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Full Length Research Article

EFFECT OF TITANIA ADDITION ON THE CRYSTALLIZATION CHARACTERISTICS OF GLASS-CERAMICS MATERIAL

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ABSTRACT
The effect of 8wt% TiO_2 incorporation on the microstructure of glass-ceramics prepared using two-step heat treatment temperatures at 356/656°C has been carried out. The crystallization behaviour was investigated using X-ray diffraction (XRD) and field emission scanning microscopy (FESEM). The crystalline phases were precipitated and identified as wollastonite, andradite, monticellite and titanate dispersed in the matrix of residual glassy phase. The microstructure is characterized by dense, needle, circular, ellipsoidal, flake and lamellar twinning-like crystals dispersed in the amorphous phase. Also, fewer micro sized pores were detected between grains. The glass-ceramics showed excellent resistance to acid and alkali attack due to the presence of crystalline phases that were dispersed in the matrix of residual glassy phase. The glass-ceramics heat treated for 4 hours duration showed excellent density as well as excellent chemical durability in both acidic and alkali media.

Keywords: Crystallization, Microstructure, Glass-ceramics

INTRODUCTION

Glass-ceramics are polycrystalline materials prepared by controlled crystallization of host glass (Holand & Beall, 2002). The material contains small volume fraction of glass surrounding each crystal grain acting as a binder. Glass-ceramics material is not fully crystals because the microstructure usually contains between 50%-95 % crystals dispersed in the residual glassy phase (Aliyu, 2018). Two or more crystalline phases may precipitate during controlled heat treatment and their compositions are completely different from the corresponding base glass.

Efficient nucleation leads to the production of large numbers of small crystals rather than small numbers of large crystals which is the target of the glass-ceramics process (El-Meliegy & Richard, 2012). According to Holand & Beall (2002), glass ceramics offer the possibility of combining the special properties of conventional sintered ceramics with distinctive characteristics of glasses. They are materials prepared by controlled crystallization process such that large numbers of crystal grains rather than few big ones are grown. This is usually accomplished using a suitable nucleation catalyst. The crystallization is composed of two-stage heat treatment. During the first stage or the nucleation stage, the glassy material is soaked for duration of time at a temperature that promotes the formation of nuclei or small crystallites throughout the bulk of the glass. During the second or crystal growth stage, the temperature is increased further at about 300°C above the nucleation temperature to allow nuclei grow onto the nuclei (El-Meliegy & Richard, 2012). To improve nuclei formation and subsequent crystal growth, nucleation catalyst is often incorporated to the glass composition. There are wide ranges of nucleation catalyst for glass-ceramics production notable among which include: metallic oxides such as Titania (TiO_2), zirconia (ZrO_2); metallic fluorides such as CaF_2, NaF and noble metals such as gold (Au) and platinum (Pt) among others. When the Titania crystals exist in the glass matrix, the crystals would be dispersed in the glass matrix exhibiting a stable characteristic property. The basis of controlled crystallization depends on efficient nucleation which results in the formation of fine-grained and uniform microstructure without micro cracks or voids suitable for a wide range of applications such as cookware, prototype for automobile components, prostheses for dental restoration and bone implant among others (Bahman *et al*., 2012; Hussaini *et al*., 2010). The study aims at establishing the crystallization characteristics and microstructure of glass-ceramics prepared from calcium-magnesium-alumino silicate primary glass system.

MATERIALS AND METHOD

Materials

Limestone, magnesite and feldspar were used as starting material for primary glass production
(El-Meliegy & Richard, 2012). In addition, Titania (TiO_2) and Sodium chloride (NaCl) were incorporated as nucleation catalyst and fining agent respectively.

Preparation

The glass composition in Table 1 was prepared from locally available raw materials such as feldspar, limestone, magnesite and 8wt% chemical grades TiO_2 as well as 0.3wt% NaCl were incorporated as nucleation catalyst and fining agent respectively. The constituents of the batch were accurately weighed and thoroughly mixed to ensure complete homogeneity. The weighed batch was melted in a crucible in an electric furnace at 1600 °C at heating rate of 5°C/min. The homogeneity of the melt was achieved by stirring the melt several times at 30 minutes interval. The melt was cast into four rods which were then properly annealed in a muffle furnace at 600°C for 1 hour to reduce residual stresses and then cooled to room temperature.

Table 1: Chemical composition of glass samples

Oxide	SiO_2	CaO	MgO	Al_2O_3	NaCl	K_2O	TiO_2	Trace
Wt%	54.00	8.00	8.00	16.00	0.30	2.00	8.00	3.70

Differential scanning calorimetry analysis (DSC)

The transition temperature (T_g) of the powdered glass (75 μm) was studied using differential scanning calorimeter (DSC) Mettler Toledo Model. The powdered glass was heated in platinum holder with another one containing Al_2O_3 as a reference material. A

uniform heating rate of 10°C /min was used. Data was recorded using a computer driven data acquisition system. The result achieved was utilized as a guide to determine the required heat treatment temperatures applied to nucleate and crystallize the produced glasses.

Heat treatment of produced glasses

Four glass samples of the same composition were heat treated using double-stage schedules which involves nucleation and crystallization processes. The four samples were heat treated to the nucleation temperature at 356°C and then held for 1-4 hours for nuclei formation and then heat treated further to crystal growth temperature at 656°C and then held for 1-4 hours to permit the growth of crystals onto the formed nuclei. Thereafter, the samples were cooled to room temperature.

X-ray Diffraction and Electron Microscopy (XRD)

Identification of crystalline phases was made using X-ray diffraction PAN analytical X'pert Pro powder diffractometer with X'celerator detector at 40 Kv and 30 mA using Fe filtered Co-Kα radiation. The phases were identified using X' high score software. Furthermore, electron microscopic observation of the crystalline sample coated with gold was carried out using JEOL JSM-7500F electron probe micro analyzer.

Scanning Electron microscopy (SEM)

Microstructural details of the sample heat treated for duration of 4 hours was obtained using scanning electron microscopy (SEM JEOL JSM-7500F) on previously polished and etched (by dipping for 2 minutes in IM HF aqueous solution) glass-ceramic sample.

Effect of acid and alkali resistance

Four samples of known weight were immersed in 1M HCl at 80°C for 12 hours. The samples were then washed with distilled water and then dried. Each sample was reweighed to check for any loss in weight after washing off acid. Similarly, a set of four samples of known weight were immersed in 1M NaOH at 80°C for 12 hours. The above procedure was applied to the samples. The weight loss of each sample was calculated and chemical durability values were represented in terms of weight loss per unit of surface exposed.

Determination of apparent density

The measurement of density was conducted using Achimedes method which was in accordance with the ASTM C 373-88 standard. The Apparent density of each sample was calculated using expression below:

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

Where, *D* is the weight of the sample in g, *W* is the weight of the soaked in distilled water in g and *S* is the weight of the sample suspended in distilled water in g.

RESULTS AND DISCUSSION

Figure 1 shows glass transition (T_g) of produced glass which was 256°C as determined by differential scanning calorimetry. The produced glass samples were nucleated at 356°C and then crystallized at 656°C for 1-4 hours holding time. This was supported by El-Meliegy & Richard (2012) who reported that the nucleation and crystal growth temperatures of glass sample should be 100°C above transition temperature and 300°C above nucleation temperature respectively.

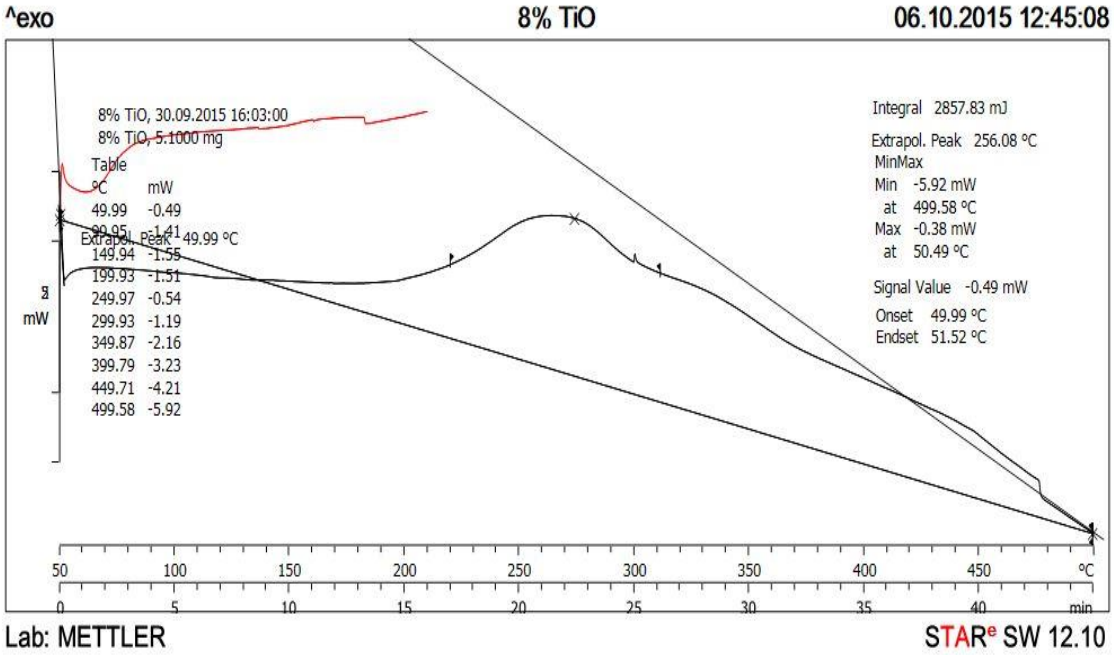

Figure 1: DSC of produced glass containing showing 256°C as glass transition (T_g) temperature

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Figure 2 displayed the diffraction pattern of glass-ceramic sample that was heat treated for duration of 4 hours as soaking time. Crystalline phases in the sample identified by X-ray diffraction analysis are anorthite, wollastonite, andradite and hematite dispersed in matrix of the glassy phase. This is in agreement with the finding of Deubener *et al*. (2018) and He *et al*. (2014) who mentioned that glass-ceramics must contain at least a crystal phase dispersed in the matrix of residual glassy phase

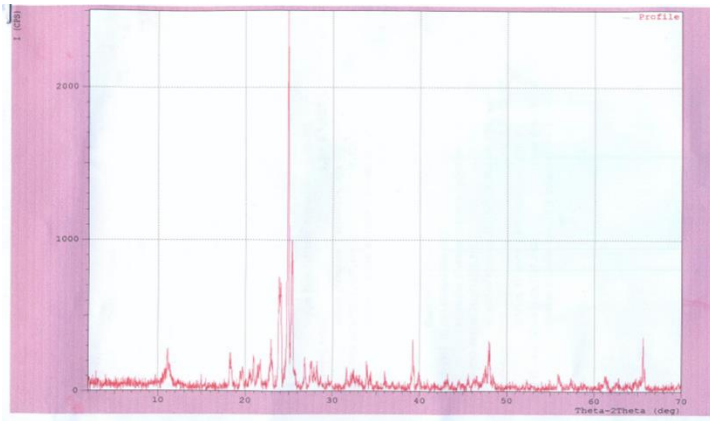

Figure 2: X-ray diffractogram of glass-ceramic sample to which 8 wt% TiO_2 was added and then heat treated for 4 hours

Similarly, Plate 1 depicts the micrograph of the heat treated sample for 4 hours duration. The microstructure has dense and collection of randomly distributed flake-like crystals alongside fewer micro sized pores dispersed in the matrix of the amorphous phase. This is supported by Salama *et al*. *(*2002) and Holand & Beall (2002) who reported that a wide range of crystalline phases would be precipitated when 8 wt % titania as nucleating agent is incorporated into glass composition and subjected to prolong heat treatment.

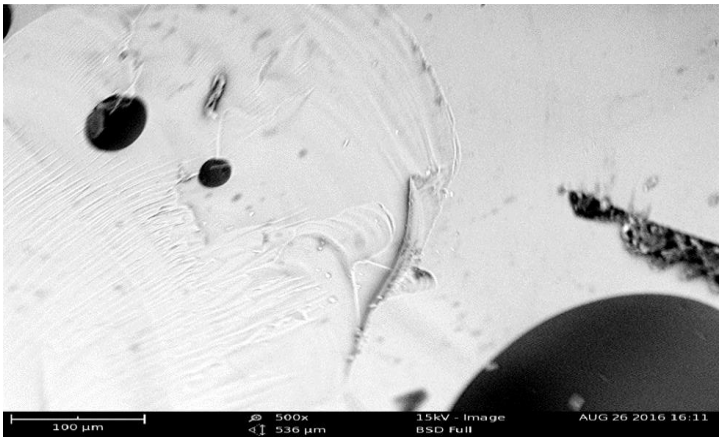

Plate1: Shows SEM image of glass-ceramic sample heat treated for duration of 4 hours

Table 2: Effect of acid and base on glass-ceramic samples prepared from local materials

Sample	Resistance to acid (wt. loss per unit area g/cm³)			Resistance to base (wt. loss per unit area g/cm³)				
	Heat Treatment time (h)	Temp. (°C)	Immersion time (h)	HCl (1M)	Heat treatment time (h)	Temp. (°C)	Immersion time (h)	NaOH (1M)
GlC_1	1	80	12	0.58	1	80	12	0.72
GlC_2	2	80	12	0.53	2	80	12	0.67
GlC_3	3	80	12	0.44	3	80	12	0.59
GlC_4	4	80	12	0.30	4	80	12	0.46

There was progressive decreased in weight loss as heat treatment time was increasing across the samples that were immersed in 1M HCl solution for 12 hours at 80°C. The decrease in weight loss was recorded on glass-ceramics samples heat treated at varying heat treatment time (1-4 h). However, minimum weight loss was recorded on sample heat treated for 4 hours duration. This might be due to precipitation of large volume of crystalline phases dispersed in the residual glassy phase (Naruporn *et al*. 2013; Salah, 2016).

In a similar manner, it has been observed that samples heat treated at various heat treatment times inhibit alkali attack using 1M NaOH solution. This result was expected because the presence of titanium ions served as driving forces for inhibition of alkali attack as well as the presence of phases assemblages scattered in the matrix of the glassy phase could be hindrance factors for alkali attack (Salah, 2016). However, decrease of alkali attack was noticeable as heat treatment time increases progressively from 1-4 hours. The results showed that heat treatment time has great influence on weight loss because; as heat treatment time increases, weight loss decreases progressively.

Table 3: Apparent density of glass-ceramics samples heat treated for 1-4 hours

S/N	Heat treatment time	Apparent density values (g/cm³)
1	1 hr.	2.7
2	2 hrs.	2.8
3	3 hrs.	2.8
4	4 hrs.	2.9

Apparent density of glass ceramic samples heat treated at various heat treatment times (1-4 hrs.) increased slightly as heat treatment time increases progressively. The increase in apparent density might be due to the precipitation of large volume of crystal phases dispersed in the residual glass (Strnad, 1986).

Conclusion

The conclusion of the study is summarized as follows:

1. The transition temperature (T_g) of the produced glass was 256°C.
2. Crystalline phases precipitated in the sample heat treated for duration of 4 hours as identified by X-ray diffraction (XRD) analysis are wollastonite, andradite, monticellite and titanate dispersed in matrix of the residual glassy phase.

3. The microstructure of sample heat treated for duration of 4 hours is characterized by dense, circular, flake-like, ellipsoidal, needle and lamellar twinning-like crystals dispersed in the matrix of the amorphous phase.
4. Minimum weight loss (0.30 g/cm^3) was recorded on sample heat treated for 4 hours and immersed in dilute acid for 12 hours. The resistance to weight lost might be due to precipitation of large volume of crystalline phases dispersed in the residual glassy phase.
5. Sample heat treated for duration of 4 hours shows minimal alkali attacks (0.46g/cm^3) due low Si-O content in the residual glass structure as well as the presence of large volume of crystal phases dispersed in the residual glassy phase.

Glass-ceramic sample heat treated for 4 hours shows maximum apparent density due to the presence of large volume of crystalline phases presence in the residual glass

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