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Full Length Research Article

EFFECT OF TITANIA ADDITION ON THE MICROSTRUCTURE AND CRYSTALLIZATION BEHAVIOUR OF GLASS-CERAMICS PREPARED FROM LOCAL RAW MATERIALS

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ABSTRACT
The effect of titania and composition on the microstructure of glass-ceramics prepared from local raw materials was investigated using two-step heat treatment at 321-621°C as nucleation and crystal growth temperature, respectively. The crystallization behaviour was investigated using X-ray diffraction (XRD) and emission scanning microscopy (SEM). The phases assemblage was 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 prolong heat treatment and the presence of crystalline phases that were dispersed in the matrix of residual glass. The glass-ceramics to which 10wt% TiO_2 was incorporated and heat treated for 4 hours showed excellent chemical durability.

Keywords: Titania addition, microstructure, crystallization, glass-ceramics, local raw materials

INTRODUCTION

Selection of raw materials for making glass-ceramics is vital. Broad spectrums of naturally occurring rocks are being increasingly utilized for the production of glass-ceramics. Hamzawy *et al*. (2005) reported that igneous and sedimentary rocks are used successfully in the production of glass-ceramic materials. Glass-ceramics are partly glassy and partly in crystalline state caused by controlled nucleation and crystallization of base glasses. Daniela *et al*. (2010), further stated that they are normally produced from specially formulated compositions which usually contain nucleating agent, melted and shaped by desirable glass forming technique and then cooled to room temperature.

Also, Gamal (2012) reported that the base glasses would be subjected to thermal treatment to initiate nuclei formation and subsequent crystals growth. Debasis and Sudip (2016) further reported that the thermal treatment is done in two steps, namely at temperature somewhat above transition region to develop nuclei in the bulk glass and then followed by further heat treatment at high temperature to promote crystals growth on the formed nuclei. 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 that might be suitable for a wide range of applications such as cookware and dental restoration among others (Hussaini *et al*., 2010; Bahman and Mehdikhani, 2012).

Wide ranges of nucleating agents are generally incorporated into glass to induce crystallization. According to Garai *et al*. (2014), Beall and his team used a wide variety of nucleation catalysts for crystallization of various silicate glass systems. When the titania crystals exist in the glass matrix, the crystals would be dispersed in the glass matrix exhibiting a stable characteristic property.

MATERIALS AND METHODS

Glass preparation

Local raw materials (such as Matari feldspar, Kalambaina limestone and Tsakesimptah magnesite) were the main starting materials for making base glass for this study. Batch for making glass specimen was formulated from chemical compositions of the starting materials by XRF as presented in (Tables 2-4). Also, chemical grade titania (10wt% TiO_2) was included in the batch composition as nucleation catalyst. The components of the batch in Table 1 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 for 3 hours. The homogeneity of the melt was achieved by stirring the melt several times at 30 minutes interval. The glass melt was cast into 8 rods and then transferred to a preheated muffle furnace at 600°C for 1 hour to reduce residual stresses.

Table 1: Chemical composition of produced glass specimens

Oxide	SiO_2	CaO	MgO	Al_2O_3	NaCl	K_2O	TiO_2
Wt%	52.00	8.00	8.00	16.00	0.30	2.00	10.00

Table 2: 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: (Aliyu, 2018)

Table 3: 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: (Aliyu, 2018)

Table 4: 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: (Aliyu, 2018)

Differential scanning calorimetry analysis (DSC)
The transition temperature (T_g) of the powdered glass (75 µm) was studied using differential scanning calorimeter 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 heat treatment schedule was based on result of DSC achieved.

Heat treatment of produced glasses
A pair of four glass specimens of the same composition were subjected to heat treatment using the conventional method which involves nucleation and crystallization processes. The specimens were heat treated to the nucleation temperature at 321°C and then soaked for 1-4 hours for nuclei formation and then heat treated further to crystal growth temperature at 621°C and then soaked for 1-4 hours to allow the growth of crystals onto the formed nuclei. Thereafter, the specimens were cooled to room temperature. The specimens were further subjected to characterization using XRD and SEM analyses as follows:

X-ray diffraction analysis (XRD)
Identification of crystalline phases was made from glass-ceramics specimen that was heat treated for duration of 4 hours 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.

Scanning electron microscopy (SEM)
Microstructure of the glass ceramic specimen that was heat treated for duration of 4 hours was investigated by scanning electron microscope. After heat treatment of the specimen, the surface was polished and then edged using Keller's reagent. The specimen was coated with gold at a current of 15 mA per 150 seconds and the analysis was carried out using JEOL JSM-7500F electron probe micro analyzer.

Effect of acid and alkali resistance
Four specimen of known weight were immersed in 1M HCl at 80°C for 12 hours. Similarly, a set of four specimen of known weight were immersed in 1M NaOH at 80°C for 12 hours. The specimens were then washed with distilled water, dried and reweighed. Chemical durability values were represented in terms of weight loss per unit of surface exposed.

RESULTS AND DISCUSSION
Figure 1 shows glass transition (T_g) of produced glass which was 221°C as determined by differential scanning calorimetry. The produced glass specimens were nucleated at 321°C and then crystallized at 621°C for 1-4 hours soaking times. This was supported by El-Meliegy and Richard (2012) who reported that the nucleation temperature of glass should be 100°C above glass transition (T_g) and crystallization temperature ought to be 300°C above glass transition.

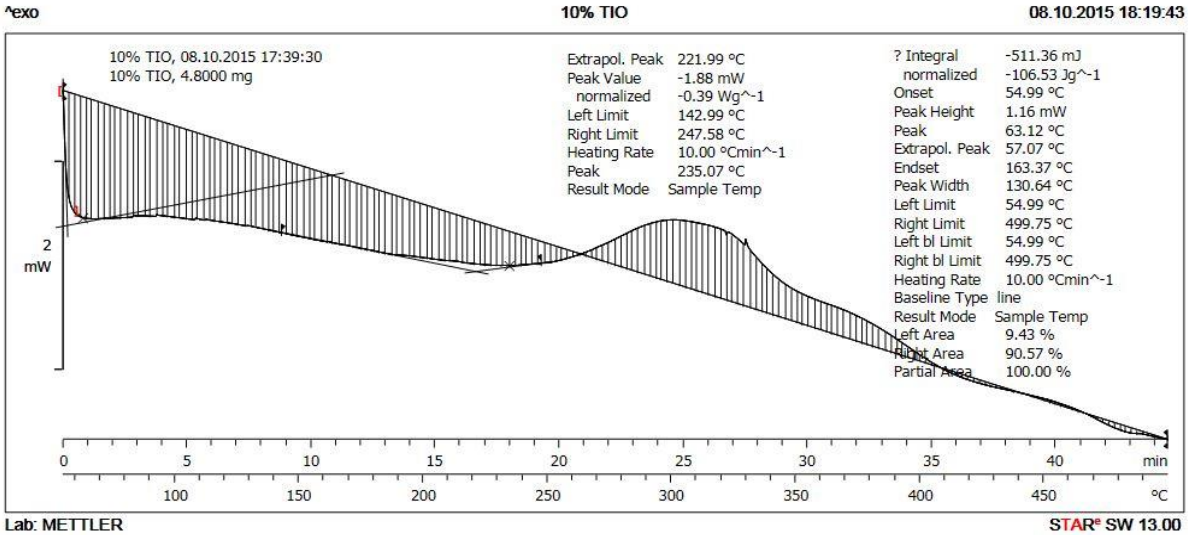

Figure 1: DSC of produced glass containing 10wt% TiO_2 showing 221°C as glass transition (T_g) temperature.

Figure 2 shows the diffraction pattern of glass-ceramic specimen that was subjected to heat treatment for duration of 4 hours as soaking time. Phases assemblage in the specimen identified by X-ray diffraction (XRD) analysis were wollastonite, andradite, monticellite and titanate dispersed in matrix of the residual glassy phase. This is in consonance with the findings of Deubener *et al*. (2018) and He *et al*. (2014) who showed that glass-ceramic must contain at least a phase assemblage dispersed in the matrix of a glassy phase.

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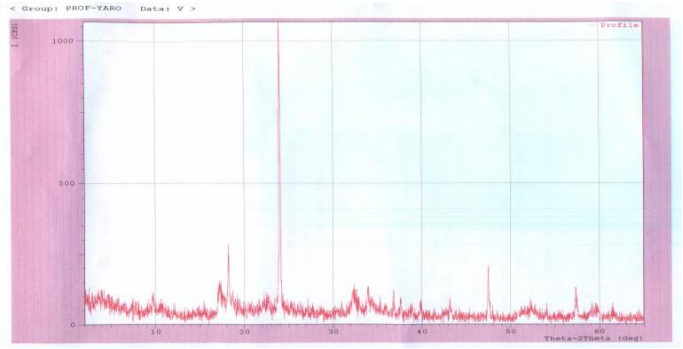

Figure 2: X-ray diffractogram of crystallized specimen heat treated for 4 hours as soaking time

In a similar manner, Plate 1 displays the micrograph of a specimen that was subjected to heat treatment of 4 hours duration as soaking time. The microstructure showed dense, circular, flake-like, ellipsoidal, needle and lamellar twinning-like crystals dispersed in the matrix of residual glassy phase. This is supported by Salama *et al*. (2002) who reported that a wide variety of phases assemblage including titanate phase might be precipitated when 10 wt % titania as nucleating agent is incorporated into glass composition and subjected to prolong heat treatment time.

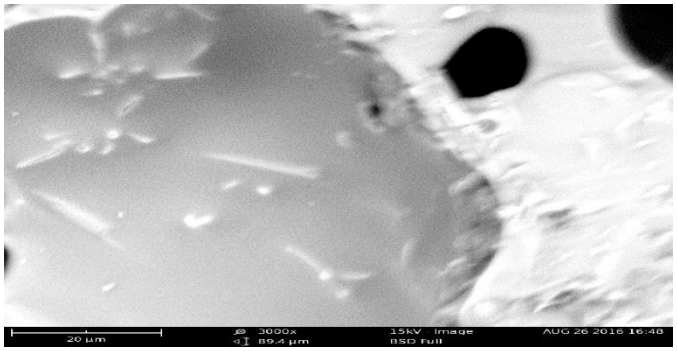

Plate 1: Displays SEM micrograph of crystallized specimen that was subjected to heat treatment of 4 hours as soaking time

Figure 3 demonstrates weight loss plotted against time for the glass-ceramics specimen when treated with 1M HCl solution at 80°C for 12 hours. The specimen that was subjected to prolong heat treatment time of 4 hours was more resistance to the attack of acid solution than the specimens of the same basic composition but subjected to short heat treatment time. Therefore, the result shows that resistance to acid attack increases with titania addition and prolong soaking time. This was expected because according to Salah (2016), the resistance to acid attack was due to the presence of large volume of phases assemblage precipitated in the matrix of residual glassy phase as a result of crystallization.

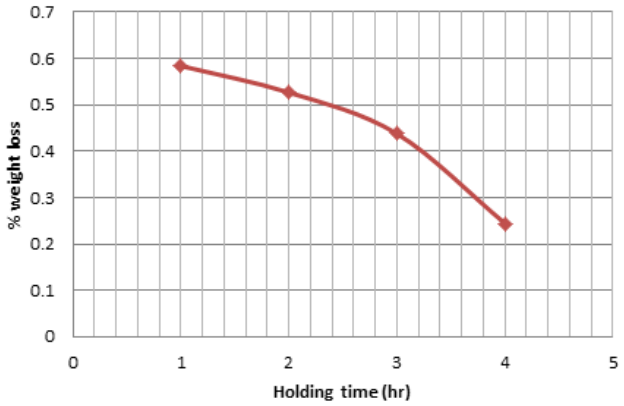

Figure 3: Effect of weight loss using 1 M HCl solution against time on crystallized specimens

In a similar vein, Figure 4 depicts the effect of weight loss on crystallized specimen when treated with 1 M NaOH solution at 80°C for 12 hours. Progressive decrease in weight loss was noticeable as heat treatment time (1-4) hours increases across the crystallized specimens. The decrease in weight loss was induced by prolong heat treatment time. Therefore, maximum alkali attack was recorded on the crystallized specimen that was subjected to heat treatment of 1 hour. The specimen suffered considerably alkali attack than it corresponding specimens heated treated for 2- 4 hours. However, minimum weight loss was recorded on the specimen that was subjected to prolong heat treatment time of 4 hours. Naruporn *et al*. (2013) and Salah (2016) have shown that prolong heat treatment time has great influence on weight loss because, as soaking time increases, weight loss decreases progressively.

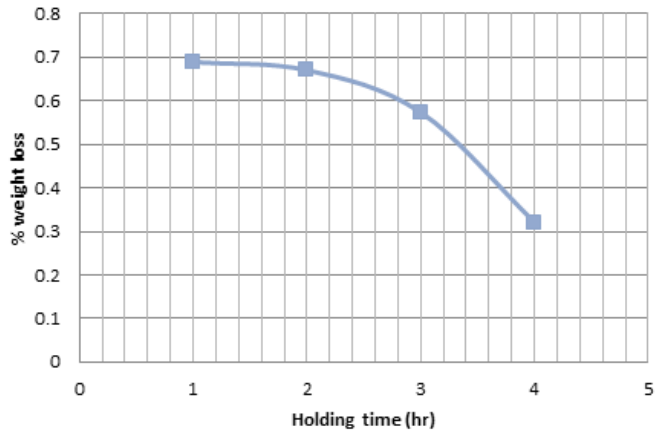

Figure 4: Effect of weight loss using 1 M NaOH aqueous solution against time on crystallized specimens

Conclusion

Base glasses of the same chemical composition containing 10 wt% titania as nucleating agent and heat treated at various holding times (1-4 hours) were prepared from local raw materials for this investigation. The results achieved are summarized as follows:

1. The glass batch prepared from local raw materials was melted at 1600 °C for 3 hours.

2. The melted glass was transformed into glass-ceramic material at 321℃ and 621℃ as nucleation and crystallization temperatures respectively using 1-4 hours as soaking times.

3. XRD analysis detected that the specimen heat treated for duration of 4 hours as soaking time precipitated wollastonite, andradite, monticellite and titanate dispersed in the matrix of residual glassy phase.

4. SEM has revealed that the microstructural configuration of the specimen subjected to prolong soaking time of 4 hours is characterized by dense, needle, circular, ellipsoidal, flake and lamellar twinning-like crystals dispersed in the matrix of the residual amorphous phase.

5. The specimen heat treated for 4 hours as soaking time showed excellent chemical durability than its corresponding specimens that were crystallized at short length of times

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