as albite, quartz, wollastonite and witherite. The SEM result revealed that the microstructure of the sample is characterized by dense, circular-like and needle-like clusters alongside micro-sized voids dispersed in the residual glassy phase matrix. The density and hardness values were found to increase while weight loss decreased with increase in soaking time across the samples. The sample soaked for 4 hours has the lowest weight loss but with the highest density and hardness values making it suitable for use for abrasion due to its excellent properties.

Keywords: Crystallization, Characterization, Some Glass-ceramic Properties

### I. Introduction

Glass-ceramics is defined as an inorganic, nonmetallic material prepared through controlled crystallization of glasses via different processing methods. The material contains at least one type of crystalline phase and a residual glassy phase [6]. Therefore, glassceramic is a solid material, partly crystalline and partly glassy, formed by controlled crystallization of glass. The properties of glassceramic material depend on the kind and percentage of crystalline phase precipitated as well as the composition of the residual glassy phase [2]. According to [13], they are produced by controlling the heat-treatment schedule from glass to achieve new material with superior properties in comparison with the parent glass. The chemical composition and microstructure of the glass-ceramics determine its properties and main applications [10]. Due to the controlled crystallization process, the parent glass is transformed into a new material with improved properties. According to [7], crystallization is the process of precipitating array of crystals from less ordered glassy material. Glass as less ordered material is defined as a non-equilibrium, noncrystalline condensed state of matter that exhibits a glass transition [15]. The crystallization process of the parent glass consists of double-stage heat such nucleation treatment as and crystallization processes. During the nucleation stage, the glass is held for a while at a temperature which promotes the formation of nuclei throughout the glassy material [1]. crystallization the temperature is increased to allow nuclei to

Aliyu, Z.S. (Department of Glass & Silicate Technology, Ahmadu Bello University, Zaria-Nigeria) Corresponding author: <u>zainabsagarba@gmail.com</u> Telephone Number: +234-817-360-3916 grow. Therefore, crystallization of a glassy material is accomplished by subjecting suitable glass to a carefully regulated heat treatment schedule, which results in nuclei formation and subsequent crystal growth within the glass [5].

To enhance both nucleation rate and crystal growth rate, nucleating agents are often incorporated to the glass melt. There are wider varieties of nucleating agents for different glass-ceramic systems, with the most common being metallic oxides such as TiO<sub>2</sub>, ZrO<sub>2</sub>, Cr<sub>2</sub>O<sub>3</sub> and P<sub>2</sub>O<sub>5</sub> among others to enhance the precipitation of crystalline phases CaO.MgO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (CMAS) and other glass-ceramic materials [3]. Basically, glassceramics are superior to their corresponding parent glasses as a result of excellent properties like mechanical, chemical, thermal and biological properties and this allows the formation of reproducible fine-grained and uniform microstructure without micro crack or other porosity [5]. It is possible to design their microstructure for a given application because their properties can be tailored by changes in composition and heat treatment [3]. A glassceramic is usually not fully crystalline with the microstructure being 50-95% crystalline and the remainder being residual glassy [2]. When a primary glass undergoes heat treatment, one or more crystalline phases may form, and both the compositions of the crystalline phases and residual glass are different from the parent glass.

In order to develop a glass-ceramics with desirable properties, it is important to control the crystallization process so that even distribution of crystals can be formed [9]. In glass-ceramic materials, selecting optimum composition and controlled heat treatment schedule allows the precipitation of a wide range of microstructures, and consequently, various specific properties are achieved and this further allowed these materials to be used in diverse technological applications. Glass-

ceramic materials have a wide variety of base glass systems which can be prepared from a broad spectrum of chemical compositions focusing majorly on the final area of application. According to [11], the most widely studied base glass systems include; MgO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (MAS),CaO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> Li<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (CAS), (LAS) and CaO.MgO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub> (CMAS) among others. [4], reported that the composition of a parent glass is different from the precipitated crystalline phases as residual glassy phase changes its composition and density as a function of the crystallization process. Similarly, chemical durability directly affects strength and hardness of glass-ceramic sample which significantly influences abrasion [12].

The aim of this work is to study the crystallization and microstructure of calcium-magnesium-aluminosilicate

(CaO.MgO.Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>) primary glass system in relation to the effect of the nucleating agent on composition as well as some properties for the beneficial application.

### II. Experimental Procedure

### A Glass preparation and production

The batch composition of the studied glass is as follows; 52.00wt% SiO<sub>2</sub>, 16.00wt% Al<sub>2</sub>O<sub>3</sub>, 12.00wt% CaO, 8.00wt% MgO, 2.00wt% K<sub>2</sub>O, 6.00wt% TiO<sub>2</sub>, 0.30wt% NaCl and 3.70wt% trace. The batch composition was thoroughly mixed and poured into a crucible which was transferred into an electrically heated furnace. The batch was melted at 1600°C for 3 hours with an interval of 30 minutes swirling to ensure complete homogenization of the melt. Thereafter, the melt was cast into rods using a mould and the rods were quickly transferred to a muffle furnace preheated at 600°C for annealing to reduce the residual stresses. The rods were gradually cooled to room temperature and

physical appearance of the samples was observed.

# B Heat Treatment Regime

The glass-ceramic samples were obtained by controlled nucleation and crystallization processes via double stage heat-treatment regimes. The glasses were crystallized at 363°C and 663°C as nucleation and crystal growth temperatures respectively. The samples were soaked for ranges of 1-4 hours duration. After the heat treatment, the muffle furnace was switched off and the samples were allowed to cool gradually to room temperature.

### C X-ray Diffraction (XRD)

The presence of the crystalline phase in a sample heat-treated for 4 hours duration were identified using Philips/ PANanalytical X'pert Pro MPD Powder Diffractometer with an X'celerator detector, and Fe filtered Cu Kα radiation in the 2 range from 5° to 100° operating at 40 kV and 35 mA.

The precipitated crystalline phases were detected using X' pert high score software.

# D Scanning Electron Microscope (SEM)

The morphological characteristics of the crystallized sample heat-treated for 4 hours duration were carried out using a scanning electron microscope (SEM) JEOL Model JSM-7500F. Scanning electron microscopy (SEM) characterization was carried out using freshly fractured surface crystalline sample etched through immersion in a 1M HF aqueous solution for 30 minutes. Thereafter, the sample was thoroughly washed with distilled water and oven-dried at 110°C for 2 hours.

# E Physico-Mechanical and Chemical Characterization

### i. Density measurement

Density measurement of four samples heat-treated for 1-4 hours' time were carried out using the Standard Archimedes Principle. The weights of the four samples heat-treated for 4 hours duration in the air and in distilled water were measured using an electrical digital weighing balance. Their respective densities were calculated using the expression as follows:

Density = 
$$\frac{D}{W-s}$$
 g/cm<sup>3</sup>

where, D is the weight of sample in the air (g), W is the weight of sample soaked in distilled water (g) and S is the weight of sample suspended in distilled water (g).

#### ii. Hardness measurement

Measurement of four samples heat-treated for 1 to 4 hours was carried out using Micro Vickers Hardness Tester Model MV1- PC. 0.3 Kgf load was applied to each sample and the indenter was square based diamond pyramid.

# iii. Chemical Durability Test

Four samples heat-treated for 1-4 hours were oven dried at 110°C for 4 hours duration and then weighed to the nearest 0.1 mg as (Wa). Each sample was individually immersed in 50 ml glass bottle containing 1M HCl. The bottle was closed with its cap and then placed in the oven at 90°C for 10 hours. Thereafter, each sample was thoroughly washed and then oven dried at 110°C for 1 hour to achieve a constant weight. Thereafter, each of the samples were reweighed to obtain the mass after immersion as (Wb), then, total weight loss per cent of each sample was calculated and chemical durability was expressed as weight loss per cent.

### III. Results and Discussion

Each rod of glass sample yielded a brownish colouration. The undesirable colour might be due to an Fe3+ charge transfer formed by trace impurities of iron oxide present in the starting materials [8]. The nucleation and crystallization processes were completed via double stage heat-treatment schedules. Figure 1 shows Xray diffraction pattern of the sample subjected to heat treatment for 4 hours duration. The crystalline phases precipitated in the sample are quartz (SiO<sub>2</sub>), albite (Na<sub>2</sub>O.Al<sub>2</sub>O<sub>3</sub>.3SiO<sub>2</sub>), wollastonite (CaO.SiO<sub>2</sub>) and witherite (BaCO<sub>3</sub>). This is in agreement with [1] and [11] who stated that glass-ceramic material must contain at least one or more crystalline phases dispersed in the residual glassy phase.

The SEM image in Plate 1 is the microstructure of sample heat-treated for 4 hours duration. The microstructure is characterized by circular-like and flake-like crystals alongside voids all dispersed in matrix of the residual glassy phase.

Figure 2 shows the density values of the samples that were soaked for 1 to 4 hours. The density values were increasing gradually as heat treatment times were increasing progressively from 1 to 4 hours. The slight increase in density was due to precipitation of large volume of crystalline phases dispersed in the glassy phase. According to [14] and [3], the density of glass-ceramic material is always larger than the density of its corresponding parent glass. In a similar way, density variation revealed the degree of crystallization processes when the difference between the densities of glass-ceramic and the corresponding parent glass is significantly great.

Figure 3 depicts the hardness results of samples heat-treated for 1 to 4 hours duration. The results revealed that there was

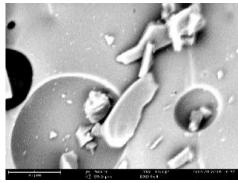


Plate 1: SEM micrograph of glass-ceramic sample soaked for 4 hours duration.

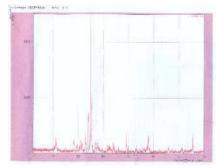


Figure I: XRD patterns of glass-ceramic sample Heat treated for 4 hours

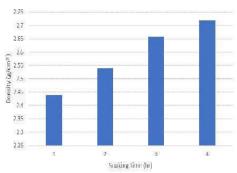


Figure 2: Variation of density and soaking time in the heat treatment furnace from 1to 4 hours duration

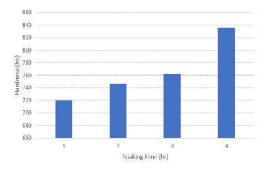


Figure 3: Variation of hardness and soaking time in the heat treatment furnace from 1 to 4 hours duration.

a gradual increase of hardness as heat treatment time increases from 1 to 4 hours. This result is in harmony with [2], who stated that hardness changes with precipitation of large volume of crystalline phases and prolong soaking time. In addition, the increase in hardness might result from viscous flow formation induced by prolonging soaking time.

Figure 4 portrays the weight loss results of samples soaked for 1-4 hours duration. A progressive decrease in weight loss was noticeable as soaking time (1-4 hours) was increasing across samples that were immersed in 1M HCl aqueous solution at 90°C for 10 hours.

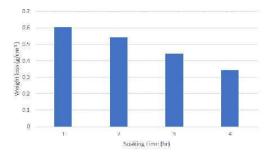


Figure 4: Weight loss values of samples that were soaked for 1-4 hours duration in 1M HCl

This is in agreement with [1, 11], who reported that decrease in weight loss would be noticeable when glass-ceramic material is heat-treated for a considerable period, as prolong soaking allows of large precipitation volume crystalline phases dispersed in residual glassy phase, and this hinders weight loss. Therefore, the reduction of weight loss observed in the sample heattreated for 4 hours duration was due to precipitation of crystalline phases dispersed in the matrix of a residual glassy phase.

### IV. Conclusion

The characterization and some properties of

calcium-magnesium-aluminosilicate (CaO. MgO. Al<sub>2</sub>O<sub>3</sub>.SiO<sub>2</sub>) glass-ceramic were studied and the conclusion has been drawn as follows:

- The physical appearance of calcium-magnesium-aluminosilicate (CaO. MgO.Al<sub>2</sub>O3.SiO<sub>2</sub>) primary glass system was brownish due the presence of iron oxide impurities in the starting materials.
- The crystalline phases dispersed in the residual glassy phase as identified by XRD were quartz, albite, wollastonite and witherite.
- 3. The microstructural configuration of the sample heat-treated for a duration of 4 hours as detected by SEM is characterized by circular-like and flake-like crystals randomly distributed alongside fewer micro-sized voids dispersed in the residual glassy phase.
- 4. The sample that was soaked for 4 hours duration has the highest density and hardness values as well as the lowest weight loss value and this might result from the presence of a considerable volume of crystalline phases embedded in the residual glassy phase. Therefore, the sample can be applied for abrasion resistance usage.

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